

# Expanded Carbon Lattices and Congener Hydrocarbons with *directionally* Inserted Triple Bonds

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**Abstract:** The diamond or graphene lattices may be expanded theoretically by replacing one or several CC bonds of each carbon atom by the sequence  $C-(C\equiv C)_k-C$  with  $k = 1, 2$ , etc. In this communication a systematic approach is described, by operating these replacements according to the *four directions around an  $sp^3$ -hybridized carbon atom* (affording “*m*-directional diamond-yne”) with  $m = 1$  to 4 or the *three directions around an  $sp^2$ -hybridized carbon atom* (affording “*n*-directional graphen-yne”) with  $n = 1$  to 3. The “*n*-directional graphen-yne” sheet may be folded to yield various types of directionally-expanded nanotube-yne, nanocone-yne, nanotor-yne, or fullrene-yne. Analogous di-yne are briefly mentioned. In addition to infinite lattices, various possibilities for molecules (diamondoid and benzenoid hydrocarbons) obtained by analogous expansions are briefly mentioned. For applications such as hydrogen storage and lithium batteries, new possibilities for selecting the shape and size of rings are available by these directional insertions of triple bonds.

**Keywords:** Expanded carbon lattices and hydrocarbons with intercalated triple bonds, diamond lattice, graphene, graphyne, graphdiyne, graphenylene, nanotube-yne, nanocone-yne, fullerene-yne.

## 1. INTRODUCTION

The element carbon constitutes not only the basis of organic chemistry and life on our planet, but presents also interesting challenges in elemental form. Scientists are familiar with the carbon allotropes having  $sp^3$ -hybridized carbon atoms (diamond, lonsdaelite, and various other related *macromolecular lattices*) or  $sp^2$ -hybridized carbon atoms (graphene or graphite *macromolecular lattices*). In both cases it is likely that the peripheral carbon atoms do not have unpaired electrons (i. e. dangling bonds) but are connected to oxygen or, more likely, hydrogen atoms. Anyhow, the effects of these marginal atoms are negligible.

In the first attempt (published in 1968) to compute energies of carbon lattices that are different from diamond or graphite, lattices that included triple bonds were also mentioned [1]. More recently, after the unexpected discoveries of fullerenes [2, 3], nanocones [4-7], nanotubes [8-10], nanoscrolls [11], nanotori [12-15], and graphene [16], a large number of publications on carbon has appeared, discussing both experimentally accessible carbon lattices and molecules as well as hypothetical ones. The number of possible carbon allotropes is staggering if one considers combinations of various hybridization states of carbon atoms. Theoretically, several kinds of carbon allotropes that contain both  $sp^2$  and  $sp^3$ -hybridized carbon atoms have been described, and they will be mentioned here only briefly [17-24]. Other contributions to problems involving carbon allotropes by the present author [25-28] and other authors [29-38] are also mentioned.

The effect of peripheral hydrogen atoms cannot be neglected, however, in *hydrocarbon molecules* which are small fragments of the diamond lattice (diamondoid hydrocarbons, or diamondoids for brevity), or small fragments of graphene lattices (benzenoid hydrocarbons, or benzenoids for brevity). Helicenes are not covered by this last categorization, because they are ‘benzenoids escaped into the third dimension’. Thus benzenoids can be either ‘graphene molecules’, or ‘helicene molecules’. Fullerenes or doubly-capped nanotubes – single-wall or multiple-wall variants – are also *molecules*, but they have only carbon and no hydrogen atoms.

Unlike *macromolecules* which give rise to mixtures that are polydisperse, *molecules* give rise to substances in which all particles are identical. In the former case one has to consider an infinite number of monomer units, neglecting peripheral atoms and bonds, whereas in the latter case one considers the actual molecular unit with all its atoms and bonds.

The literature contains conflicting views about the so-called “carbyne” having very long chains of  $sp$ -hybridized carbon atoms, based on evidence that such chains or the corresponding dinitriles have been detected in interstellar cosmos, and that conjugated polyynes with terminal bulky substituents could be synthesized. However, in condensed phase, simple very long and unprotected “carbyne molecules” should immediately polymerize exothermally; compressed acetylene is known to explode, therefore for its use in welding it is conserved in pressure containers dissolved in acetone. Conjugated diynes polymerize photochemically even in single crystals forming colored insoluble polymers with conjugated alternating double and triple bonds.

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At normal pressure, graphite is thermodynamically more stable than diamond, but there is a huge activation barrier for the interconversion between these allotropes. Synthetic diamond can be obtained from graphite at high pressure and temperature in the presence of metallic catalysts, and under special conditions diamond may be formed by epitaxial deposition.

Graphene sheets have extraordinary properties, making them fit for many practical applications. Among these applications one can cite materials for lithium batteries, for isolation, purification, storage, and selectivity of gaseous hydrogen, and for components of electronic equipment. However, the small size of rings in graphene causes limitations in such applications, for instance in accommodating hydrogen molecules, and lithium atoms or ions.

In the 1968 paper [1], among the plane lattices with  $sp^2$ -hybridized carbon atoms having larger rings than hexagons there was a lattice where each vertex was common to a 4-membered, a 6-membered, and a 12-membered ring (this lattice is now called graphenylene). The regular polygonal angles are  $90^\circ$ ,  $120^\circ$ , and  $150^\circ$ , respectively, adding up to  $360^\circ$ ; however, it was expected that the energy factor of aromaticity/antiaromaticity would cause deviations from regularity, and indeed all the 4-membered rings avoid antiaromaticity by having exocyclic double bonds, despite the fact that the bonds in the 6-membered rings become unequal, namely alternatively shorter and longer than the benzene CC bonds, as shown by Müllen and coworkers [39].

Another way for having larger rings than hexagons in a plane lattice with  $sp^2$ -hybridized carbon atoms is to insert one or several triple bonds into a graphene sheet; these triple bonds with linear geometry leave polygonal bond angles unchanged, but of course they modify the distance between polygon vertices, hence rings areas.

