Oriental Journal of Chemistry Vol. **24**(3), 785-794 (2008)

Number of rings in carbon nanostructures (Fullerenes and Nanotubes)

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(Received: July 15, 2008; Accepted: October 03, 2008)

ABSTRACT

One of the questions is determining the number of rings in Fullerenes and Nanotubes. Here, for solving this problem, a simple, fast and high accuracy method is explained. Application of this method has shown very good results. Determining the number of rings (N_R) in carbon nanostructures such as Fullerenes, Nanotubes (SWNT) and other nanocarbon structures is the main aim in this study. This structural index that is based on the degrees of unsaturation may useful in the QSAR and QSPR studies concern to the carbon nanostructures.

Key words: Carbon nanostructuresm, Number of rings, Structural index, Stone-Wall transformation, QSAR, QSPR, Molecular topology.

INTRODUCTION

Carbon nanostructure compounds in an attractive variation of structures and wonderful forms have been synthesized and identified. These structures have several rings that share number of carbons. The system could be illustrated with super polycyclic compounds such as Fullerenes and Nanotubes single walls (SWNT)[1-7].

One of the questions in the chemistry of carbon nanostructures is determining the number of rings in Fullerenes, Nanotubes and carbon nanostructures. Here, for solving this fundamental question, a simple, fast and high accuracy method is explained. Application of this method in a course of organic chemistry showed very good results[9]. The calculation of the number of rings in these complex carbon nanostructure compounds can be very difficult. The results may utilize in the Graph theory studies[9,10].

Graph theory has been found to be a useful tool in *QSAR* (Quantitative Structure Activity Relationship) and *QSPR* (Quantitative Structure Property Relationship)[11-15]. Numerous studies have been made related to the above mentioned fields by using what are called topological indices (TI)[15,19,20]. The use of effective mathematical methods for making good correlations between several data properties of chemicals is important. In 1993 and 1997 were reported a related complex of application of the Wiener and Harary indices in fullerene science[17-18].

The results were utilized for calculating the number of rings in other nanocarbon structures (such as: Fullerenes, Nanotubes SWNT, Phenylenic and Naphthylenic Tori, Polyhex (x,y) tori, Nanotube Covering Modified, Nanotube isomerized, Nanobuds and so on).

Mathematical method

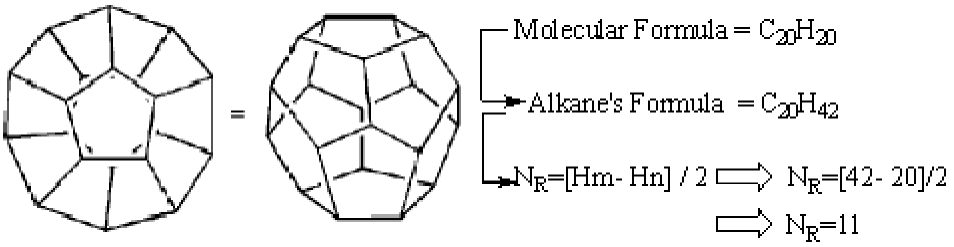
The number of rings (N_R) in carbon nanostructures as a structural index for compounds (Fullerenes 1-25 and Nanotubes SWNT: 1–20), was determined by these stages

- Recognition of skeletal structure of favored compounds.
- Counting the carbon (and hydrogen) atoms.
- Add to each unsaturated carbon atom 1H atom For example for C_{60} could reach to $C_{60}H_{60}$ in accordance with this manner. Write the molecular formula of carbon nanostructure compounds (C_nH_n). The number of hydrogen atoms in the compounds are shown by "H_n" symbol.
- Write the molecular formula of an Alkane (C_nH_{2n+2}) according to the number of carbons that were counted in stage-3. The number of hydrogen atoms in the molecular formula are shown by "H_m" symbol. The symbol "m" is equal to 2n+2.
- Calculation the "number of rings (N_R) in carbon nanostructures," by comparing the number of H-atoms between stages –4 & 3. See equation (1).

$$N_R=[H_m-H_n] / 2 \qquad \text{Eq.-1}$$

The results, after some simple mathematical operations are shown in Tables 1-2 for the carbon nanostructures.

