



## DFT Investigation of Structure, stability, NBO charge on Titanium-Nitrogen Nanoheterofullerenes evolved from a small nanocage

Iman Sabeeh Hasan<sup>1</sup>, Alhussein Arkan Majhool<sup>2</sup>, Mustafa Humam Sami<sup>3</sup>, Mohaned Adil<sup>4</sup>, Saripah Salbiah Syed Abdul Azziz<sup>5</sup>

<sup>1</sup> Department of Pharmacy, Al-Zahrawi University College, Karbala, Iraq

<sup>2</sup> College of Applied Medical Sciences, University of Kerbala, Kerbala, Iraq

<sup>3</sup> Department of Pharmacy, Al-Noor University College, Nineveh, Iraq

<sup>4</sup> Medical technical college, Al-Farahidi University, Iraq

<sup>5</sup> Chemistry Department, Faculty of Science and Mathematics, Sultan Idris Education University, 35900, Tanjong Malim, Perak, Malaysia

### ARTICLE INFO

### ABSTRACT

#### Article history:

Received 8 April 2023

Received in revised form 26 July 2023

Accepted 26 July 2023

Available online 26 October 2023

#### Keywords:

Heterofullerene

Heteroatom

Stability

NICS

NBO

In this DFT (density functional theory) approach, we are performed geometric and electronic properties of Ti—N hallow cages improved from C<sub>20</sub> *i.e.*, C<sub>20-2n</sub>Ti<sub>n</sub>N<sub>n</sub> (n = 1-8), at (U)B3LYP, (U)M062X, (U)B3PW91//6-311++G\*\*, AUG-cc-pVTZ. Except for C<sub>4</sub>Ti<sub>8</sub>N<sub>8</sub>, other structures are real minima and none deform as segregated open cage. Substituting causes different  $\Delta E_{\text{HOMO-LUMO}}$  values (the frontier molecular orbital energy separation) and C<sub>18</sub>Ti<sub>1</sub>N<sub>1</sub> is distinguished as the suitable insulated structure, while C<sub>12</sub>Ti<sub>4</sub>N<sub>4</sub> is considered as the proper conductive structure. There is good reliability among polarizability, and ionization potential with substituting Ti—N units. The NICS (0) shows aromaticity decreases as n increases. Due to eight Ti—N units in the symmetrical positions of C<sub>4</sub>Ti<sub>8</sub>N<sub>8</sub> cage, it shows dipole moment of 0.00 Debye, and the smallest charge of +0.526 on Ti. Considering the least |*E*<sub>ads</sub>|; |−18.9 kcal/mol|; and the greatest charge of +1.269 on titaniums of C<sub>18</sub>Ti<sub>1</sub>N<sub>1</sub>, it is recommended for hydrogen storage. The NBO of C<sub>18</sub>Ti<sub>1</sub>N<sub>1</sub> points out higher intramolecular charge transfer (ICT) from donor orbitals to acceptor orbitals through the appropriate overlapping between LP(1)<sub>N</sub> → π\*<sub>C=C</sub>, π<sub>C=C</sub> → σ\*<sub>C-Ti</sub>, π<sub>C=C</sub> → σ\*<sub>C-Ti</sub>, σ<sub>C-Ti</sub> → π\*<sub>C=C</sub> and LP(1)<sub>N</sub> → σ\*<sub>C-Ti</sub> orbitals of C<sub>18</sub>Ti<sub>1</sub>N<sub>1</sub>.

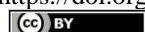
### 1. Introduction

The C<sub>20</sub> is comprising pentagons with great curvature. Due to interesting construction of this hollow cage, it has been subject of many theoretical surveys [1-7]. Initially, interaction of C<sub>20</sub> with the lithium heteroatom does not give significant modification in the cage geometry. It is inspected to be more reactive than it's bowl and ring analogue, even though the relative energy among these isomers is influenced by sophistication of the applied theoretical methods [1-7]. It is distinguished as the most stable twenty vertex polyhedral with the minimum energy amid the mathematically probable fullerenes. From an experimental point of view, this

