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ORIGINAL PAPER

Computational chemistry calculations of stability for bismuth nanotubes, fullerene-like structures and hydrogen-containing nanostructures

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Abstract Using molecular mechanics (MM+), semi-empirical (PM6) and density functional theory (DFT) (B3LYP) methods we characterized bismuth nanotubes. In addition, we predicted the bismuth clusters {$Bi_{20}(C_{5V})$, $Bi_{24}(C_{6v})$, $Bi_{28}(C_1)$, $B_{32}(D_{3H})$, $Bi_{60}(C_I)$} and calculated their conductor properties.

Keywords Bismuth · Fullerene-like nanostructures · Hydrogen · Nanotubes

Introduction

Metallic bismuth is an important element, having a lot of distinct industrial applications as a component of low-melting alloys, catalysts [1, 2], or for measuring super-strong magnetic fields. Bismuth in nanostructurized forms has been mentioned in some recent monographs [3–7], reviews [8–10], patents [11, 12], and several experimental articles. Bismuth nanoparticles, nanopowders, nanowires, nanofilms and other nanostructurized forms including nanotubes [13–19] have been produced by diverse methods, such as, classic chemical reduction of bismuth salts and microwave treatment.

The structure, stability and electronic properties of bismuth nanotubes were discussed in detail by several authors [20–23]. At the present, the bismuth nanotubes are considered the only elemental nanotubes as morphologically identical analogues of carbon nanotubes [24]. Bismuth clusters Bi_n (n=2–13) were also investigated by first-principle simulations [25, 26]. In this paper, we applied a series of computational methods to characterize open and closed bismuth nanotubes and yet undiscovered fullerene-like nanostructures.

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Computational methods

We optimized 16 bismuth structures using molecular mechanics (MM+), semi-empirical (PM6) and density functional theory DFT (B3LYP) methods implemented in the programs Hyperchem 8.0.4 [27] and Gaussian 09 [28]. We calculated their vibration modes and visualized the results in the program Chemcraft v1.6 [29]. Table 1 presents a brief and general description of the computational methods we used.

The geometries for bismuth nanotubes with both open and closed extremes were optimized. In both cases, the Hamada index (n,m) was used; it corresponds to armchair (m=n) and zigzag (m=0) configurations of Bi nanotubes, varying the "n" value in the range of 3÷6. The tubular structures with open extremes were initially constructed on the basis of carbon atoms using the program VMD 1.8.7 (University of Illinois) [30], then, the program Chemcraft was used to change them to bismuth atoms. The geometry was optimized using the molecular mechanics method "MM+" in the HyperChem program v8.0. Since, bismuth atoms prefer to form tri-coordinated structures, to generate closed tubes, we added bismuth atoms manually and optimized every time in order to form the pentagons in the

Table 1 Classification and brief description of the computational methods used

Method	Brief description
Molecular mechanics methods	Each method is a particular system and it is based on a series of equations, which define the total potential energy of structure or molecule. This energy is given by a sum of energies describing the atoms outside equilibrium values {Eq. 1}: $U = \Sigma_s + \Sigma_b + \Sigma_t + \Sigma_{vdw}$ (1) (U is molecular potential energy; U_s is the energy describing the change of bond lengths; U_b is energy describing the change of bond angles; U_t is the torsional energy for rotation around a bond; U_{vdw} is the energy describing the van der Waals forces/ interactions).
Electronic structure methods	
Semi-empirical methods	These methods combine the theoretical physics with experimental results. In order to be able to approximate solution of Schrödinger equation, some integrals are depreciated and the others are estimated on the basis of experimental results.
Ab-initio methods	These methods do not use experimental parameters in computational calculations; instead, the quantum mechanics laws are used, such as application of the electron mass and charge, light speed and Plank constant.
DFT	These methods are not based on the wave function. Their basis is the electronic density function and the correlation effects, in which each electron react at a medium electronic density.

extremes and close the structure. Otherwise, the presence of pentagons would generate curvature defects in the nanostructure.

An optimization was carried out using the semi-empirical method PM6, implemented in the program Gaussian 09. The molecular dynamic calculations were performed with 2000 steps at 1 ps each one at ambient temperature (298.15 K) with the same method. For the optimized structures, where imaginary vibrational modes were not found, the calculations were refined at a higher level using the method B3LYP in combination with a series of bases def2-SVP.

As is shown below, some bismuth nanotubes tend to form the structures, which are analogues to carbon fullerenes after geometry optimization. In this respect, we selected the structures Bi_{20}, Bi_{24}, Bi_{28}, B_{32} and Bi_{60} and optimized them using the DFT theory. We constructed these Bi "fullerenes" in a similar manner using the technique described above, starting from short tubes (one hexagon ring only). The structures were then, optimized again using the electronic method B3LYP/ SBKJC ECP. Additionally, we performed computational calculations in order to investigate the possible application of fullerene-like bismuth nanoparticles as hydrogen storage.

Results and discussion

Bismuth nanotubes

The size of bismuth nanotubes we studied ranges from 60 to a maximum of 144 atoms. Zigzag- and armchair-type nanotubes with closed or open tube extremes were discussed (Table 2). In each case we tried to construct a structure with major symmetry.