For example, N_R for Eicosahedron is calculated as:



Graphs

All graphing operations were performed using the Microsoft Office Excel- 2003 program. For modeling, linear (MLR) model was used in this study.

DISCUSSION

According the mentioned rules in the above phrases for determining the number of rings in polycyclic compounds and the nanostructures, the students must break some of the bonds and convert it to an open-chain compound. But, there are two important questions: 1) Which bonds? and, 2) How could we break the bonds to receipt the open-chain compounds. For students, answer to these main questions in the great number of polycyclic, Fullerenes and Nanotube compounds is very difficult. The lecturers for teaching these points have partially some difficulties during the process of lecture and answer to these questions.

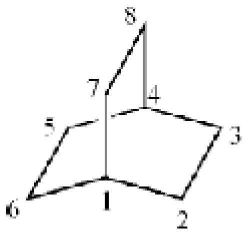
There were two identified methods to determining the number of rings in multi cyclic hydrocarbons, previously[21-25].

Breaking C-C bonds method

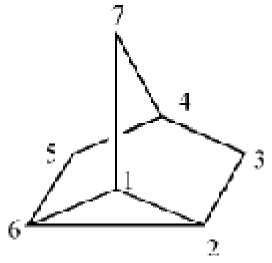
The systematic name of **I** is bicyclo[2.2.2] octane: (a) Octane, since compound (I) contains eight carbon atoms; (b) bicyclo, because it has two rings, that is converted into an open chain when we break two C-C bonds; (c) [2.2.2], since the number of carbons on the bridge (shared carbons) are two carbon atoms (C2 & C3), two carbons (C5 & C6), and two atoms of carbon (C7 & C8).[9, 21-25] The method and scheme of *bicyclo[2,2,2]octane* was imitated directly from Reference 21.

Counting the number of rings

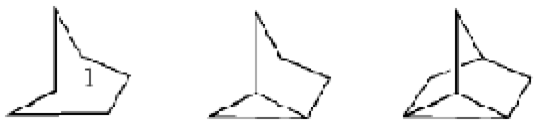
In identifying the rings in a structure such as compound **II** (nortricyclene), a student should begin by tracing any ring of carbons in the polycyclic ring structure (generally the largest ring, but this is not required); this is the parent ring (ring number =1). Next connect remaining atoms to the parent ring, by any path, but being careful not to retrace any paths previously used. Finally, connect remaining segments by the longest path available, again being careful not to retrace (Young's method)[9,25]. The possible sequences for **II** (tricyclo [2.2.1.02,6]heptane) followed in Figures.



Bicyclo[2.2.2] octane (I)



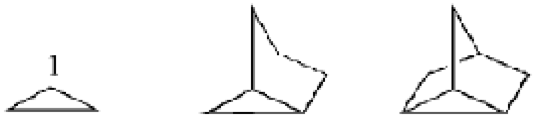
Tricyclo [2,2,2,1,0^{2,6}] heptane Noriricylclene (II)



Starting on a six membered ring of compound II

Starting on a five membered ring of compound II

Starting on another six membered ring of compound II



Starting on three another membered ring of compound II

The method that has explained on compound I, and all the possible sequences for I were imitated from reference[25].

Utilizing these two methods to calculation the number of rings is very difficult for the complex polycyclic compounds as well as Fullerenes and Nanotubes.

The method which is mentioned here, could be illustrated with known super polycyclic compounds such as Fullerenes, Nanotubes (SWNT), Phenylenic and Naphthylenic Tori, Polyhex (x,y) tori, Nanotube Covering Modified, Nanotube isomerized and so on.

Number of rings in fullerenes

Since the discovery of the fullerenes (C_n) one of the main class of carbon compounds, the unusual structures and properties of these molecules and by the many potential applications and physicochemical properties have been discovered and were introduced. Up to now, various empty carbon fullerenes with different magic number "n", such as C_{20}, C_{60}, C_{70}, C_{80}, C_{180}, C_{240} and so on, have been obtained. Many studies of the chemical, physical and mechanical properties of empty fullerenes have been carried out[1-7,12].