In the present communication we discuss lattices and hydrocarbons derived from diamond or graphene by replacing, for every carbon atom, one or more CC bonds by connected pairs of  $sp$ -hybridized carbon atoms: by this replacement a single C–C bond in the diamond lattice becomes a sequence of C–C≡C–C bonds, whereas an aromatic CC bond in graphene becomes a resonant sequence of bonds: (C–C≡C–C ↔ C=C=C=C). More generally, one can imagine replacing one or several CC bonds of each carbon atom by the sequence C–(C≡C)<sub>k</sub>–C with  $k = 1, 2$ , etc. For the products of such  $C_{2k}$  insertions Chauvin has proposed the name carbo<sub>k</sub>-mers [40-42] but this name has not been adopted in the rich literature on graphyne and graphdiyne [43-56] or yne-diamond [57-59] and will not be used here. With very few exceptions, the inclusion of triple bonds into carbon lattices and molecules has so far disregarded their *directions*; the present paper attempts to fill in systematically information in order to close this gap. We do not include computation of energies or other properties but we include numerous literature references to papers that provide such computations. In figures showing *portions of infinite lattices* the peripheral hydrogens will not be shown. However, in figures of *molecules* the peripheral hydrogens will always be shown.

In a graphene sheet,  $sp^2$ -hybridized carbon atoms are bonded to their neighbors by covalent bonds oriented along three directions, with bond angles of  $120^\circ$ . Accordingly, if one inserts into such bonds one or several pairs of triply-bonded carbon atoms, one should discuss uni-, bi-, and tri-directional combinations of  $sp$ - and  $sp^2$ -hybridized carbon atoms. When the graphene sheet is folded to form nanocones, nanotubes, nanoscrolls, nanotori, or fullerenes, the bond angles are slightly different from  $120^\circ$  but one can still have the same three separate cases for inserting  $sp$ -hybridized carbon atoms. One may also consider, in addition to replacing each C–C bond tridirectionally by a C–C≡C–C bond sequence, *semiconservative structures* in which one conserves certain benzenoid rings.

In the diamond lattice,  $sp^3$ -hybridized carbon atoms are bonded to their neighbors by covalent bonds oriented along four directions, with bond angles of  $109.5^\circ$ . Accordingly, if one inserts into such bonds one or several pairs of triply-bonded carbon atoms, one should discuss uni-, bi-, tri- and quadri-directional combinations of  $sp$ - and  $sp^3$ -hybridized carbon atoms. In this case there are no further subclasses, i. e. neither “folded” lattices, nor conserved adamantane units, may possibly be taken into account, unless one considers the fourth dimension. However, one can replace in the adamantane lattice some carbon atoms in certain positions by a tetrahedral unit of carbon atoms leading to the so-called T-carbon [60]; of course, such a replacement will lead to considerable angle strain.

## 2. THE FOUR DIAMOND-YNES: LATTICES WITH $sp^3$ - AND $sp$ -HYBRIDIZED CARBON ATOMS

Around each  $sp^3$ -hybridized carbon atom in the diamond lattice, the four single covalent bonds are oriented along four directions in the tridimensional space. Based on this observation, Balaban and Schleyer have introduced a naming and coding system for constitutional isomers of diamond hydrocarbons (diamondoids) using the dualist graph approach and the four digits 1, 2, 3, and 4 for these directions [61]. When the procedure for isolating and purifying diamondoids from petroleum revealed the richness of diamondoid structures, this coding system proved its usefulness. However, for specifying the location and stereochemical features of substituted diamondoids, one needs more information; the complicated IUPAC (von Baeyer) nomenclature can provide this information, and for three classes of diamondoids a general algorithm was found for providing this IUPAC nomenclature and numbering of carbon atoms: zigzag blade-like diamondoids [62], tight-helical diamondoids, and diamondoids whose dualists are *all-trans*-perhydroacenes [63].

### 2.1. Lattices with Unidirectional Triple Bonds Along $sp^3$ -Hybridized Bonds

Fig. (1) shows what happens when all C–C bonds in the diamond lattice that are parallel to one of the four tetrahedral directions become replaced by a sequence of C–C≡C–C bonds. As seen in Fig. (1), the MM2 minimal-energy optimization for the small fragment of the “unidirectional diamond-yne” leads to slight curving of the peripheral C–C≡C–C bonds, but in the center one sees that bond angles

for internal  $sp$ -hybridized carbon atoms are indeed  $180^\circ$ . As a result of this uni-directional elongation, each adamantane unit looks *stretched* along one of the four tetrahedral directions; there are two kinds of the four chair-shaped hexagons: one hexagon with all six short sides, and three hexagons with two longer sides than the remaining four short sides.

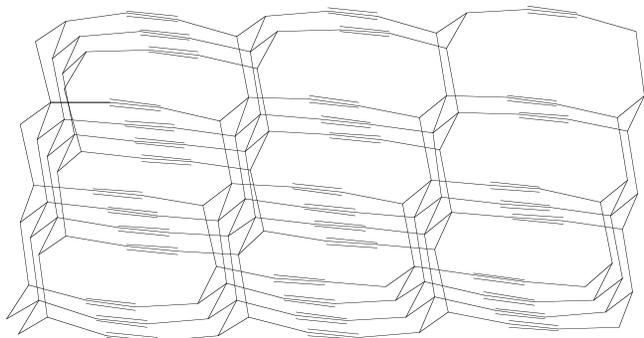


Fig. (1). A small fragment of “unidirectional diamond-yne”.

## 2.2. Lattices with Bidirectional Triple Bonds Along $sp^3$ -Hybridized Bonds

When the diamond lattice is expanded along two directions, one can see in Fig. (2) that now each adamantane unit has become a flattened, almost square box, in which there are two kinds of chair-shaped hexagons: either with four longer sides than the two shorter remaining ones, or vice-versa with two longer sides than the four shorter remaining ones. There is no observable curvature for the  $C-C\equiv C$  bond sequence.

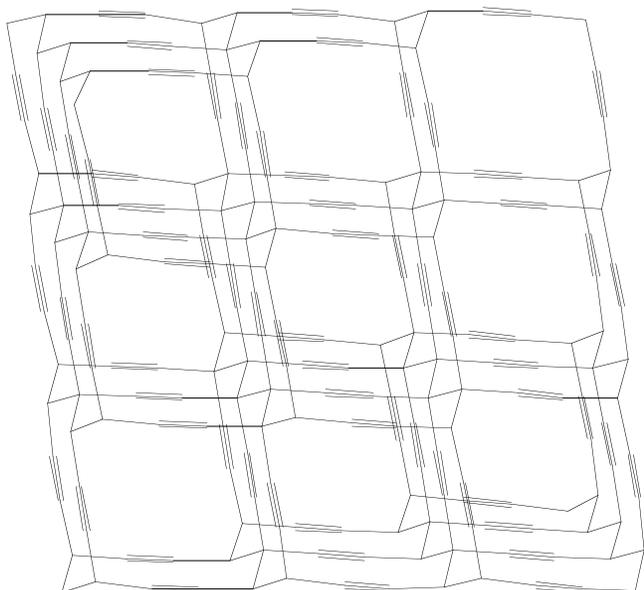


Fig. (2). A small fragment of “bidirectional diamond-yne”.