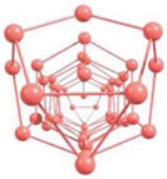
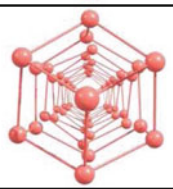
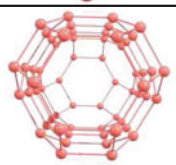
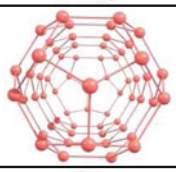
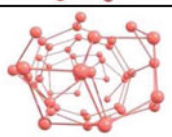
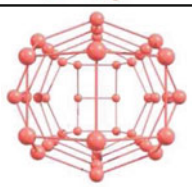
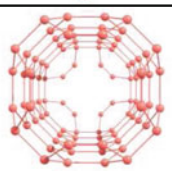
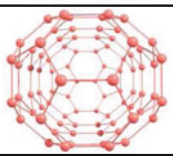
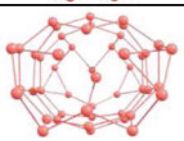
We propose that the diameter of bismuth nanotube in the function of Hamada indexes is given by Eq. 1, in which the value of the unitary vector for a sheet of bismuth hexagons is a=5.23 Å. This equation considers that the nanotubes are formed by regular hexagons. However, after relaxing this structure, the change of bond angles and lengths generates slightly major diameters. A comparison of expected diameters according to Eq. 1 and observed experimentally is shown in Fig. 1. It is seen that, for the armchair-type nanotubes, this difference increases conformably with increase of the Hamada index. In case of zigzag-type nanotubes, the difference is expressed more clearly for diameters of open nanotubes.

$$d = \frac{a\sqrt{n^2 + m^2 + nm}}{\pi} \quad (1)$$

As it was mentioned above, Bi atoms were added to form pentagons in the tube extremes and molecular mechanics was used to be able to close the nanotubes manually. However, optimizing the geometry of the open nanotubes with PM6 program, the tendency to close the extremes in these structures is observed in all cases. For nanotubes with diameters less than 10 nm, this is reached forming squares in the extremes (Table 3), but for higher-diameter structures, structure relaxation is insufficient for closure of the extremes. So, it is expected that these structures are less stable in comparison with those closed manually. Even, relaxing the open (5,0) and open (4,0) structures, the atoms in the tube wall displace to the interior zone and to the extremes, losing the tubular form (Table 2).

It is known in computational chemistry, that the stability of a molecule is only relative in comparison with another molecule with equal type and number of atoms and this is associated with the potential energy surfaces in the structures. So, in order to compare nanotube

Table 2 Bismuth nanotubes, optimized with use of PM6 method

n	m	Structural type	Symmetry	No. atoms	Image	Diameter (Å)
3	**0**	open	C_2	60		5.34
3	**0**	closed	C_2	62		6.70
3	**3**	open	C_{3v}	60		9.92
3	**3**	closed	C_{3v}	62		9.93
4	**0**	open	D_{4h}	48		8.50
4	**0**	closed	C_{2v}	42		8.39
4	**4**	open	C_{4v}	96		13.32
4	**4**	closed	C_{2v}	92		12.98
5	**0**	open	C_{5v}	60		9.15

energies, the nanotubes with equal number of atoms were constructed for the cases of the open (6,6) and closed (6,6) tubes. Both model tubes are made of 144 atoms. Their energy difference of 132.924 kcal mol^{-1} was

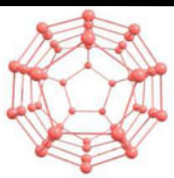
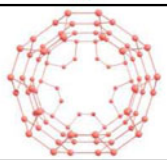
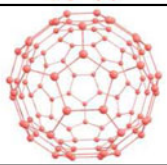
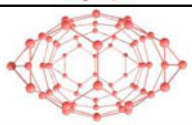
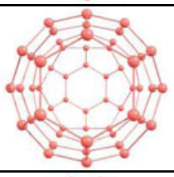
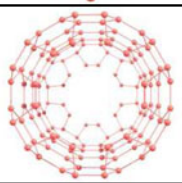
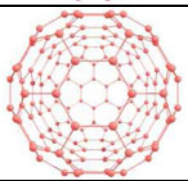
n	m	Structural type	Symmetry	No. atoms	Image	Diameter (Å)
5	**0**	closed	C_{5v}	50		10.35
5	**5**	open	C_{5v}	90		16.72
5	**5**	closed	C_i	100		16.61
6	**0**	open	C_{6v}	72		12.42
6	**0**	closed	C_{3v}	60		12.16
6	**6**	open	C_{6v}	144		20.14
6	**6**	closed	C_{6v}	144		19.92

Table 2 (continued)

obtained, taking into account the closed structure (6,6) (0 kcal mol^{-1}). These energies were calculated for the same stationary point (potential energy surface), using the DFT method (B3LYP/SBKJC VDZ ECP) resulting in more precise results. A similar analysis was carried out for the open tubes, formed of 60 atoms {(3,0) and (3,3), zigzag and armchair, respectively). For this comparison, the lowest-energy structures are of a zigzag type, which are taken as a reference to obtain ΔE (see Table 4).

Using these calculations, the gap between HOMO and LUMO molecular orbitals was analyzed. Figures 2 and 3 show the structures of the type zigzag (m=0) and armchair, respectively. It is observed in both graphics, that a better conductivity corresponds to open nanotubes. This seems to indicate that this property is geometry dependent. For the armchair-type nanotubes, the tendency to improve the conductivity is seen conformably increase of diameter.