fullerene produced through stable C<sub>20</sub>H<sub>20</sub> in gas phase [8]. Furthermore, the synthesis and the doped nanosheets can be confirmed with some categorizations. Moreover, encapsulation of metal—endohedral fullerenes such as Ti@C<sub>28</sub>, Zr@C<sub>28</sub>, and U@C<sub>28</sub> are investigated *via* a bottom-up growth process [8-13]. The substituted aluminum and/or titanium heteroatoms stabilize the highly strained C<sub>20</sub>, C<sub>24</sub>, C<sub>28</sub> fullerenes *via* charge transfer (CT) from the electropositive dopant to carbon [14]. Regardless of Ti—decorated boron cages that B<sub>38</sub> and B<sub>40</sub> have been achieved as the first experimentally full-heterofullerene, H<sub>2</sub> storage of the designed transition metals at heptagon and hexagon rings of these structures have been surveyed through DFT [15].

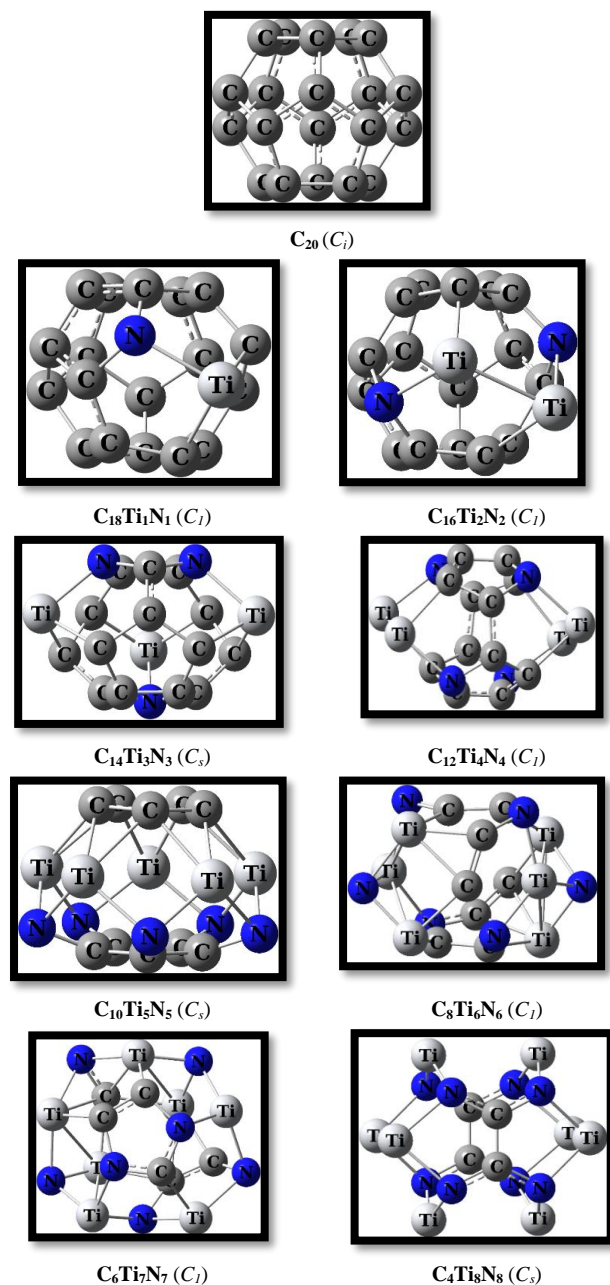
\* Corresponding author.; e-mail: shadaldlymy747@gmail.com

<https://doi.org/10.22034/CRL.2023.392371.1223>



This work is licensed under Creative Commons license CC-BY 4.0

Experimental and theoretical inspections have revealed that Ti—clusters significantly improve H<sub>2</sub> storage [15]. Our enquiry further proofs theoretical insight into substituent effect of Ti—N units on C<sub>20</sub>-<sub>2n</sub>Ti<sub>n</sub>N<sub>n</sub> structures, to respect which of them are suitable for H<sub>2</sub> storage (Figure 1).



