Scientific paper

Hyper-diamonds and Dodecahedral Architectures by Tetrapodal Carbon Nanotube Junctions

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Abstract

Tetrapodal junctions are used to construct diamond-like networks and dodecahedral architectures. They can be associated with the already synthesized spongy carbon, consisting only of sp^2 covalent carbon atoms, and the zeolites, periodic structures in the Euclidean space. In this paper, the structure and stability of two zigzag tetrapodal junctions are discussed. Series of objects are built up by connecting a various number of junctions. Geometry optimization and single point computations (total energy E_{tot} and HOMO-LUMO gap energy E_{gap}) were performed at the Hartree-Fock level of theory in view of evaluating their stability. The genus of such nanostructures was calculated from the number of consisting tetrapodal junctions.

Keywords: Tetrapodal junctions, hyper – structures, multitori

1. Introduction

In 1991 Mackay and Terrones[1] studied the effect of introducing rings larger than the hexagon in the planar graphitic sheet. They designed structures embedded in surfaces of negative curvature, called „schwarzites", in honor of the German mathematician Schwarz.[2,3] Modeling such structures led to the conclusion that they are more stable than the closed fullerenes and could compete in this respect with C_{60}, the reference structure in Nanoscience. Their stability has the origin in the very low strain induced by heptagons and octagons contained in such structures while keeping the sp^2 character of the graphite. The genus of schwarzite[4–6] units is 2 (for tetrahedral symmetry) or 3 (for octahedral symmetry). Such structures can be viewed as carbon nanotube junctions.

The tetrahedral/tetrapodal junctions are particularly interesting due to their similarity with the tetrahedral sp^3 hybridized carbon atom: the valences are now nanotubes while the atom is an opened cage embedded in a surface of genus 2. Similar to the tetrahedrally coordinated carbon atom, a tetrapodal junction can be used to build various hyper-nanostructures such as dendrimers and multitori, which could act as molecular sieves.[7]

Multitori[8] are complex structures consisting of more than one single torus;[9] they are supposed to result by self-assembly of some repeating units/monomers, formed by opening of cages/fullerenes and appear in spongy carbon and in natural zeolites. Networks of sp^2 spongy carbon, with large porosity, have already been synthesized[10] and their properties studied.[11,12] The high porosity of these materials has found applications in catalysis,[13–15] in hydrogen storage,[16] thermal insulators[17,18] and molecular sieving,[19] as well.

2. Results and Discussion

We have investigated the structure and stability of two tetrapodal junctions T_{j40} and T_{j52}, their optimized geometries are presented in Figure 1. At each opening a (3,0) zigzag carbon nanotube can be attached, which were found to be narrow-gap semiconductors.[20] The junctions were designed from the corresponding tetrahedral non IPR fullerenes[21] C_{44} (T) and C_{56} (T_d) by deleting the central atom in the pentagon triples. The tetrapodal junctions have only hexagonal rings, and can be connected by three octagons at each junction.[22]

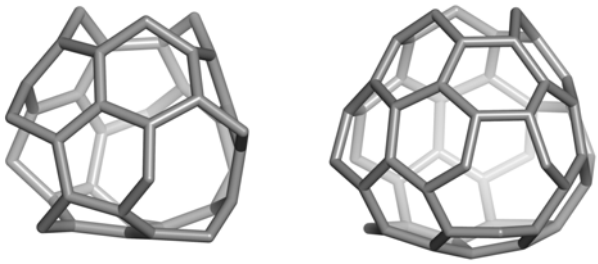

Figure 1. Tetrapodal open units: T_{j40} (left) and T_{j52} (right)

2. 1. Energetics of Tetrapodal Junctions

The geometry optimization was performed (by Gaussian 09)[23] at the Hartree-Fock level of theory, with HF/6-31G(d,p) set of parameters for the junctions and fullerenes and HF/3-21G* for the hyper pentagons and hexagons. All the structures were optimized in hydrogenated form. According to the simple Hückel model the studied fullerenes have pseudo-closed, while the junctions have pseudo-open electron configuration.[24] Therefore, to obtain the highest possible symmetry in case of the T_{j40}^{-4} junction, charges were added as required. The framework of both junctions consists of four phenalene motifs, in case of T_{j40} each fragment shares one bond with the neighboring motifs, and in case of T_{j52} the fragments are disjoint separated be one bond. It has been reported[25] that the 13-carbon phenalene cation an anion motif has a diatropic perimeter ring current like in the case of coronene,[26] predicted by the ipsocentric model.