For calculating the number of rings in the fullerene classes of was utilized the method which is mentioned in the mathematical method section. The results were demonstrated at Table 1 for fullerenes (C_n, n = 20, 24, 26, 36, 56, 58, 60, 70, 76, 78, 80, 82, 84, 120, 132, 140, 146, 150, 160, 162, 180, 240, 276, 288 and 300).

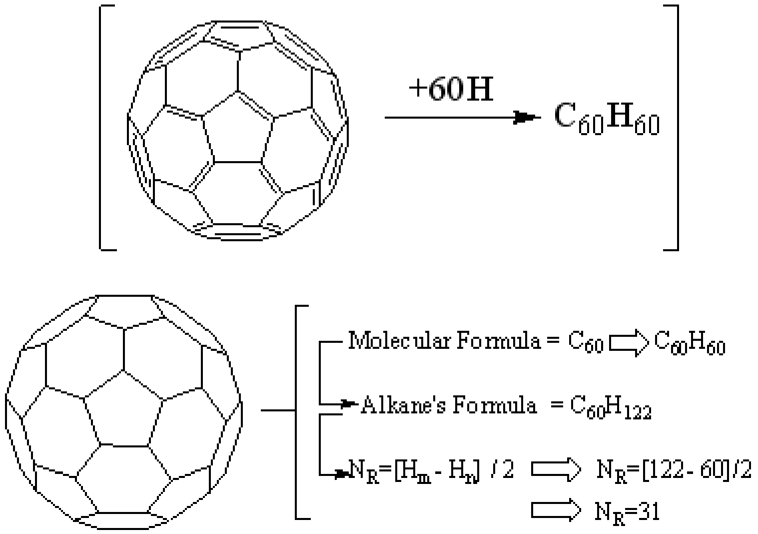


Figure 2 shows a very good linear relationship between the "N_R" versus the number of carbon atoms (C_n) in the fullerenes **1-25** that were shown in the Table-1. Equation 2 is relevant to Fig.-2. The R-squared value (R^2) for this graph is equal to 1.00.

$$N_R = 0.5(C_n) + 1 \qquad \text{...(Eq.-2)}$$

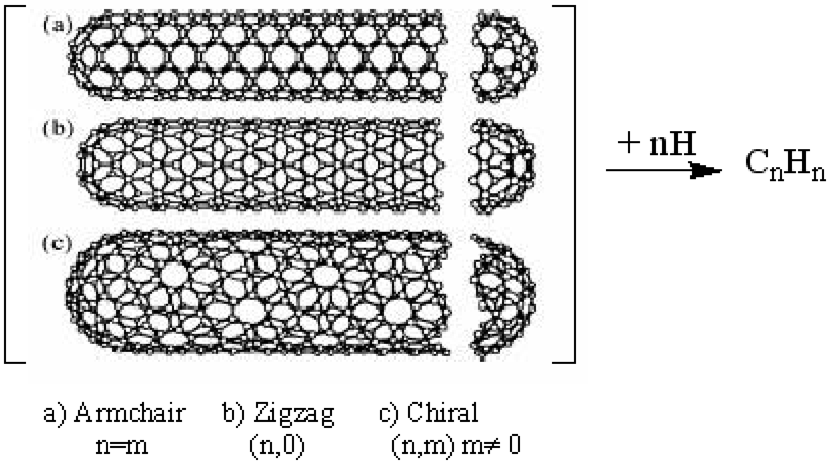
Number of rings in nanotubes

Study about properties of nanotubes with medicinal and electronic applications have been made the highly useful and effective results for applications in different areas of science. One of the main recognized structures of nanotubes is single wall tube (SWCN).

Since their discovery in 1991, SWNTs and MWNTs have displayed exceptionally strong and stable mechanical properties along the nanotube's axis and flexible characteristics along the normal to the tube's axis[3-6]. Researchers have tried to exploit nanotubes' strength in reinforcing fibers in nanotube–polymer composite materials[3-7].