## 2.3. Lattices with Tridirectional Triple Bonds Along $sp^3$ -Hybridized Bonds

Through expansion of the diamond lattice along three directions, as seen in Fig. (3), in an adamantane unit there are again two kinds of chair-shaped hexagons: one kind with all longer sides, and three kinds with four longer sides than

the two remaining shorter ones. Adamantane units look now larger, but *compressed* along one direction.

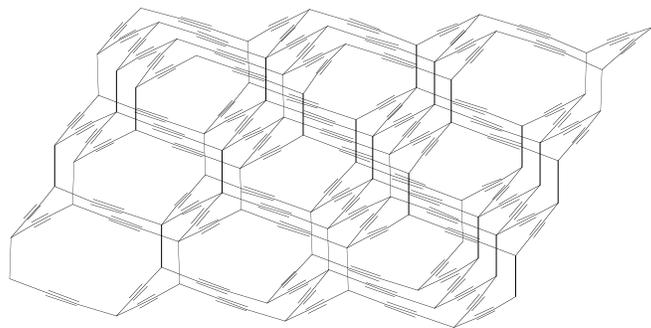


Fig. (3). A small fragment of “tridirectional diamond-yne”.

## 2.4. Lattices with Quadridirectional Triple Bonds Along $sp^3$ -Hybridized Bonds

By expansion of the diamond lattice along four directions, adamantane units have now regained their symmetry and are completely expanded along all four directions. Each adamantane unit has four identical chair-shaped larger hexagons (Fig. 4).

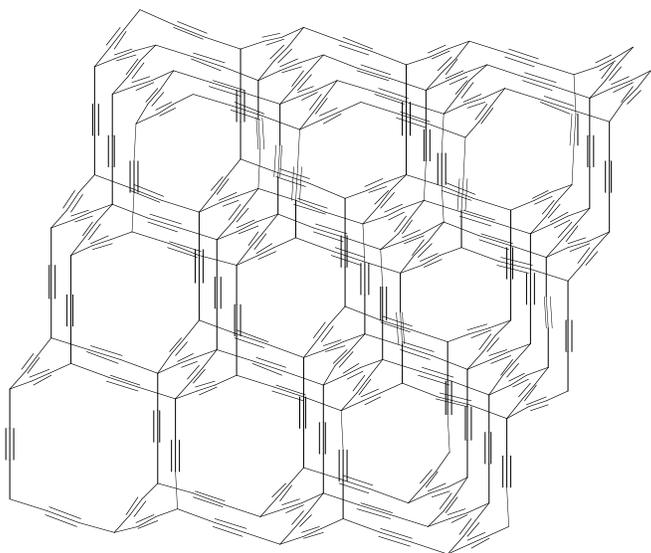


Fig. (4). A small fragment of “quadridirectional diamond-yne”.

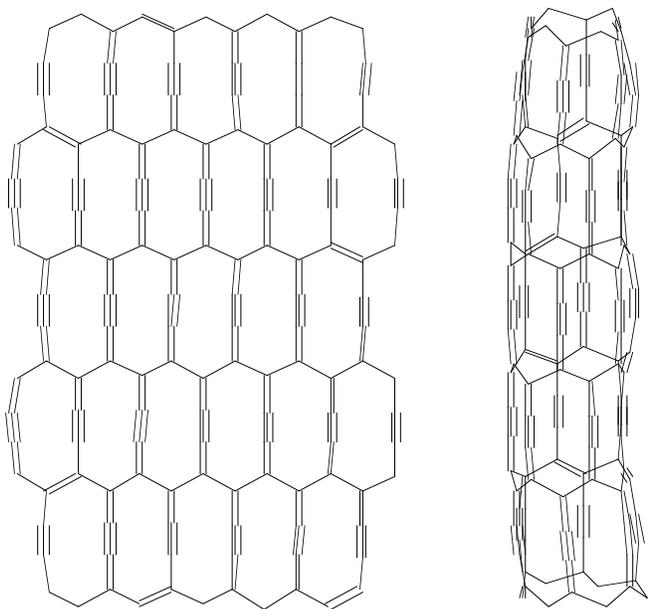
## 3. THE THREE GRAPHEN-YNES AND THE CORRESPONDING EXPANDED NANOTUBES

Expansion of an infinitely large graphene sheet along the three separate directions around each  $sp^2$ -hybridized carbon atom can be followed by folding the expanded sheet so as to form an infinitely long nanotube or nanocone; by curving the nanocone and closing the ends one would obtain an “infinitely large nanotorus” (although it is hard to imagine and infinitely large doughnut).

### 3.1. Lattices with Unidirectional Triple Bonds Along $sp^2$ -Hybridized Bonds

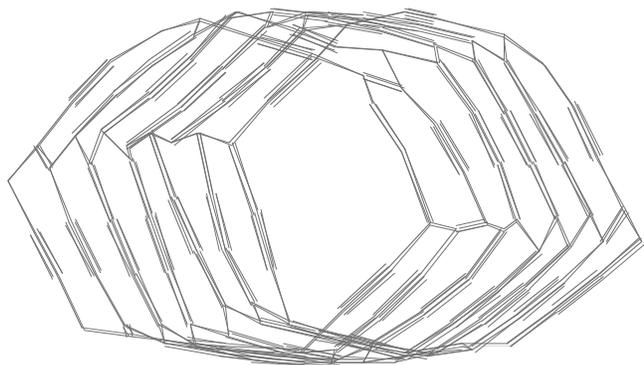
By intercalating a pair of  $sp$ -hybridized carbon atoms at each carbon in graphene according to one of the trigonal directions one obtains “unidirectional-graphen-yne”, and by folding it the result is a nanotube elongated in one direction parallel to the nanotube axis, as seen in Fig. (5). Folding and

curvature orthogonal to this direction (as in armchair nanotubes) would cause a large angular strain, and therefore we will ignore this alternative. The CambridgeSoft representation of cumulenic bonds is not correct, and owing to this deficiency of the program, the next figures will adopt a different representation (with cylindrical bonds), in which the bond multiplicity is not apparent.