**Fig. 1.** The optimized C<sub>20</sub> and its derivatives as well as their point groups, at B3LYP/AUG-cc-pVTZ.

## 2. Computational Methods

The optimization is done for closed-shell multiplicity ( $n = 0, 2, 4, 6, 8$ ) at the restricted spin-symmetry methods and for opened-shell multiplicity ( $n = 1, 3, 5, 7$ ) at the unrestricted spin-symmetry methods using the GAMESS [16-18]. Harmonic frequencies are obtained to realize nature

and ZPVE value [18]. The NBO [19], aromaticity [20], MEP as well as reactivity [21] calculations are individually achieved, at three methods. The reactivity is accomplished *via*  $N = E_{\text{HOMO}(\text{Nu})} - E_{\text{HOMO}(\text{tetracyanoethylene})}$ ,  $\omega = \mu^2 / 2\eta$ ,  $\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2$ ,  $\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2$ ,  $\chi = -\mu$ ,  $S = 1 / 2\eta$ , and  $\Delta N_{\text{max}} = -\mu / \eta$ .

## 3. Results and Discussion

In the succeeding parts we will discuss substituted heteroatom effects by increasing the Ti—N units, however there are many other likely isomers but we are investigated eight of them.

### 3.1. Structural investigation

The structures of studied molecules are explained in terms of bond distances close to the substituting elements. The C—C bond distances of C<sub>20</sub> are around 1.44 – 1.54 Å (Tables 1 and 2) which insert amid the values of H<sub>2</sub>C=CH<sub>2</sub> and H<sub>3</sub>C—CH<sub>3</sub> (1.35 and 1.54 Å, respectively).

**Table 1.** The bond lengths per Å, at B3LYP/AUG-cc-pVTZ.

Species	C=C	Ti—C	N—C
C <sub>20</sub>	1.444-1.537	-	-
C <sub>18</sub> Ti <sub>1</sub> N <sub>1</sub>	1.398-1.538	1.444	1.443
C <sub>16</sub> Ti <sub>2</sub> N <sub>2</sub>	1.410-1.523	2.006-2.021	1.408-1.432
C <sub>14</sub> Ti <sub>3</sub> N <sub>3</sub>	1.397-1.501	1.877-2.074	1.424-1.491
C <sub>12</sub> Ti <sub>4</sub> N <sub>4</sub>	1.402-1.493	1.079-2.080	1.395-1.448
C <sub>10</sub> Ti <sub>5</sub> N <sub>5</sub>	1.402-1.523	1.587-1.609	1.587-1.609
C <sub>8</sub> Ti <sub>6</sub> N <sub>6</sub>	1.336-1.482	1.943-2.165	1.355-1.488
C <sub>6</sub> Ti <sub>7</sub> N <sub>7</sub>	1.408-1.414	2.117-2.162	1.376-1.419
C <sub>4</sub> Ti <sub>8</sub> N <sub>8</sub>	1.449	-	1.375

**Table 2.** The bond lengths per Å, at B3LYP/AUG-cc-pVTZ.

Species	Ti-N	Ti-Ti
C <sub>20</sub>	-	-
C <sub>18</sub> Ti <sub>1</sub> N <sub>1</sub>	1.442	-
C <sub>16</sub> Ti <sub>2</sub> N <sub>2</sub>	2.006-2.027	2.380
C <sub>14</sub> Ti <sub>3</sub> N <sub>3</sub>	1.953-1.984	-
C <sub>12</sub> Ti <sub>4</sub> N <sub>4</sub>	2.041-2.065	2.305
C <sub>10</sub> Ti <sub>5</sub> N <sub>5</sub>	1.674-1.697	-
C <sub>8</sub> Ti <sub>6</sub> N <sub>6</sub>	1.882-2.031	2.502-2.775
C <sub>6</sub> Ti <sub>7</sub> N <sub>7</sub>	1.872-2.078	2.701-2.798
C <sub>4</sub> Ti <sub>8</sub> N <sub>8</sub>	1.873-2.028	2.360

The considered Ti—C, and N—C bond lengths are expanded to approximately 1.77 - 2.61 Å which are followed with sum of covalent radii of the scrutinized atoms; C = 0.70 Å, Ti = 1.40 Å and N = 0.65 Å. Shrinking 0.11 Å in C=C bond length of heterofullerenes vs. C<sub>20</sub> is attributed to dopants. The bond angles of C—C—C (99.59° – 118.82°), C—Ti—C (37.03° – 91.73°), and C—N—C (98.74° – 113.96°) are changed vs. C—C—C (103.99° to 111.31°) of pure C<sub>20</sub> (Table 3).