Nanotubes of type (n,n) are called armchair nanotubes because of their "W" shape perpendicular to the tube axis. They have asymmetry along the tube axis with a short unit cell (0.25 nm) that can be repeated to make the entire section of a long nanotube. Nanotubes of type (n,0) are called zigzag, because of their *N\N* shape they have a short unit cell (0.43 nm) along the tube axis. All remaining nanotubes are called chiral nanotubes and have longer unit cell sizes along the tube axis[3-7]. One of the main recognized structures of nanotubes is the (5,5) tube. In the (5,5) tube, the structure can be built up by successively adjoining sections of 10 C atoms. In the infinite tube, the periodic unit cell is two such sections consisting of 20 C atoms. As an example, were calculated the number of rings for this class of nanotubes.

For calculating the number of rings in the classes of nanotubes was utilized the method which is mentioned in the mathematical method section. The results for Nanotubes **1-20** were demonstrated at Table 2.



As an example for C_{200} the number of rings (N_R) are:

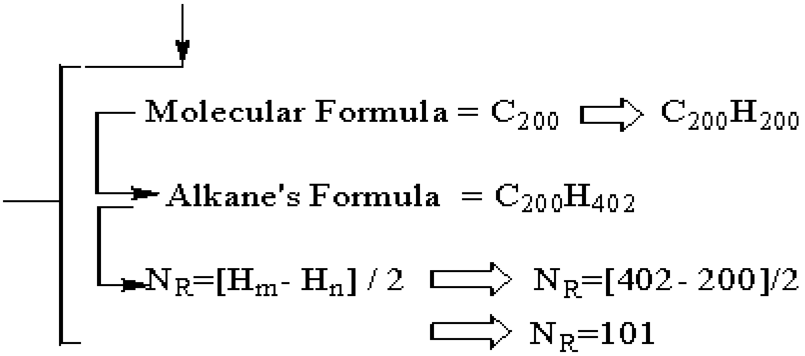


Figure 3 similar to Fig. 2, shows a very good linear relationship between the "N_R" versus the number of carbon atoms (C_n) in the nanotubes **1-20** that were shown in the Table-2. Equation 2 is also relevant to Fig.-3. The R-squared value (R^2) for this graph is equal to 1.00. The linear equations 2 show same results for the fullerenes and the nanotubes.

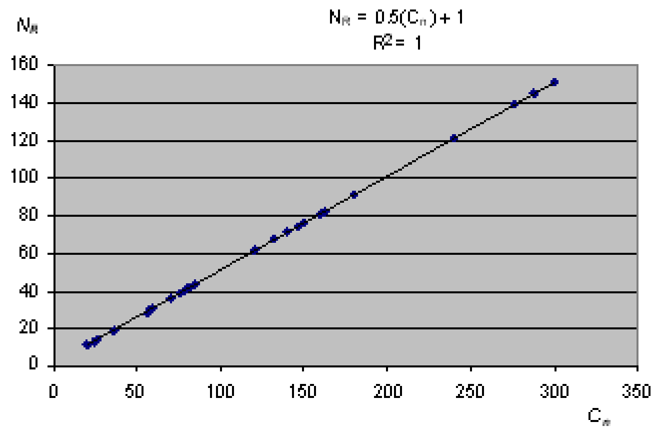


Fig. 2: The linear relationship between the "N_R" versus the number of carbon atoms (C_n) in the Fullerenes 1-25

Table 1: The number of rings in Fullerenes 1-25. (C_n, n = 20, 24, 26, 36, 56, 58, 60, 70, 76, 78, 80, 82, 84, 120, 132, 140, 146, 150, 160, 162, 180, 240, 276, 288 and 300)