Calculations of vibration modes suggest difficulties to be stable structures for those with more than one vibration imaginary frequency. For bismuth nanotubes, using these calculations, two negative frequencies for the open (4,4) nanotube, four negative frequencies for the open (5,5)

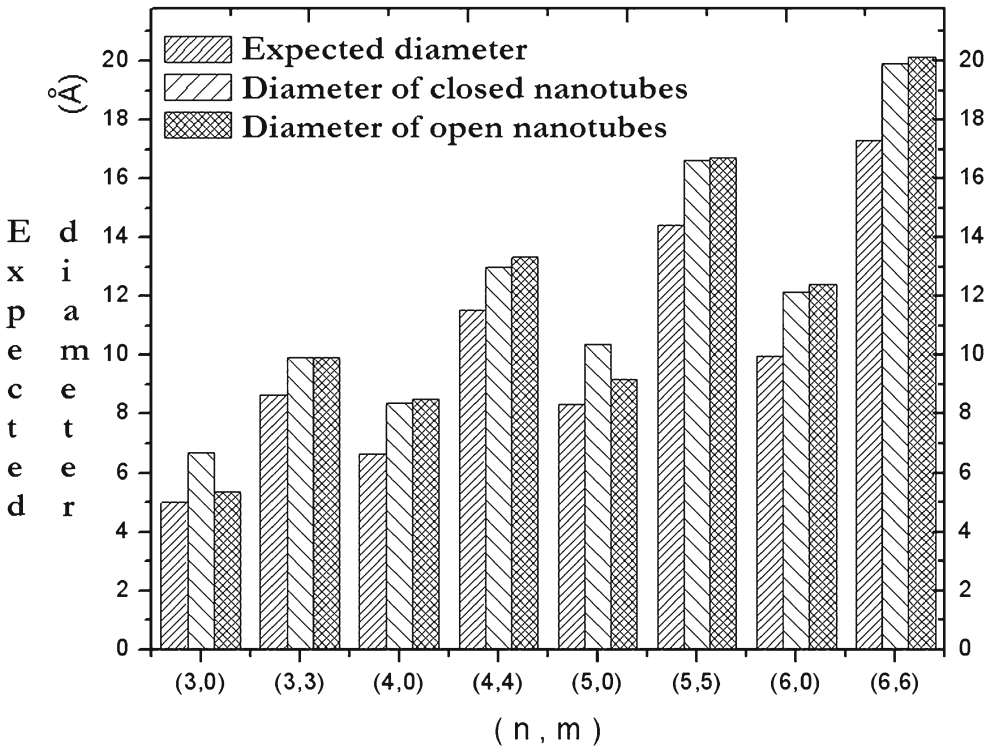


Fig. 1 A comparison of expected diameters according to Eq. 1 and obtained by PM6 method

Table 3 Comparison of nanotube extremes before and after optimization of nanostructures

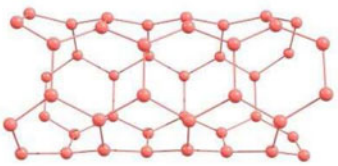
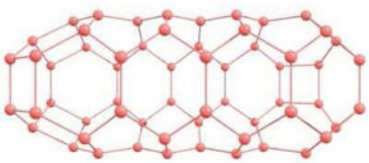
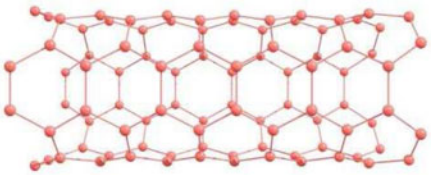
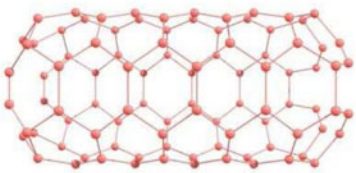
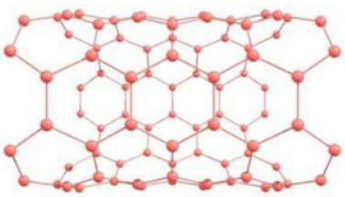
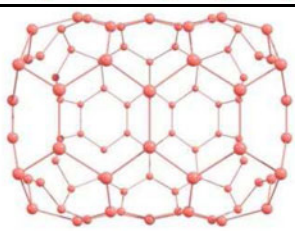
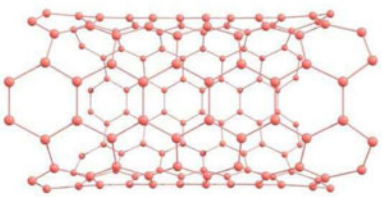
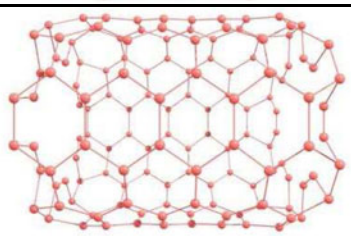
(n, m)	Before optimization	After optimization with PM6
(3,3)		
(4,4)		
(5,5)		
(6,6)		

Table 4 Comparison of nanotube energies for zigzag and armchair types

Structure type	Index	Form	Relative energy
Open nanotubes	(3,0) (3,3)	zigzag armchair	ΔE=22.88 kcal/mol
Closed nanotubes	(3,0) (3,3)	zigzag armchair	ΔE=33.04 kcal/mol

nanotube, and four frequencies for the (6,6) open nanotube were obtained.