Data obtained using HF/6-31G(d,p) method are listed in Table 1 while the data computed by HF/3-21G* are listed in Table 2. The strain energy, evaluated according to POAV theory of Haddon[27,28] is also included in these tables. One can see that the closed fullerenes (Table 1, entries 1, 4 and 6) show a higher strain in comparison to the open structures, the lowest value being for the IPR fullerene C_{60}, the reference structure in nanoscience. Observe the higher symmetry of the charged T_{j40}^{-4} resulted in higher strain, when compared with the neutral lower symmetry T_{j40}. Even the presence of hydrogen atoms on the open structures prohibits a direct comparison with the close fullerenes, data in Table 1 suggest the stability of the tetrapodal structure stability is close to that of C_{60}.

The strain decreases in structures with more than one repeating unit (see Table 2) while the HOMO-LUMO gap increases for the (hyper) cycles (Table 2, entries 3 and 6), with T_{j40}-hexagon being the most stable structure in Table 2.

2. 2. Hyper-Structures

The T_{j40}–hexagon, obtained by connecting six tetrapodal units and having the structure of the chair conformer of cyclohexane, is favored by the "intercalate" structure of T_{j40}-dimer.[4] Further addition T_{j40}-units, one can build adamantane-like T_{j40}–ada and diamantane-like T_{j40}–dia and finally a hyper-diamond structure (Figure 2).

The T_{j52}-pentagon is favored by the "eclipsed" T_{j52}-dimer. Twelve such hyper-pentagons can self-assembly to form a hyper-dodecahedron (Figure 3).

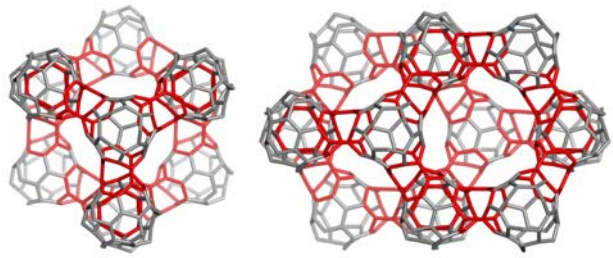

Figure 2. Hyper-diamond substructures designed by T_{j40}–unit: T_{j40}–ada (left) and T_{j40}–dia (right)

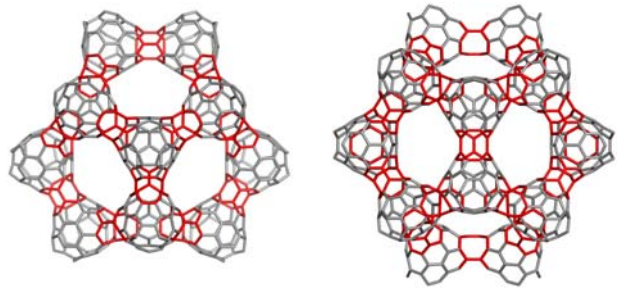

Figure 3. Multitori by T_{j52}–unit: 10 units (left) and 20 units, closing a hyper-dodecahedron (right)

Design of the above structures was made by our software programs CVNET[29] and Nano Studio.[30]

Table 1. Energetic data of tetrapodal junctions and their spanned fullerenes using HF/6-31G(d,p).

	Structures	E_{tot} (eV) / C atom	E_{gap} (eV)	Strain Energy (kcal/mol)	Sym
1	C_{44}	–37.852	6.595	12.73	T
2	T_{j40}	–38.021	6.681	5.80	D_2
3	T_{j40}^{-4}	–38.006	7.414	6.70	T
4	C_{56}	–37.854	5.505	10.65	T_d
5	T_{j52}	–37.986	6.144	5.44	D_{2d}
6	C_{60}	–37.864	7.418	8.256	I_h

Table 2. Energetic data of tetrapodal junctions using HF/3-21G*.