No.	Fullerenes	H_n	H_m	N_R
1	C_{20}	20	42	11
2	C_{24}	24	50	13
3	C_{26}	26	54	14
4	C_{36}	36	74	19
5	C_{56}	56	114	28
6	C_{58}	58	118	30
7	C_{60}	60	122	31
8	C_{70}	70	142	36
9	C_{76}	76	154	39
10	C_{78}	78	158	40
11	C_{80}	80	162	41
12	C_{82}	82	166	42
13	C_{84}	84	170	43
14	C_{120}	120	242	61
15	C_{132}	132	322	67
16	C_{140}	140	342	71
17	C_{146}	146	362	74
18	C_{150}	150	382	76
19	C_{160}	160	402	81
20	C_{162}	162	422	82
21	C_{180}	180	362	91
22	C_{240}	240	482	121
23	C_{276}	276	554	139
24	C_{288}	288	578	145
25	C_{300}	300	602	151

Table 2: The number of rings in Nanotubes SWNT 1-20 (For example (5,5)armchair nanotube)

No.	Nanotubes	H_n	H_m	N_R
1	C_{20}	20	42	11
2	C_{30}	30	62	16
3	C_{40}	40	82	21
4	C_{50}	50	102	26
5	C_{60}	60	122	31
6	C_{70}	70	142	36
7	C_{80}	80	162	41
8	C_{90}	90	182	46
9	C_{100}	100	202	51
10	C_{110}	110	222	56
11	C_{120}	120	242	61
12	C_{130}	130	262	66
13	C_{140}	140	282	71
14	C_{150}	150	302	76
15	C_{160}	160	322	81
16	C_{170}	170	342	86
17	C_{180}	180	362	91
18	C_{190}	190	382	96
19	C_{200}	200	402	101
20	C_{210}	210	422	106

Other nanocarbon structures

One of the plausible processes for isomerization of the fullerene is the so-called Stone-Wales or “pyracylene” transformation, which is the 90° rotation of two carbon atoms with respect to the midpoint of the bond. The Stone-Wales transformation is also used to describe the structural changes of sp^2-bonded carbon nanosystems. For example, it has been proposed that the coalescence process of fullerenes or carbon nanotubes may occur through a sequence of such a rearrangement. By the Stone-Wales transformation, four hexagons are changed into two pentagons and two heptagons. It is a kind of Stone-Wales defect. See Fig. 4 [27-29].

The Ston-Walls rearrangments were studied on Fullerenes by H. F. Bettinger et.al. [29] In accordance with this investigation, General-gradient approximation (PBE) and hybrid Hartree-Fock density functional theories (B3LYP) have been applied to study the Stone-Wales transformation of buckminsterfullerene to yield a C_{60} isomer of C_{2v} symmetry with two adjacent pentagons[29]. Two different transition states and reaction pathways were identified for the rearrangement from fullerene to C_{60}-C_{2v} on the C_{60} potential energy surface (PES)[29]. One has C_2 molecular point group symmetry with the two migrating carbon atoms remaining close to the fullerene surface. The other one has a high-energy carbene-like structure where a single carbon atom is significantly moved away from the C_{60} surface. The carbene intermediate and the second transition state along the stepwise reaction path characterized previously at lower levels of theory do not exist as stationary points with the density functionals utilized here. The classical barriers of both mechanisms are essentially identical, 6.9 eV using PBE and 7.3 eV with B3LYP. [29]

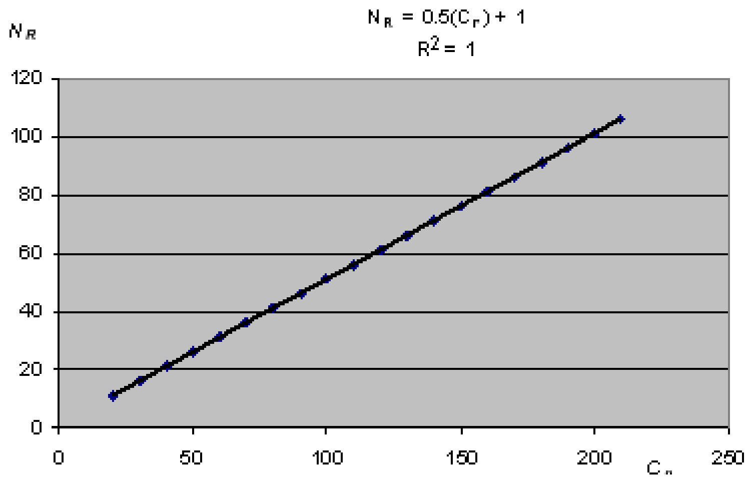


Fig. 3: The linear relationship between the "N_R" versus the number of carbon atoms (C_n) in the nanotubes 1-20