Another analysis by calculations of molecular dynamics was carried out to evaluate the stability of bismuth nanotubes. On the basis of the results obtained, we considered performing calculations for closed nanotubes, since, none of these nanostructures collapsed during geometry optimization and none of these structure presented imaginary frequencies. These calculations were carried out also by the PM6 method, paying attention to the interaction between atoms per a determined period of time (2000 ps) at 298.15 K. Table 5 shows images of bismuth nanotubes before and after the molecular dynamics simulation for closed nanotubes. It can be observed that the structures are not collapsed; their changes are minimal. The structures (3,0) and (5,5) seem open in their extremes; however, the interatomic distance is considerably shorter than the van der Waals radii.

Bismuth "fullerenes"

The tendency of open nanotubes, seen in Table 5, to close their extremes, and the stability, - acquired by the closed structures, suggest the existence of structures, - similar to fullerenes. For example, in order to close the (5,5) tube, an arrangement of pentagons, surrounded by hexagons, is formed. If this "tube" has only one ring of hexagons in its length, the resulting structure is spherical containing 20 hexagons, 12 pentagons, and 60 atoms, *i.e.*, this is fullerene analogue. We studied by PM6 technique five of such fullerenes: Bi_{20}, Bi_{24}, Bi_{28}, Bi_{32}, and Bi_{60}. The structures were optimized using molecular mechanics method (MM+) in order to form spheres in the same manner, as the nanotube extremes are closed. Additionally, the optimization by DFT/B3LYP/SBKJC ECP method was applied, resulting that all structures were characterized as local minimums. Their vibration modes were also calculated; all frequencies were found to be positives. The bond lengths vary from 2.91 Å to 3.45 Å; these values are less than the van der Waals radii for bismuth (4.0 Å). Table 6 shows a summary of these structures. Among them, Bi_{20} and Bi_{60} are spherical; the other three structures are described using the major diameter (D1) and minor diameter (D2). Comparing C_{60} and Bi_{60}, the diameter of the fullerene is 7.1 Å, meanwhile the diameter of Bi_{60} is 15.1 Å. Regarding the conductivity we can affirm that