**Table 3.** The bond angles (in degree), at B3LYP/AUG-cc-pVTZ.

Species	C—C—C	C—Ti—C	C—N—C
C <sub>20</sub>	103.99-111.31	-	-
C <sub>18</sub> Ti <sub>1</sub> N <sub>1</sub>	103.46-117.93	85.79	101.64
C <sub>16</sub> Ti <sub>2</sub> N <sub>2</sub>	99.59-118.82	-	99.81-99.94
C <sub>14</sub> Ti <sub>3</sub> N <sub>3</sub>	103.75-132.89	83.81-117.40	89.89-105.85
C <sub>12</sub> Ti <sub>4</sub> N <sub>4</sub>	99.78-114.38	-	98.74-99.63
C <sub>10</sub> Ti <sub>5</sub> N <sub>5</sub>	107.33-108.77	38.92-39.89	-
C <sub>8</sub> Ti <sub>6</sub> N <sub>6</sub>	-	37.03-74.44	104.66-113.96
C <sub>6</sub> Ti <sub>7</sub> N <sub>7</sub>	-	91.73	108.16
C <sub>4</sub> Ti <sub>8</sub> N <sub>8</sub>	-	-	-

These variations create pyramidalization on dopant sites;  $\theta_C = 360 - [(C-C-C)_1 + (C-C-C)_2 + (C-C-C)_3]$ ,  $\theta_{Ti} = 360 - [(C-Ti-C)_1 + (C-Ti-N)_2 + (N-Ti-C)_3]$  and  $\theta_N = 360 - [(C-N-C)_1 + (C-N-Ti)_2 + (Ti-N-C)_3]$  (Table 4) [22-25].

**Table 4.** The pyramidalization angles of  $\theta_{Ti}$ ,  $\theta_N$  (in degree), at B3LYP/AUG-cc-pVTZ. The pyramidalization angle of C<sub>20</sub> is 31.623 - 42.254°.