	Structures	E_{tot} (eV)/ C atom	E_{gap} (eV)	Strain Energy (kcal/mol)	Sym
1	T_{j40}-dimer	–37.768	1.698	5.31	C_3
2	T_{j40}-trimer	–37.755	0.927	5.03	C_2
3	T_{j40}-hexagon	–37.728	7.382	4.57	D_3
4	T_{j52}-dimer	–37.741	1.247	4.90	D_{3h}
5	T_{j52}-trimer	–37.731	0.891	4.67	C_{2v}
6	T_{j52}-pentagon	–37.711	6.755	4.25	D_{5h}

2. 3. Genus in Multitori

An embedding is a representation of a graph on a surface S such that no edge-crossings occur.[31] A polyhedral lattice, embedded in an *orientable surface S* obeys the Euler formula:[32] $v - e + f = \chi(M) = 2(1 - g)$, with χ being the Euler *characteristic*. The genus g (*i.e.*, the number of simple tori consisting a given network) is related to the Gaussian curvature of the surface S by means of Euler's characteristic χ of S (Gauss-Bonnet theorem[33]) as: for $g = 0$ (case of sphere) $\chi > 0$ (positive curvature); for $g = 1$ (case of torus) $\chi = 0$ while for $g > 1$ (surfaces of high genera), $\chi < 0$, S showing a negative curvature. A surface is *orientable*, when it has two sides, or it is *non-orientable*, when it has only one side, like the Möbius strip.[4,5]

In open multitori built up from u tetrapodal junction units, the genus of structure is calculated as: $g = u + 1$, irrespective of the unit tessellation. In closed unit multitori, the genus can be calculated by formula $g = u - \sum_c(u_c \times c/2) + 1$ where c represents the number of closures per unit, while u_c is the number of units with c closures. Table 3 lists examples representing the proof of the above theorem (in agreement with the Euler's formula) in both open and closed structures built up by using the tetrapodal junctions.

3. Conclusions

Tetrapodal junctions are proved to be stable structures possible to self-assembly in building diamond-like networks and hyper-dodecahedral architectures. They can be associated to the already synthesized spongy carbon, consisting only of sp^2 covalent carbon atoms. Structural relatedness to zeolites was evidenced by the presence of large hollows.

Series of objects were built up by connecting a various number of junctions. The structure stability of tetrapodal junctions, performed at the Hartree–Fock level of theory was proved to be close to the reference fullerene C_{60}.

Genus in both open and closed hyper-structures, consisting of tetrapodal units, was calculated both by applying the Euler's formula and by the newly proposed formula using the number of repeating units.

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Table 3. Genus calculation in multi-tori by Euler formula and by the number of repeating units

	v	e	f_6	f_8	f	v-e+f	g	u
T_{j40}–ada	400	576	120	36	156	–20	11	10
T_{j40}–dia	560	810	168	54	222	–28	15	14
	v	e	f_6	f_8	f	v-e+f	g	u
T_{j52} – hyper-dodecahedron	1040	1530	360	90	450	–40	21	20
	v	e	f_6	f_8	f_5	f	v-e+f	g
T_{j40}–ada-closed	416	624	120	36	48	204	–4	3
T_{j40}–dia-closed	580	870	168	54	60	282	–8	5
	v	e	f_6	f_8	f_5	f	v-e+f	g
T_{j52} – hyper-dodecahedron-closed	1060	1590	360	90	60	510	–20	11

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Povzetek

Terapodalna stičišča smo uporabili pri konstrukciji diamantnih in do dekahhedralnih omrežij. Ta so lahko povezana z že sintetiziranim gobastim ogljikom, ki ima samo sp^2 kovalentne ogljikove atome ali pa z zeoliti, to je, periodičnimi strukturami v Evklidskem prostoru. V tem članku obravnavamo strukturo in stabilnost dveh cik-cak tetrapodalnih stičišč. Izgradili smo vrsto objektov s pomočjo različnih povezav stičišč. Izvedli smo vrsto računov geometrijske in eno točkovne optimizacije (skupna energija Etot in HOMO-LUMO vrzelv energiji Egap) naravni Hartree-Fockteorije, da smo lahko ocenili stabilnost obravnavanih nanostruktur. Rodovno funkcijo tehnano struktur pa smo izračunali iz števila tetrapodalnih stičišč.