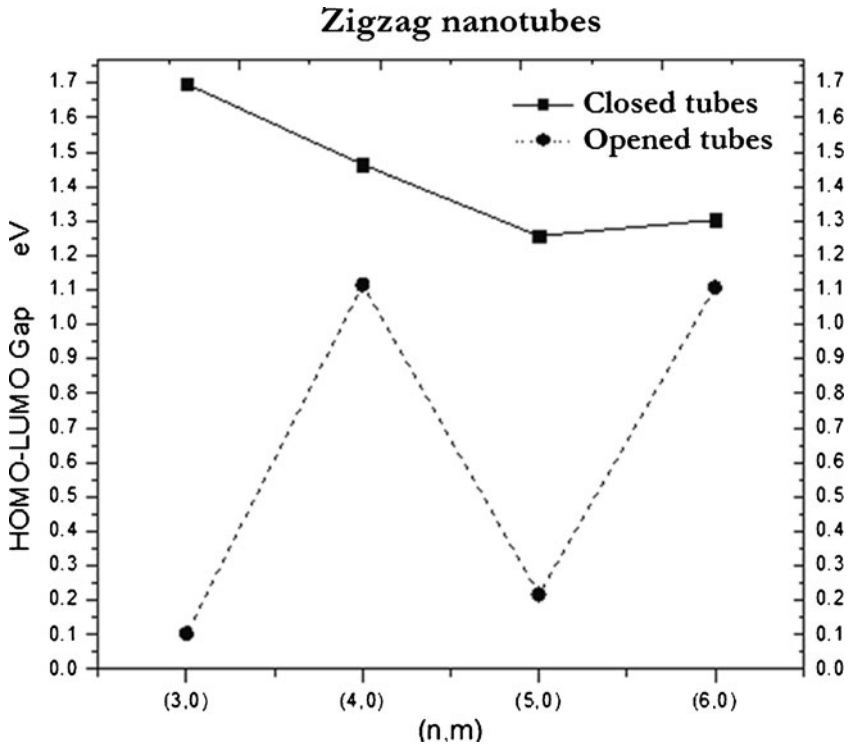


Fig. 2 Gap between the HOMO-LUMO for zigzag tubes

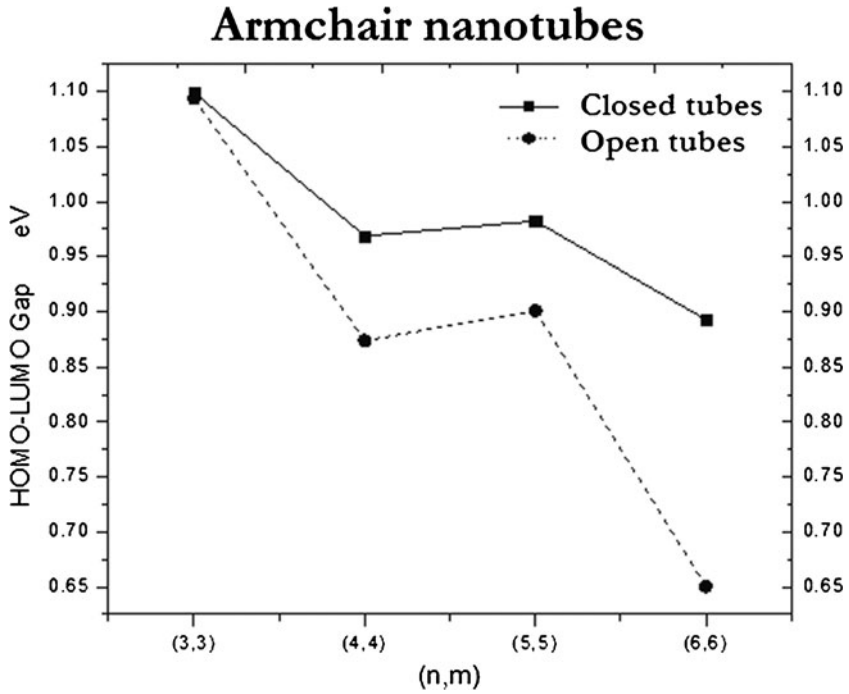


Fig. 3 Gap between the HOMO-LUMO for armchair tubes

the bismuth compounds Bi_{20}, Bi_{24}, and Bi_{28} are not conductors; the compounds Bi_{32} and Bi_{60} are semiconductors.

This behavior (conductivity dependant on the geometry) is similar to the results above for bismuth nanotubes. Table 7 shows the tendency of the HOMO-LUMO gap to decrease; increasing the size of structure accordingly. Graphics of the electron density of the HOMO and LUMO identify the zones of major reactivity in the structure. The HOMO zones tend to donate their electrons to form a bond and the LUMO zones tend to accept them.

Bismuth fullerenes containing hydrogen

A useful application of bismuth nanotubes and fullerenes could be the storage of small molecules, for instance hydrogen. In order to determine the maximal number of H_2, that a structure can hold, we added hydrogen molecules to the interior of the fullerene-like bismuth nanostructures and optimized the structures using the PM6 program. We used the same method to obtain the vibration modes. The vibration modes remained positive for five structures that optimized with the maximal possible quantity of hydrogen. These structures are shown in Fig. 4.

Percentage of gravimetric densities of hydrogen for these structures are as follows: $H_{30}Bi_{20}$ (1.77% H), $H_{30}Bi_{24}$ (1.48% H), $H_{36}Bi_{28}$ (1.52% H), $H_{52}B_{32}$ (1.99% H), $H_{210}Bi_{60}$ (4.04% H). As it was reported earlier [31], an objective of 6% in the gravimetric density of hydrogen is considered feasible for use of a material in hydrogen storage. As is shown in Fig. 4, the optimization of bismuth structures, containing hydrogen, does not destroy nor deform them. However, the bond length Bi-Bi slightly increases (some bonds up to 3.62 Å exist), expanding the structure in all directions.

Another interesting change for fullerene-like bismuth nanostructures containing hydrogen is an increase of their conductivity, which can be observed in Fig. 5. Both bismuth "fullerenes" with or without hydrogen tend to increase their conductivity conformably increasing structure size. However, even in the biggest structure among all studied nanoforms (Bi_{60} y $H_{210}@B_{i60}$), the electronic gap does not show magnitudes less than 1 eV, so none of these structures are conductive. This contrast with bismuth nanotubes seems to have a relation with presence of pentagons in the structures. For example, open nanotubes (there are no pentagons in this type of nanotubes) are, in all cases, better conductors in comparison with closed nanotubes, which, in its turn, are better conductors than fullerene-like structures.

The molecular dynamics calculations were carried out using the PM6 method, using 2000 steps at 298.15 K. The data in Table 8 shows that bismuth structures do not collapse or deform. However, in all cases the structure is not able to confine hydrogen molecules. Also, the calculations were made at lower temperatures (154 K y 0 K), obtaining the same results. With exception of the Bi_{20} structure, which is not formed by any

Table 5 Structure of closed Bi-nanotubes before and after molecular dynamics calculations