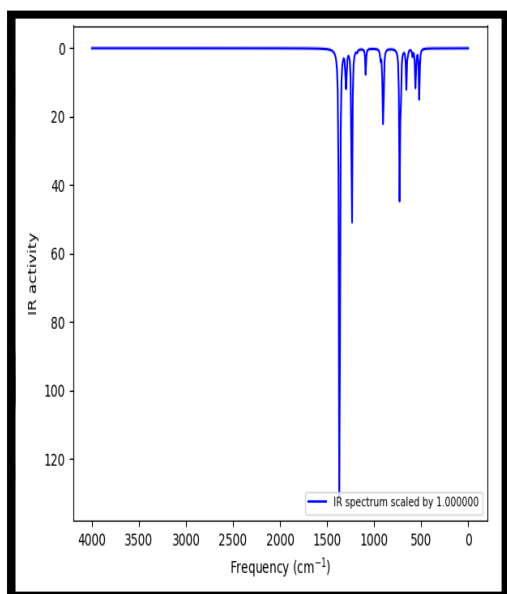
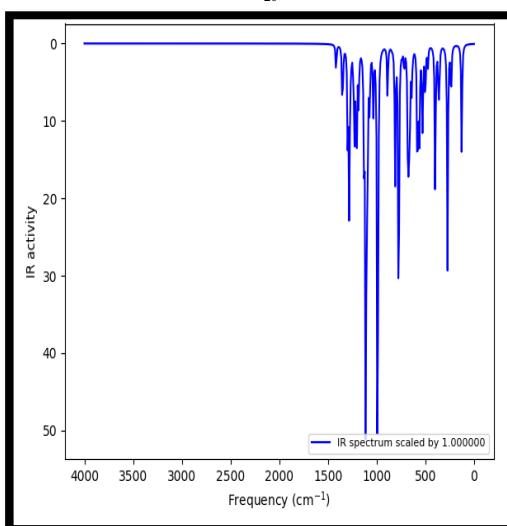
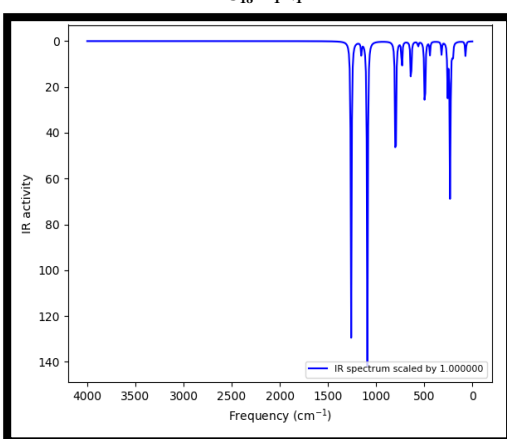
Species	$\theta_{Ti}$	$\theta_N$
C <sub>20</sub>	31.62-42.25	-
C <sub>18</sub> Ti <sub>1</sub> N <sub>1</sub>	100.95	40.84
C <sub>16</sub> Ti <sub>2</sub> N <sub>2</sub>	64.22	35.5
C <sub>14</sub> Ti <sub>3</sub> N <sub>3</sub>	26.25-98.52	34.28-101.16
C <sub>12</sub> Ti <sub>4</sub> N <sub>4</sub>	72.33-123.25	32.06-49.44
C <sub>10</sub> Ti <sub>5</sub> N <sub>5</sub>	-	-
C <sub>8</sub> Ti <sub>6</sub> N <sub>6</sub>	-	35.32-115.38
C <sub>6</sub> Ti <sub>7</sub> N <sub>7</sub>	23.39-71.26	40.86-92.14
C <sub>4</sub> Ti <sub>8</sub> N <sub>8</sub>	76.85	40.23

Here, the substituting dopants of C<sub>20-2n</sub>Ti<sub>n</sub>N<sub>n</sub> species displays more pyramidalization vs. C<sub>20</sub>, owing to their more tendency to accept  $sp^3$  hybridization than  $sp^2$ . The smallest vibrational frequency ( $\nu_{min}$ ) analysis displays one negative frequency only for C<sub>4</sub>Ti<sub>8</sub>N<sub>8</sub> as transition state and positive frequencies for others as real minima (Table 5 and Figure 2).

**Table 5.** The total energy, smallest vibrational frequency, polarizability, and polarity.

Species	$E_{tot}^{a, (b), c, [d]}$ / a.u.	$\nu_{min}^e$ / cm <sup>-1</sup>	$\langle\alpha\rangle^b$	$\mu^b$
C <sub>20</sub>	-761.60234 (-761.18425) -761.18350 [-761.67038] -1589.47147 (-1589.11869) -1589.35354 [-1589.77347]	82.23	187.27	0.00
C <sub>18</sub> Ti <sub>1</sub> N <sub>1</sub>	-2417.44789 (-2417.12013) -2417.33158 [-2417.83232]	127.09	184.04	5.96
C <sub>16</sub> Ti <sub>2</sub> N <sub>2</sub>	-3245.52935 (-3245.15983) -3245.35522 [-3245.95661]	104.94	243.27	5.95
C <sub>14</sub> Ti <sub>3</sub> N <sub>3</sub>	-4073.41358 (-4073.102759) -4073.29079 [-4073.953506]	137.84	250.89	5.64
C <sub>12</sub> Ti <sub>4</sub> N <sub>4</sub>	-4901.89785 (-4901.57717) -4901.77369 [-4902.461001]	75.13	483.89	0.54
C <sub>10</sub> Ti <sub>5</sub> N <sub>5</sub>	-5729.82262 (-5729.56165) -5729.68969 [-5730.50202]	158.28	298.21	4.37
C <sub>8</sub> Ti <sub>6</sub> N <sub>6</sub>	-6557.772910 (-6557.71081) -6557.84980 [-6558.02788]	109.37	304.89	3.12
C <sub>6</sub> Ti <sub>7</sub> N <sub>7</sub>	-7386.224877 (-7385.58105) -7385.68065 [-7385.81647]	91.56	398.25	1.54
C <sub>4</sub> Ti <sub>8</sub> N <sub>8</sub>		-269.67	633.14	0.00