**Fig. (5).** A small fragment of “unidirectional graphen-yne” and the corresponding zigzag nanotube.

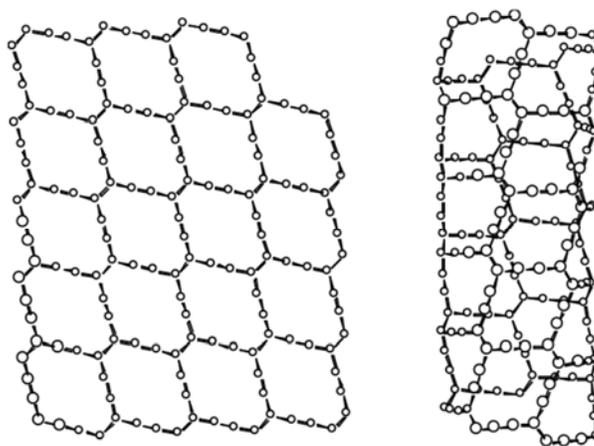
There are two opposed triads of carbons from the initial regular hexagons of graphene, which look stretched in the direction paralleling the pair of  $sp$ -hybridized carbon atoms. The folding can take place as shown in Fig. (5), along the zigzag sequence of initial CC bonds, or according to other Coxeter vectors [64], yielding armchair or chiral nanotubes; for small diameters of the nanotube, a prismatic structure results, as seen in Fig. (6).



**Fig. (6).** A small fragment of a unidirectional armchair nanotube.

### 3.2. Lattices with Bidirectional Triple Bonds Along Two $sp^2$ -Hybridized Bonds

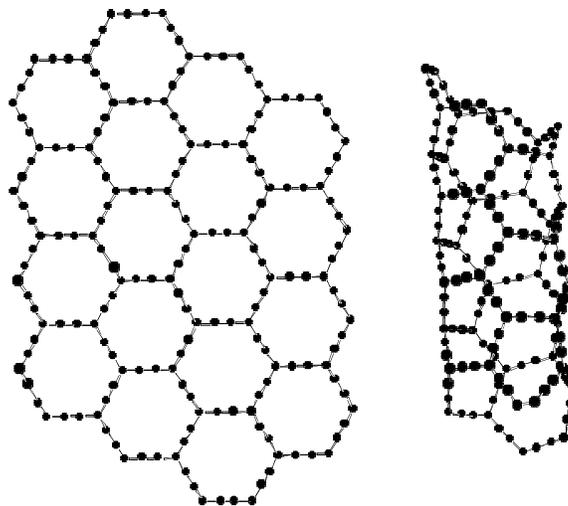
In this case the initial regular hexagons of graphene look as having been stretched by pulling two opposed sides. Again, the folding can occur according to various Coxeter vectors, such as the one presented in Fig. (7) resulting in a chiral nanotube.



**Fig. (7).** A small fragment of “bidirectional graphen-yne” and a corresponding nanotube.

### 3.3. Lattices with Tridirectional Triple Bonds Along Three $sp^2$ -Hybridized Bonds

When every CC bond is replaced by a  $C-C\equiv C-C$  bond sequence, the hexagons become regular again but their sides have become about three times larger. The folding can lead to zigzag, armchair, or chiral nanotubes as seen in Fig. (8).



**Fig. (8).** A small fragment of “tridirectional graphen-yne” and a corresponding chiral nanotube.

## 4. SEMICONSERVATIVE LATTICES WITH $sp^3$ - AND $sp$ -HYBRIDIZED CARBON ATOMS

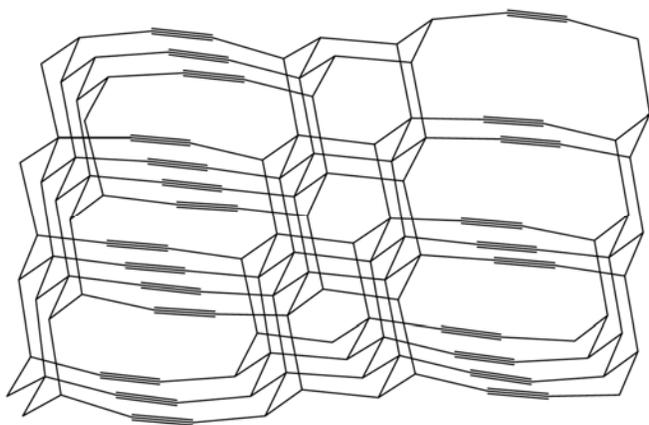
In a diamond lattice one can conserve adamantane rings and expand some surrounding C–C bonds by inserting triple bonds selectively according to the four tetrahedral directions.

### 4.1. Semiconservative Infinite Lattices with Unidirectional $sp^3$ - and $sp$ -Hybridized Carbon Atoms

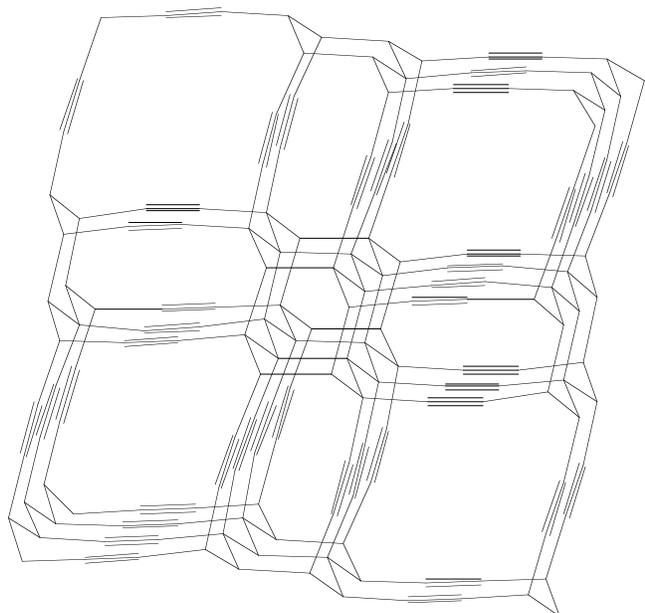
As seen in Fig. (9), layers of adamantane units can alternate with unidirectionally expanded layers.