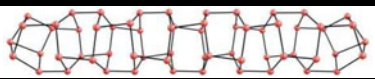
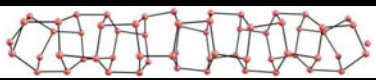
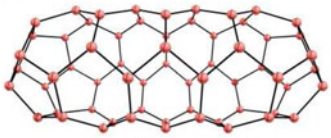
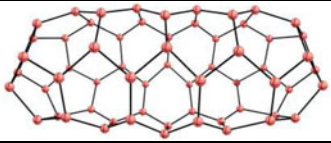
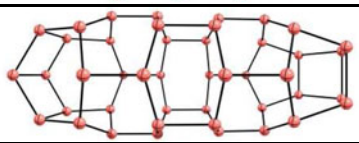
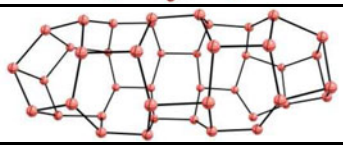
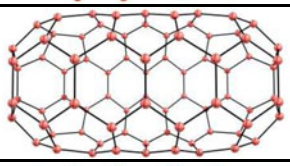
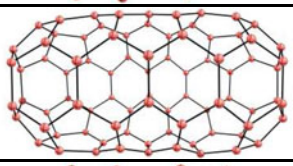
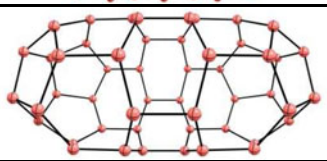
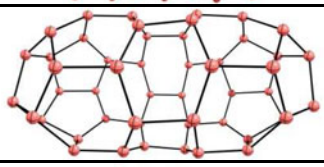
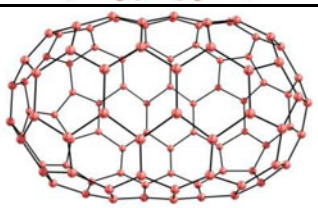
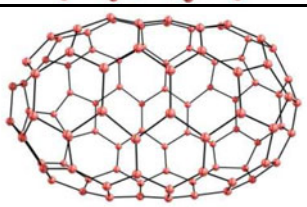
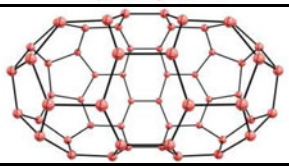
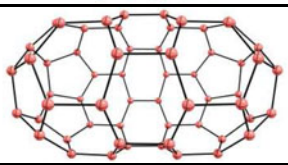
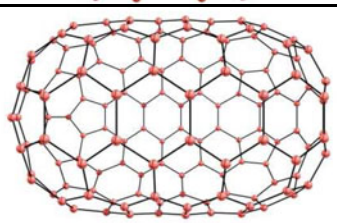
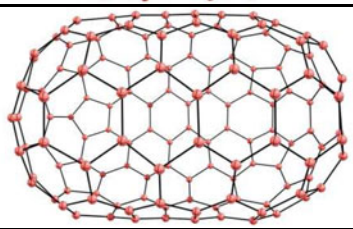
(n, m)	Structure before DM	Structure after DM
(3,0)		
(3,3)		
(4,0)		
(4,4)		
(5,0)		
(5,5)		
(6,0)		
(6,6)		

Table 6 Bismuth "fullerenes"

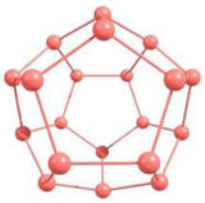
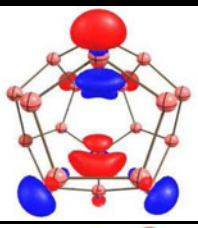
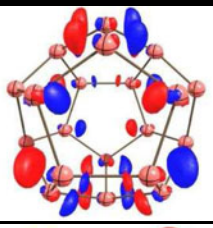
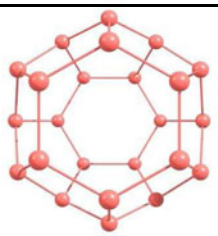
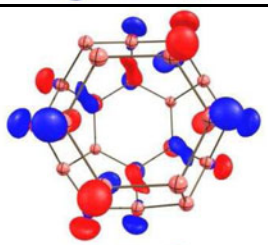
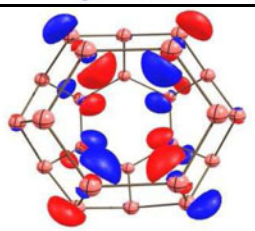
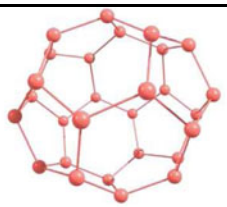
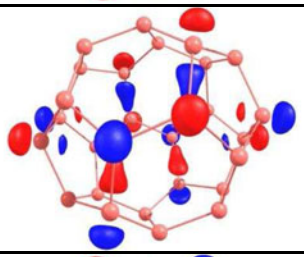
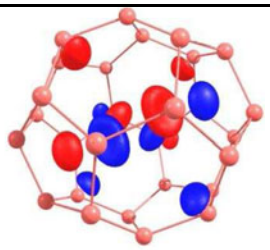
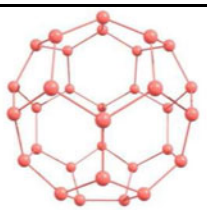
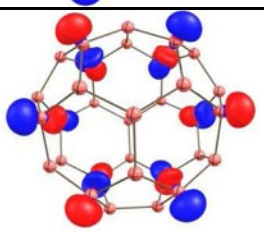
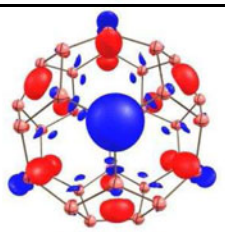
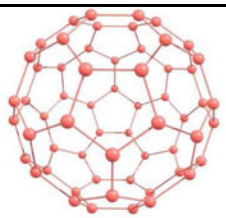
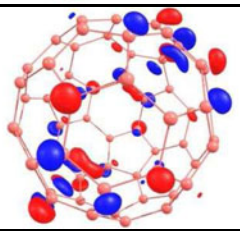
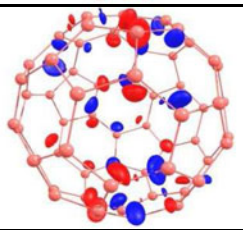
Structure	Symmetry	D_1 (Å)	D_2(Å)	Gap (eV)
Bi_{20}	C_{5v}	8.51		2.3
Bi_{24}	C_{6v}	9.54	6.62	2.2
Bi_{28}	C_1	11.06	9.59	2
B_{32}	D_{3h}	11.52	8.74	1.8
Bi_{60}	C_I	15.1		1.45

hexagon, it is observed that the hydrogen molecules escape through centers of some hexagons (diameter 0.58 nm), which form these Bi structures.