At <sup>a</sup>B3LYP/6-311++G\*\*, <sup>b</sup>M06-2X/6-311++G\*\*, <sup>c</sup>B3PW91/6-311++G\*\*, <sup>d</sup>B3LYP/AUG-cc-pVTZ, and <sup>e</sup>B3LYP/6-311+G\*.

 $C_{20}$  $C_{18}Ti_1N_1$  $C_4Ti_8N_8$ 

**Fig. 2.** The selected IR spectrum of  $C_{20}$ ,  $C_{18}Ti_1N_1$  and  $C_4Ti_8N_8$ , at B3LYP/6-311+G\*.

Here, the  $E_{tot}$  is increased as  $n$  is increased and  $C_{18}Ti_1N_1$ ,  $C_{16}Ti_2N_2$ ,  $C_{10}Ti_5N_5$ , and  $C_8Ti_6N_6$  structures compare to  $C_{20}$  fulfill “stability conditions” showing the  $\nu_{min}$  values of 127.09, 104.94, 158.28, and 109.37

$cm^{-1}$ , which are high vs.  $82.2\text{ cm}^{-1}$  [26]. Interestingly, there is good consistency between  $\langle\alpha\rangle$  and the order of  $n$ . The  $\langle\alpha\rangle$  is improved from 187.27 *a.u.* for  $C_{20}$  to 633.14 *a.u.* for  $C_4Ti_8N_8$ . It seems that the substituted Ti, N heteroatoms in  $C_{20-2n}Ti_nN_n$  heterofullerens lead to increasing  $\langle\alpha\rangle$  and  $C_4Ti_8N_8$  has more tendency to interaction with the neighboring polar molecule. The substituted doping  $C_{20}$  to  $C_{18}Ti_1N_1$ ,  $C_{16}Ti_2N_2$ ,  $C_{10}Ti_5N_5$ ,  $C_8Ti_6N_6$ , and  $C_6Ti_7N_7$  is caused considerably  $\mu$  of 5.96, 5.96, 4.37, 3.12, and 1.54 Debye, respectively (Table 5).

### 3.2. $\Delta E_{HOMO-LUMO}$ , IE or IP, and NICS

One Ti—N bond of  $C_{18}Ti_1N_1$  is increased the  $\Delta E_{HOMO-LUMO}$  (1.79, 2.06, 1.80 eV) leading to enhanced stability against electronic excitations (Table 6).