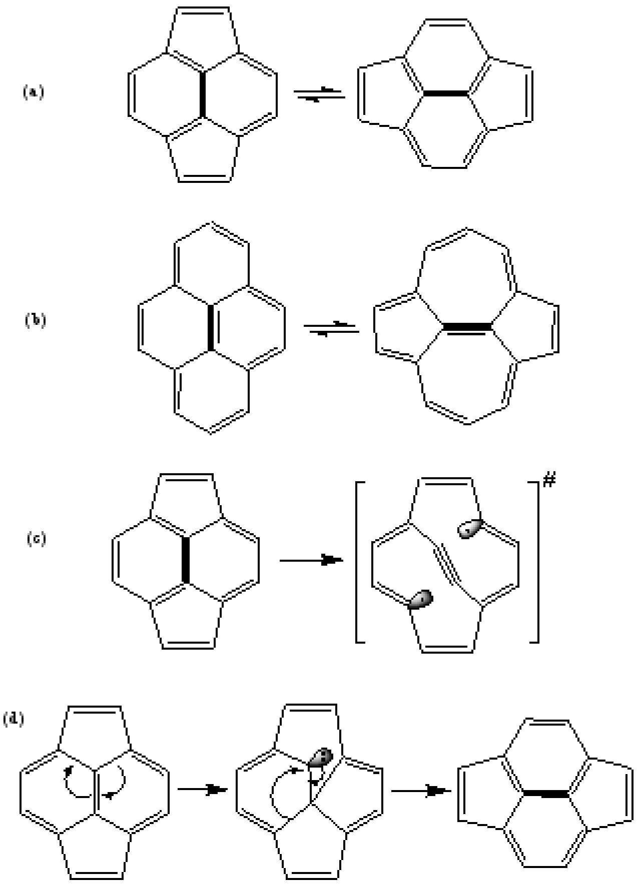
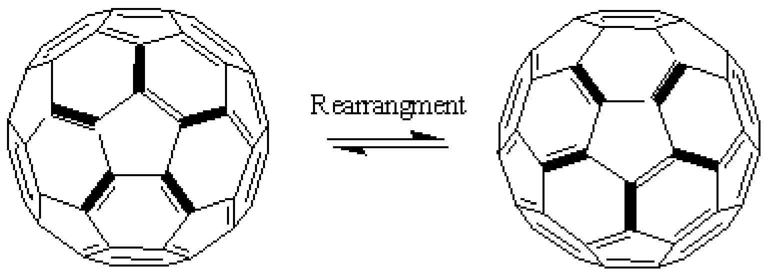


Fig. 4: The isomerization mechanisems during Stone–Wales rearrangement, a) Changing the orientation without change of the ring member carbons, b) Rearrangement with change of the ring sizes, c) by passing biradical intermediate and d) by passing singlet carben intermediate[27-29]



The Stone Wales defect is a defect that occurs on carbon nanotubes and is thought to have important implications for nanotube's mechanical properties[27-29]. The defects are thought to be responsible for nanoscale plasticity and the brittle-ductile transitions in carbon nanotubes. The number of rings (N_R) do not show changes in the isomerization process of the fullerenes. For calculating the number of the rings can use the Equation-2 ($N_R = 0.5(C_n) + 1$).

In nanotechnology, Tori systems as a kind of carbon Nanostructure form a material which make from polyhedral carbon atom rings. Several reports and investigation were published by M. V. Diudea concern to the tori systems[30]. Polycyclics tori are transformed into hexagonal and other tiling tori by several cutting procedures. The strain energy, defined as the difference between the energy of toroidal structure and the energy of its corresponding straight, open tube, is shown to decrease as the torus diameter increases, in the series 10,*n* of polyhex tori[30-39]. See Fig.-5. Graph-theoretical characterization of these structures including the Hosoya polynomial, Distance Degree Sequence, and Wiener index was also studied[30-39].