Conclusions

The existence of bismuth nanotubes is confirmed by the calculations performed and the computational chemistry

Table 7 HOMO and LUMO graphics for bismuth "fullerenes" (bismuth atoms are colored pink)

	Optimized structure	HOMO	LUMO
Bi_{20}			
Bi_{24}			
Bi_{28}			
B_{32}			
Bi_{60}			

methods we used in this study. All applied methods showed good accordance between each other; no contradiction has been noted. The bismuth nanotubes presented the following main characteristics: a) the structures correspond to local energy minimums, which imply their stability; b) up to the (6,6) arrangement, the nanotubes possess semiconductive properties; the conductivity is better for open nanotubes. In addition, using the same calculation methods, the existence of fullerene-like bismuth nanostructures was predicted, among which five structures {$Bi_{20}(C_{5V})$, $Bi_{24}(C_{6v})$, $Bi_{28}(C_1)$, $B_{32}(D_{3H})$, $Bi_{60}(C_I)$} were studied, showing the following characteristics: a) the structures correspond to local energy minimums; b) the structures Bi_{20}, Bi_{24} and Bi_{28} are semiconductors, meanwhile Bi_{32} and Bi_{60} are conductors, c) in all cases, hydrogen presence in Bi "fullerenes" improves the conductivity; d) the DFT calculations indicate that the hydrogen gravimetric density inside these structures can reach 4.04%; however, according to the molecular dynamics results, it is concluded on the unavailability of these nanoforms for hydrogen storage purposes due to the large diameters of the hexagons (0.58 nm), allowing the hydrogen molecules to escape out of the

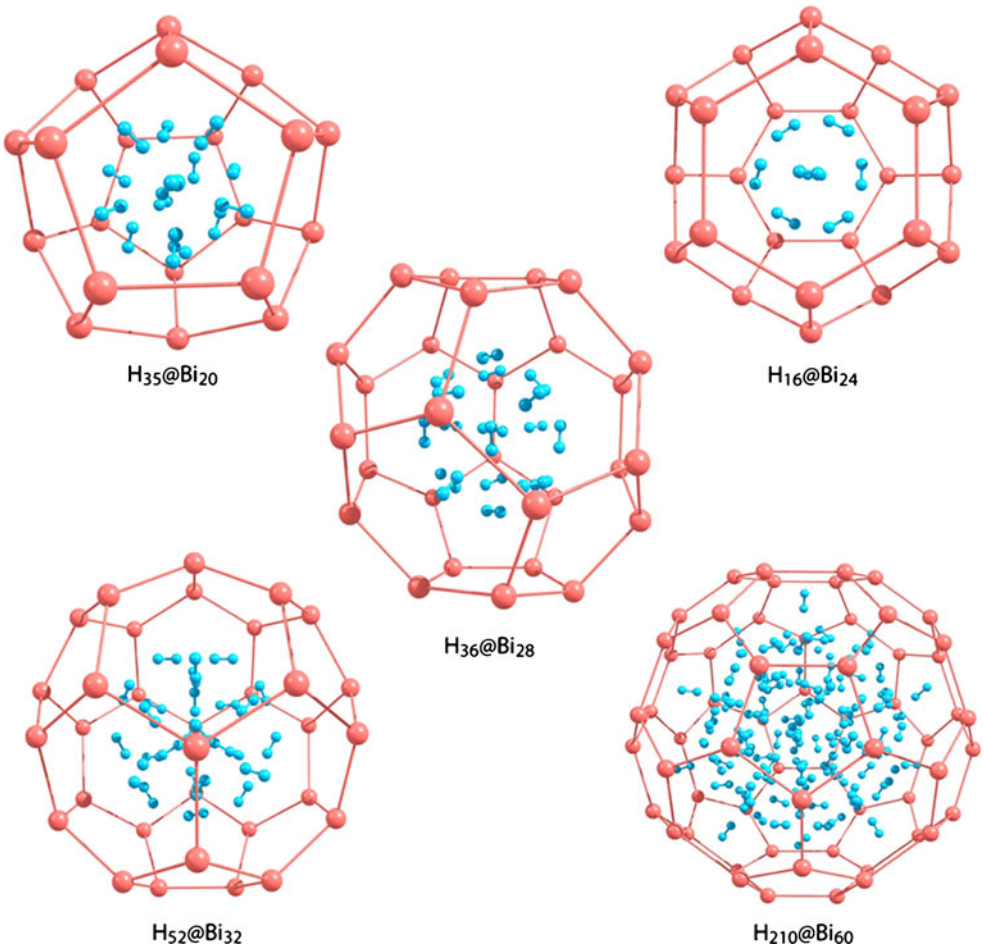


Fig. 4 Bismuth "fullerenes" with hydrogen molecules

nanostructure, d) the conductivity of Bi "fullerenes" is less in comparison with closed nanotubes. In its turn, the conductivity of open nanotubes is better than that of closed nanotubes. So, the presence of pentagons in the structure reduces the conductivity, also generating structural concavity.