### 4.2. Semiconservative Infinite Lattices with Bidirectional $sp^3$ - and $sp$ -Hybridized Carbon Atoms

Fig. (10) shows one possibility of a row with adjacent zigzag adamantane units can be surrounded by rows of unidirectionally and bidirectionally expanded structures.



**Fig. (9).** A small portion of a semiconservative lattice with adamantane and unidirectionally expanded layers.



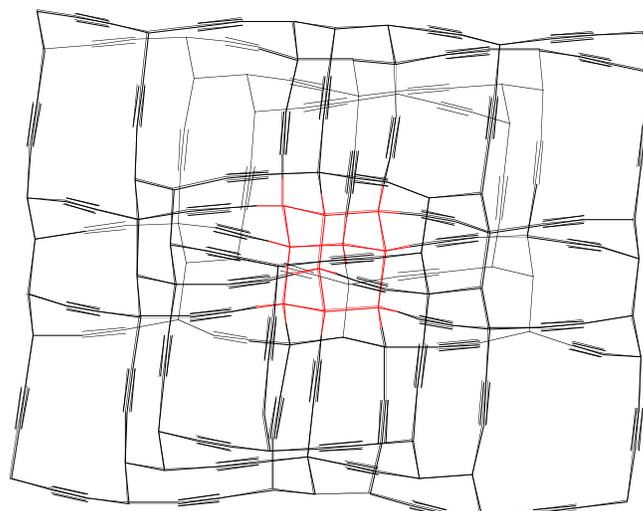
**Fig. (10).** A small portion of a semiconservative lattice with adamantane and bidirectionally expanded layers.

#### 4.3. Semiconservative Infinite Lattices with Tridirectional $sp^3$ - and $sp$ -Hybridized Carbon Atoms

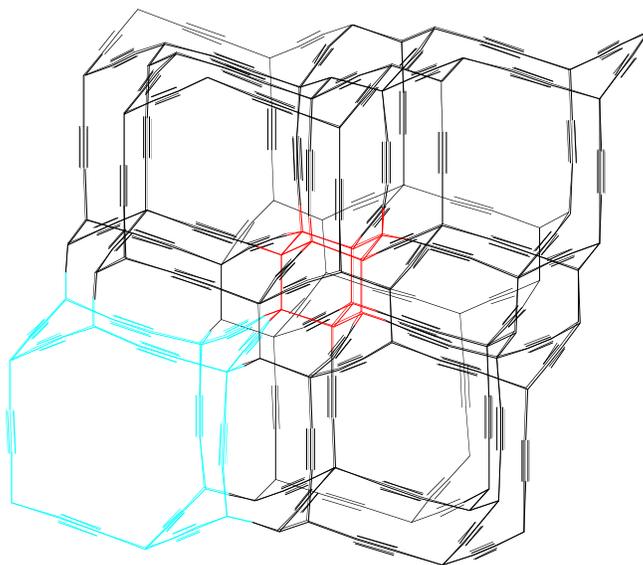
Fig. (11) presents a portion of a semiconservative lattice with adamantane units (red) and tridimensionally expanded layers.

#### 4.4. Semiconservative Infinite Lattices with Quadridirectional $sp^3$ - and $sp$ -Hybridized Carbon Atoms

One can see in Fig. (12) that a red-colored adamantane unit may be surrounded by expanded structures having triple bonds in all four possible directions. Of course, a chair-shaped hexagon of carbon atoms in an adamantane unit can be shared only with bidirectionally- or tridirectionally-expanded congeneric lattices, which still have carbon atom hexagons. A quadridirectionally-expanded unit (blue-colored in Fig. 12) can share only one carbon atom with an adamantane unit.



**Fig. (11).** A small portion of a semiconservative lattice with adamantane and tridirectionally expanded layers.



**Fig. (12).** A small portion of a semiconservative lattice having adamantane units (red-colored) surrounded by uni-, tri-, and quadridirectionally expanded layers (one such quadridirectional cell is shown in blue).

### 5. SEMICONSERVATIVE LATTICES WITH $sp^2$ - AND $sp$ -HYBRIDIZED CARBON ATOMS

One can have infinite lattices with conserved rows of benzenoid units alternating with directionally expanded rows of  $sp^2$ - and  $sp$ -hybridized carbon atoms. One such lattice called graphyne has been much discussed in the literature, as will be shown below.

#### 5.1. Unidirectional Semiconservative Lattice with Benzenoid Rings and Expanded Portions with $sp^2$ - and $sp$ -Hybridized Carbon Atoms

In Fig. (13) one can see a small portion of the unidirectional semiconservative lattice with acenic portions alternating with expanded analog portions.

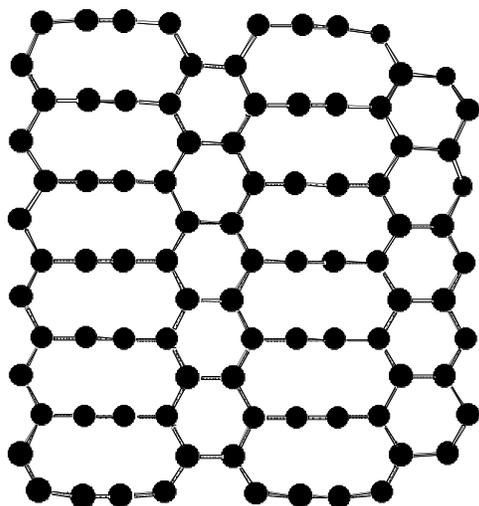


Fig. (13). A small portion of the unidirectional semiconservative lattice.

### 5.2. Bidirectional Semiconservative Lattice with Benzenoid Rings and Expanded Portions with $sp^2$ - and $sp$ -Hybridized Carbon Atoms

One can see in Fig. (14a) that benzenoid rings (red-colored) can be surrounded by two kinds of expanded rings in one and two directions; the slender unidirectionally expanded rings alternate with the plump bidirectionally expanded rings around the six CC bonds of each benzenoid ring. Slender rings can also be absent, as seen in Fig. (14b), which displays only two kinds of rings: benzenoid and plump bidirectionally-expanded rings.