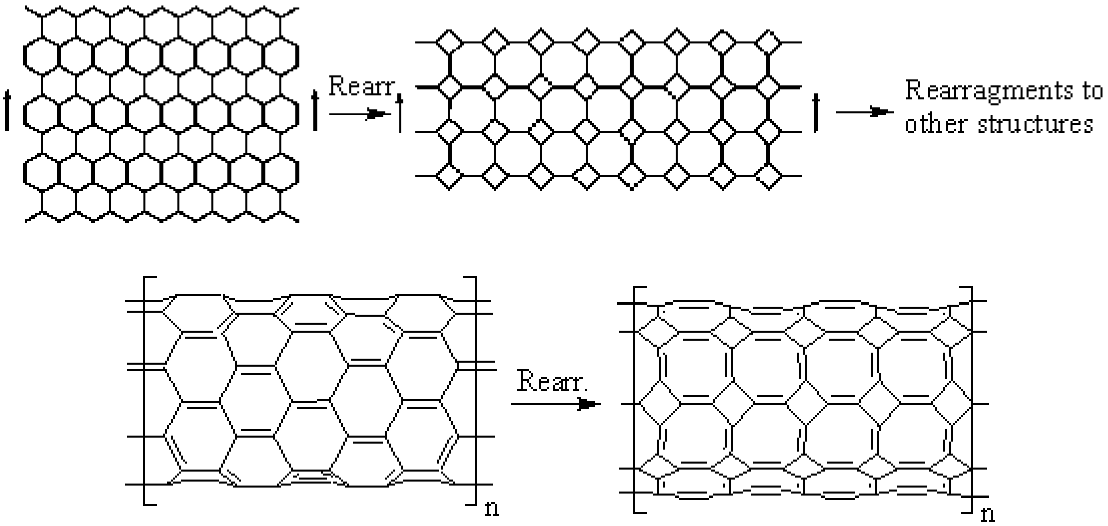


Fig. 5: The isomerization process on nanotubes concern to the tori and nanotubes systems

The number of rings (N_R) does not show changes in the isomerization process of the tori systems. It seems that remaing of carbon valances in the body of the nanocarbon structures during the process of isomerization, is the mean reasone for remaining the number of rings in the structure of the carbon nanotubes. For calculating the number of the rings can use the Eq.-2 ($N_R = 0.5(C_n) + 1$).

The results demonstrate that: The number of rings in the Nanocarbon structures (Fullerenes, Nanotubes SWNT, Phenylenic and Naphthylenic Tori, Polyhex (x,y) tori, Nanotube Covering Modified, Nanotube isomerized, Nanobuds and so on) have not changes during the isomerization. So, for calculating the number of the rings in the skeletal structure of the appropriate Nanocarbon structures can utilize the Eq.-2 (or Eq.-3) before and after the isomerization process.

CONCLUSION

Comparison of this method with other methods for recognition the number of rings in fullerenes and nanotubes shows that this manner is simple for application, fast in illustration and high accuracy for counting the number of rings in the nanostructures. All the concern evidence about using this method emphasized that the students and the lecturers confirmed the facility, rapidity and high accuracy of this method for teaching and learning. The linear behaviors between the "N_R" versus the number of carbon atoms (C_n) in the Fullerenes 1-25 and Nanotubes 1-20 show same results. The number of rings in the Nanocarbon structures (Fullerenes, Nanotubes SWNT, Phenylenic and Naphthylenic Tori, Polyhex (x,y) tori, Nanotube Covering Modified, Nanotube isomerized, Nanobuds and so on.) have not changes during the isomerization.

ACKNOWLEDGMENT

The author gratefully acknowledges colleagues in the Chemistry Department of The University of Queensland-Australia, for their useful suggestions.

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