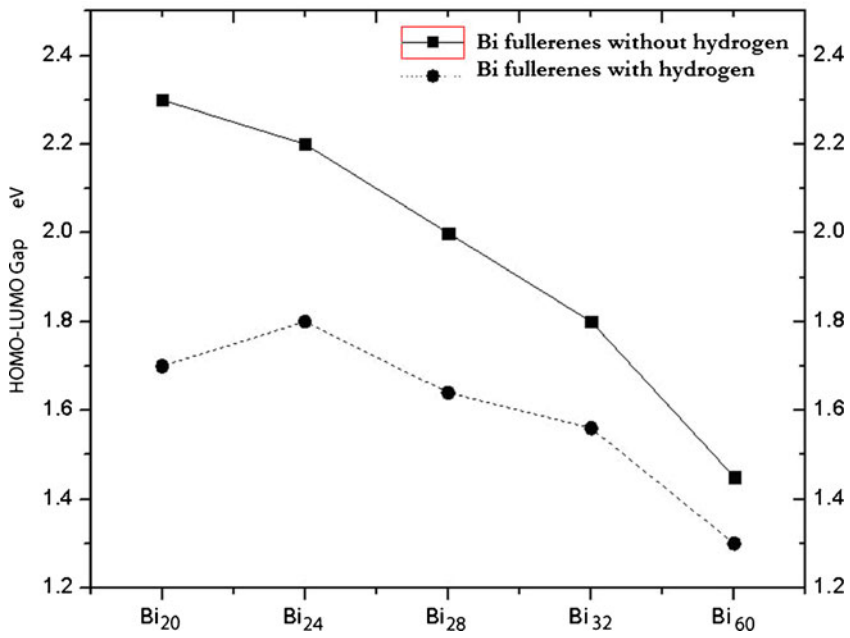
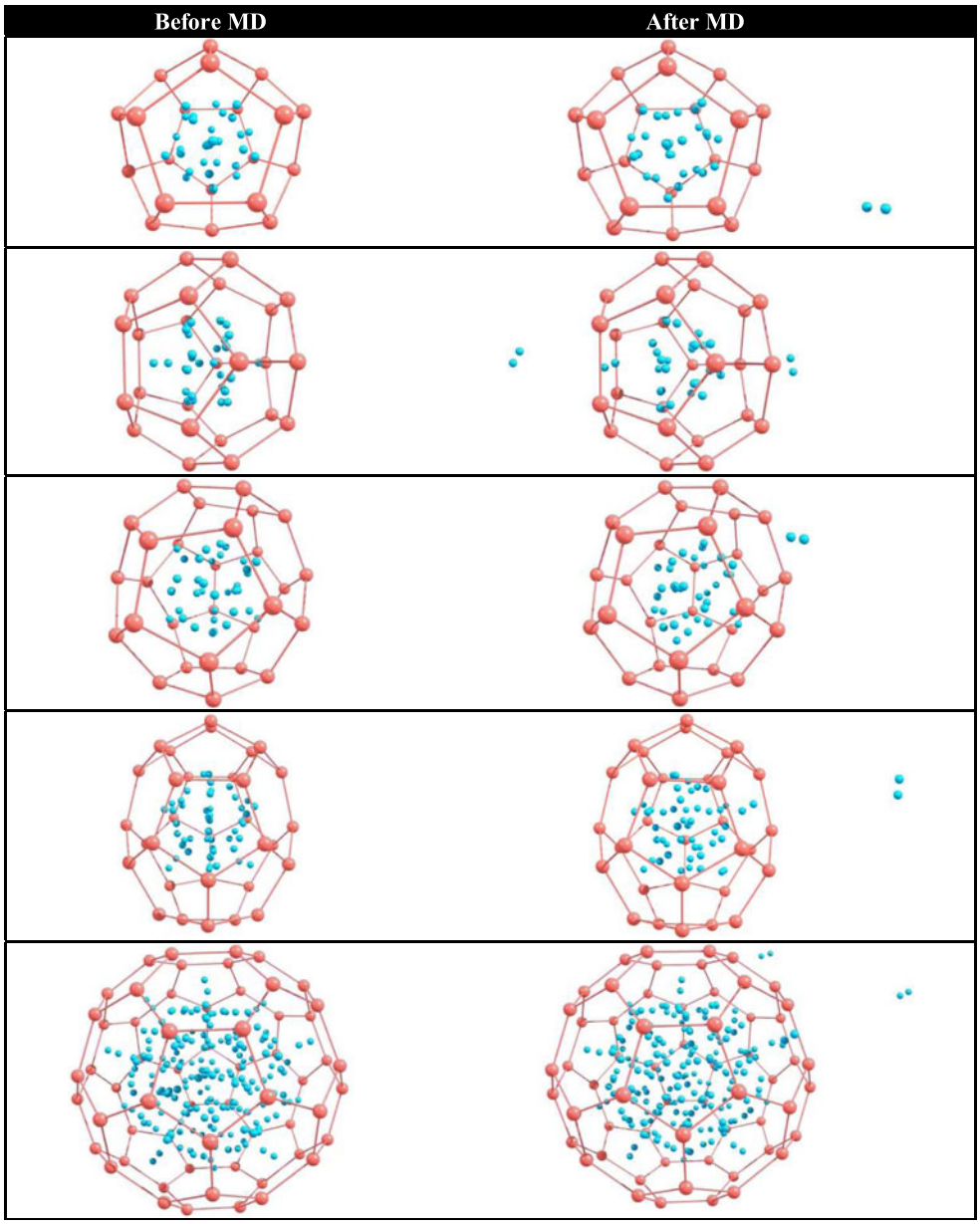


Fig. 5 Conductivity of bismuth "fullerenes" and their hydrogen composites

Table 8 Results of molecular dynamics method for hydrogen-containing bismuth fullerene-like nanostructures



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