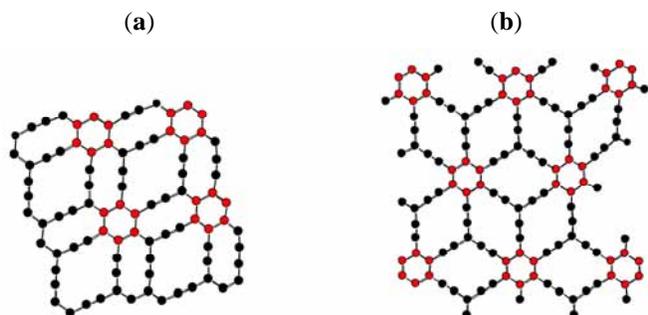


Fig. (14). Left (a): a small portion of the bidirectional semiconservative lattice with three kinds of rings. Right (b): same but with only two kinds of rings.

### 5.3. Tridirectional Semiconservative Lattice with Benzenoid Rings and Expanded Portions with $sp^2$ - and $sp$ -Hybridized Carbon Atoms

Fig. (15a) presents a lattice with benzenoid rings, again red-colored, surrounded by six bidirectionally expanded rings, which in turn are adjacent to tridirectionally expanded rings that may continue the fully expanded graphene sheet or may return to portions hosting benzenoid rings. In this case the presence of hexagonally-symmetric benzenoid rings and tridirectionally-expanded rings along with plump bidirectionally-expanded rings is unavoidable.

A different lattice, with only two kinds of rings, leaving some benzenoid rings untouched and expanding selectively the other benzenoid rings is “graphyne”, a lattice composed of  $sp$ - and  $sp^2$ -hybridized carbon atoms that has benzenoid

rings connected by triple bonds along all three directions around  $sp^2$ -hybridized carbon atoms (Fig. 16). The trisubstituted [12] annulene ring has 3-fold symmetry with alternating triple and benzene-type bonds. Baughman *et al.* predicted nonlinear optical behavior for graphyne [51].

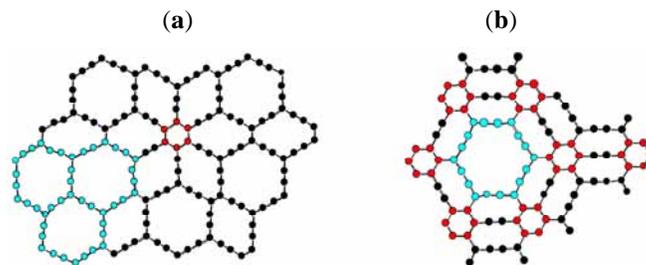


Fig. (15). (a) and (b) A small portion of the tridirectional semiconservative lattice with 3 kinds of rings; (c) Same but with only two kinds of rings. Benzenoid rings are red, tridirectionally-expanded rings are blue.

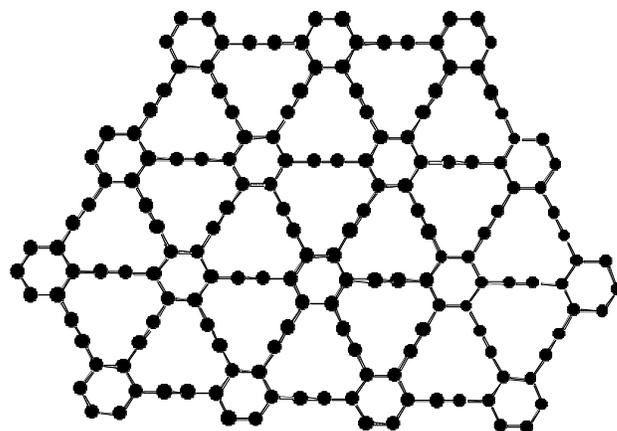


Fig. (16). A small fragment of graphyne.

Most of the hypothetical lattices and molecules discussed above have not been obtained experimentally in significant amounts; the next lattice, called graphdiyne (which is a tridirectional assembly of  $sp$ - and  $sp^2$ -hybridized carbon atoms that has benzenoid rings connected by a  $-C\equiv C-C\equiv C-$  bond sequence) has been predicted to be the most stable of the various diacetylenic non-natural carbon allotropes (Fig. 17). Again, one can imagine such an expansion along only

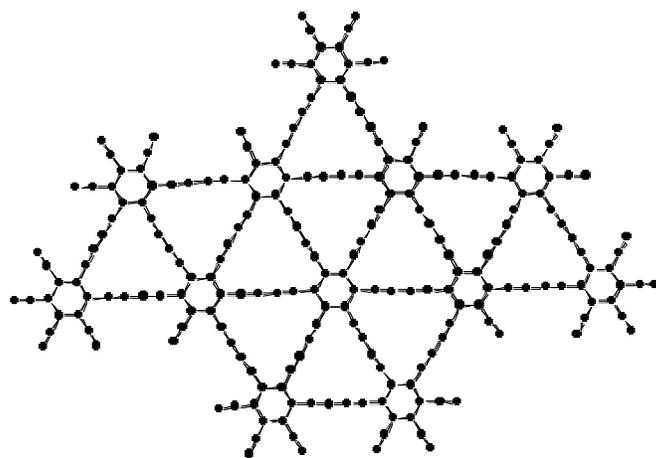


Fig. (17). A small fragment of the tridirectional graphdiyne lattice.

one or two directions around  $sp^2$ -hybridized carbon atoms in graphene or benzenoids. Of course, in  $C-(C\equiv C)_k-C$  bond sequences replacing CC bonds, instead of  $k = 2$  one may have higher  $k$  values, but then the inherent high energy content of triple bonds will lower the kinetic and thermodynamic stability of such systems.

## 6. RELATED CARBON NANOSTRUCTURES

In addition to expanding infinite carbon lattices by intercalating triple bonds into CC bonds, it is of interest to discuss similar expansions of other carbon nanostructures such as diamondoids, benzenoids, nanocones, and fullerenes.

### 6.1. Carbon Nanostructures with $sp^3$ - and $sp$ -Hybridized Carbon Atoms

In adamantane, if C–C bonds at each carbon atom that are parallel to one of the four tetrahedral directions are sequentially replaced by the bond triplet C–C≡C–C, one obtains “ $sp$ -expanded” adamantanes presented in Fig. (18).

A semiconservative expansion for diamondoids can give rise to interesting structures, for instance isomerism in unidirectionally expanded [1212]pentamantane for one marginal or internal adamantane unit (Fig. 19).

Another possibility for a semiconservative expansion of the diamond lattice results from replacing carbon atoms by a tetrahedral assembly of four carbon atoms and connecting these tetrahedra by  $-(C\equiv C)_k-$  bond sequences. Fig. (20) shows such a portion of the lattice for  $k = 1$ , in which ten tetrahedra are assembled in an analog of an adamantane unit, with red-colored and grey-colored tetrahedra corresponding to adamantane’s CH and  $CH_2$  groups, respectively. One can see that there are many rotational degrees of freedom, so that the structure presented in Fig. (20) is not the ground state. Analogous expansions may be imagined with Diudea’s diamond- $D_5$  [65].

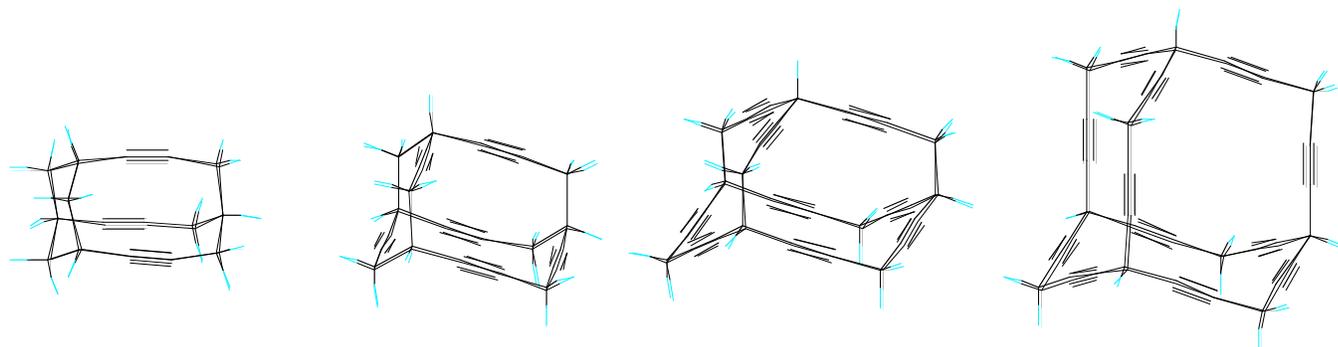
### 6.2. Carbon Nanostructures with $sp^2$ - and $sp$ -Hybridized Carbon Atoms

In benzene, if two, four and six CC bonds that are parallel to the three trigonal directions are sequentially replaced by the bond sequence C–C≡C–C, one obtains “ $sp$ -expanded” benzenoids presented in Fig. (21). It should be emphasized that these expanded rings still obey the Hückel Rule, and in the following one will see that any expansion that would lead to the formation of 8-membered rings is avoided.

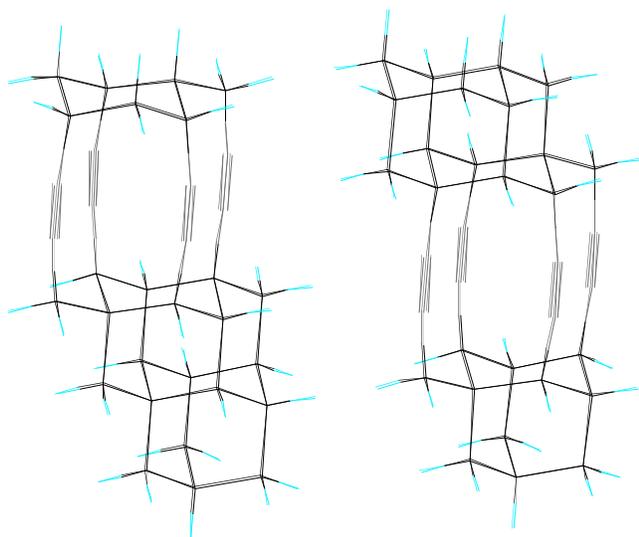
Comprehensive reviews of subunits of graphyne and graphdiyne and their subunits have been published by Haley [35-38], who was instrumental in the renaissance of annulene chemistry. In Fig. (22), the vertices symbolize benzenoid rings, shorter edges in the first row symbolize a C–C≡C–C bond sequence, and longer edges in the last two rows symbolize a C–(C≡C)<sub>2</sub>–C bond sequence. All these molecular subunits have been obtained experimentally. The graphyne subunits are robust substances insensitive to heat, light or oxygen, with m.p. around 300°C, but the graphdiyne subunits are more sensitive and decompose above 200°C. All absorb light in the visible region.

Since hexadehydro-tribenzo[12]annulene (i. e. the first graphyne subunit in Fig. 21), and the first subunit of graphdiyne (the first structure in the second row of the same figure) have low solubilities, for improving solubilities of the other structures alkyl substituents were used (decyl, or *tert*-butyl) [35-38]. Some of the structures from Fig. (21), including those two mentioned in the preceding phrase, do not obey the Hückel Rule, but they are stable plane molecules. On expanding one benzenoid ring of naphthalene by converting two CC bonds into C–C≡C–C parallel bond sequences the newly formed 10-membered ring must have its four hydrogens partitioned unequally (3+1) because the structure with 2+2 hydrogens would have divergent C–C≡C–C bond sequences, which would be therefore sterically strained. The numerous dehydrobenzannulenes synthesized by Nakagawa and coworkers in the 1970 and 1980s [52, 53] have been reviewed in the second of a three-volume book [28].

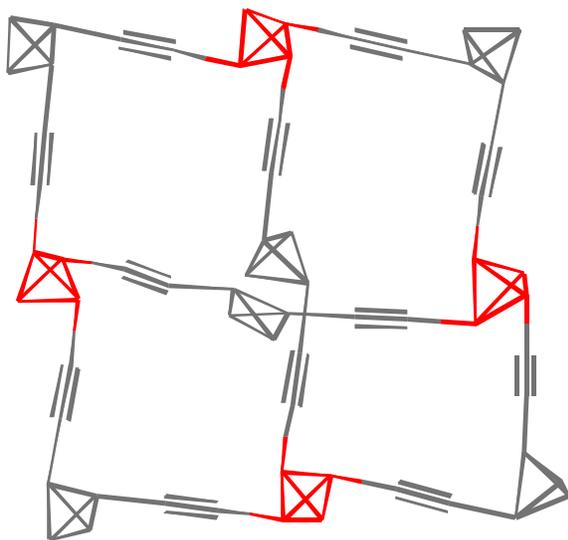
There are eight classes of nanocones as argued in several papers [66, 67]. These classes can be modeled by conical folding of graphene sheets from which one or several 60° sectors have been cut off, according to the overlapping or non-overlapping of Clar-sextet rings. Electrical properties of carbon nanotubes can also be correlated to the same Clar-sextet overlap that can occur in congruent or incongruent fashion on cylindrical folding of graphene sheets [68]. Similarly, on conical or cylindrical folding of “tridirectional graphen-yne” sheets that have been presented in Fig. (8), one can obtain  $sp$ -expanded nanocones or nanotubes. If nanotubes are not too long and if they are capped at both ends by two halves of buckyballs, they are quasi-ellipsoidal molecules composed entirely of carbon atoms.



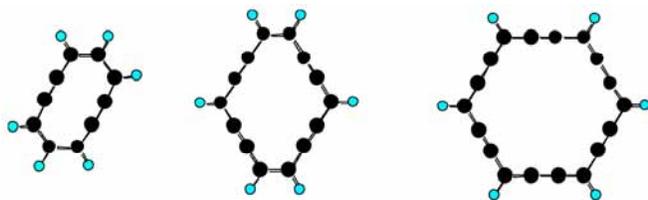
**Fig. (18).** From left to right, sequential “ $sp$ -expansion” of adamantane by replacing at each carbon atom 1, 2, 3, and 4  $H_2C-CH$  bonds by the bond sequence  $H_2C-C\equiv C-CH$ . Dangling CH bonds are blue-colored.



**Fig. (19).** Isomerism due to semiconservative unidirectional expansion of a marginal (left) or internal adamantane unit (right) in [1212]pentamantane.



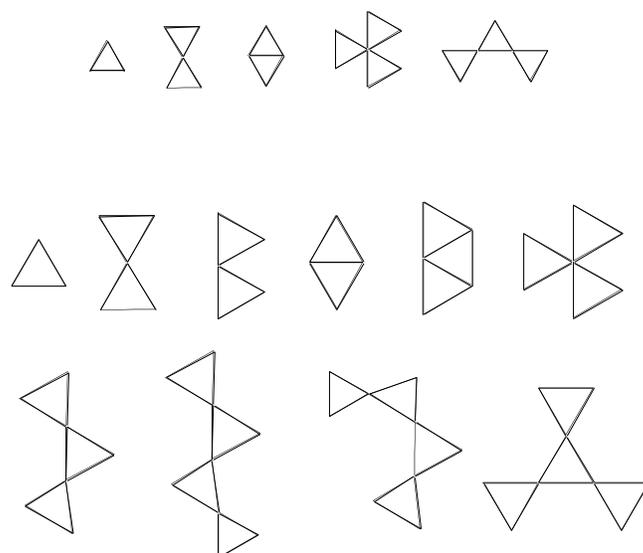
**Fig. (20).** A portion of a semiconservative expansion of T-carbon.



**Fig. (21).** Sequential “*sp*-expansion” of benzene by replacing (from left to right) 2, 4, and 6 CC bonds by the bond sequence C–C≡C–C. Hydrogens are blue-colored.

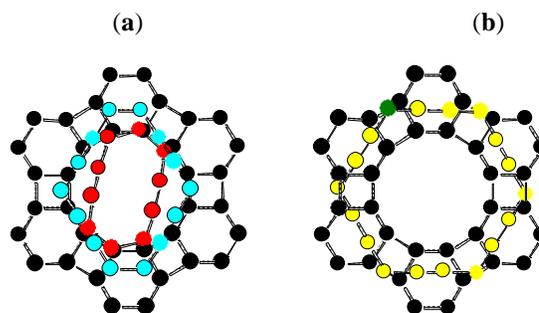
## 7. CONCLUSIONS

Expanding carbon element lattices *via* the replacement of CC bonds by C–(C≡C)<sub>k</sub>–C bond sequences (with *k* = 1, 2, etc.) may be done selectively for the four directions around carbon atoms in diamond or the three directions in graphene. Similarly, such an expansion can also be carried out “direction-selectively” for diamondoid or benzenoid hydrocarbons.



**Fig. (22).** Molecular subunits of the graphyne (upper row) and graphdiyne lattices (lower rows): vertices symbolize benzenoid rings, shorter edges in the first row symbolize a C–C≡C–C bond sequence, and longer edges in the last two rows symbolize a C–(C≡C)<sub>2</sub>–C bond sequence.

In Fig. (23a) one may see a comparison between the largest rings in graphenylene and the uni- or bidirectional graphen-yne; the 12-membered ring of graphenylene is intermediate between these two graphen-ynes; however, it is smaller than the largest ring of tridimensionally expanded graphen-yne shown in Fig. (23b), a feature that is important in the selectivity towards hydrogen molecules in mixtures with N<sub>2</sub>, O<sub>2</sub>, CO, etc. [69-72].



**Fig. (23).** Left (a): comparison between the largest rings in unidirectional graphen-yne lattices (red), bidirectional graphen-yne (blue) and graphenylene (black). Right (b): the same comparison involving graphenylene (black) and tridirectional graphen-yne (green).

Hydrogen and helium molecules differ in dimensions and shape: the ellipsoidal hydrogen molecules have dimensions that are slightly larger than those of spherical monatomic molecules of helium, so that it would be interesting to have experimental data for how mixtures of these two gases would behave towards the carbon lattices illustrated in Fig. (23). There is also a remote possibility that selectivity towards the smaller D<sub>2</sub> molecules than H<sub>2</sub> molecules may be detected in the interaction of such isotopomers with these lattices.

In the Introduction of this article it was announced that computations of energies would not be included. Suffice it to mention that references 14, 20-22, 39, 40-42, 48-51, 53-55, 70, 71 provide such calculations for infinite carbon lattices, whereas references 27-38, 52 discuss actual molecules that are stable and contain carbon atoms with sp and sp<sup>2</sup> or sp<sup>3</sup> hybridization. One may add a few other references for calculations involving carbon lattices [73-80] and for properties of the stable molecules of tri-directionally expanded benzene with phenyl and/or *tert*-butyl groups R [76]. Whereas most of the proposed carbon lattices are still to be obtained experimentally, the graphdiyne lattice has been obtained on the surface of copper [54] by cross-coupling of hexaethynylbenzene as a nanoscale film with a large area (3.61 cm<sup>2</sup>); its conductivity (2.516 × 10<sup>-4</sup> S m<sup>-1</sup>) indicates a semiconductor property.

### CONFLICT OF INTEREST

The author confirms that this article content has no conflict of interest.

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