**Table 6.** The FMO (in *a.u.*), along with band gap (in eV).

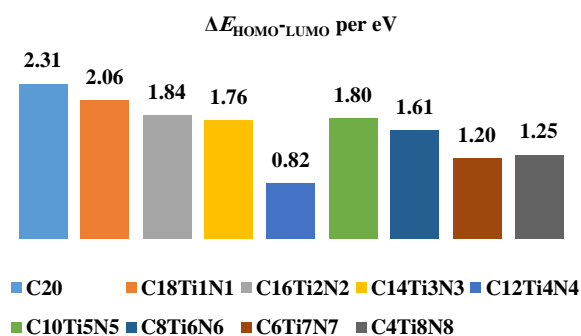
Species	$E_{HOMO}^{a, (b), (c)}$	$E_{LUMO}^{a, (b), (c)}$	$\Delta E_{HOMO-LUMO}^{a, (b), (c)}$
$C_{20}$	-0.20134	-0.13054	1.93
	(-0.21055)	(-0.12567)	(2.31)
	[-0.20455]	[-0.13351]	[1.93]
$C_{18}Ti_1N_1$	-0.19002	-0.15070	1.79
	(-0.19519)	(-0.11964)	(2.06)
	[-0.19241]	[-0.12624]	[1.80]
$C_{16}Ti_2N_2$	-0.17362	-0.11566	1.58
	(-0.18059)	(-0.11286)	(1.84)
	[-0.17470]	[-0.11676]	[1.58]
$C_{14}Ti_3N_3$	-0.19181	-0.13945	1.42
	(-0.14289)	(-0.07834)	(1.76)
	[-0.13560]	[-0.08806]	[1.29]
$C_{12}Ti_4N_4$	-0.13989	-0.10388	0.98
	(-0.13985)	(-0.10964)	(0.82)
	[-0.13950]	[-0.10395]	[0.97]
$C_{10}Ti_5N_5$	-0.17146	-0.10626	1.77
	(-0.17086)	(-0.10488)	(1.80)
	[-0.17365]	[-0.10643]	[1.83]
$C_8Ti_6N_6$	-0.14359	-0.08387	1.63
	(-0.14230)	(-0.08321)	(1.61)
	[-0.14680]	[-0.07701]	[1.20]
$C_6Ti_7N_7$	-0.14090	-0.09408	1.27
	(-0.14088)	(-0.09672)	(1.20)
	[-0.14581]	[-0.10790]	[1.03]
$C_4Ti_8N_8$	-0.13346	-0.08443	1.33
	(-0.13258)	(-0.08651)	(1.25)
	[-0.12279]	[-0.08700]	[0.97]

At <sup>a</sup>B3LYP/AUG-cc-pVTZ, <sup>b</sup>M06-2X/6-311++G\*\*, and <sup>c</sup>B3PW91/6-311+G\*.

Four Ti—N bonds of  $C_{12}Ti_4N_4$  are decreased the  $\Delta E_{HOMO-LUMO}$  of 0.98 eV at B3LYP/AUG-cc-pVTZ, 0.82 eV at M06-2X/6-311++G\*\*, 0.97 eV at B3PW91/6-311+G\* and leading to the enhanced conductivity of  $C_{12}Ti_4N_4$ . Hence,  $C_{18}Ti_1N_1$  is distinguished as the most kinethic stable derivative, whereas  $C_{12}Ti_4N_4$  with four separated Ti—N units *via* four C=C bonds is classified as the least kinethic stable one. Also, we are evaluated the ionization energy or ionization potential (IE or IP) (Table 7). Now, to probe proper connection, we compare  $\Delta E_{HOMO-LUMO}$ , IE or IP, and aromaticity based on  $|NICS(0)|$  of  $C_{20}$  and heterofullerenes with n. The  $\Delta E_{HOMO-LUMO}$  value of heterofullerenes is lower than that of  $C_{20}$ , and there is no uniformity amid band gap and n (Figure 3).

**Table 7.** The ionization potential, and NICS (0), at B3LYP/AUGcc-pVTZ.

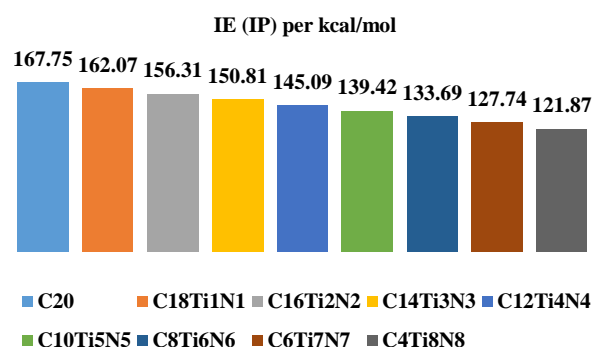
Species	IE (IP)	NICS (0)	NICS (0) <sub>zz</sub>
$C_{20}$	167.75	-23.81	3.69
$C_{18}Ti_1N_1$	162.07	-42.05	-60.98
$C_{16}Ti_2N_2$	156.31	-37.82	-52.03
$C_{14}Ti_3N_3$	150.81	-19.50	-35.12
$C_{12}Ti_4N_4$	145.09	-15.72	-55.32
$C_{10}Ti_5N_5$	139.42	-13.51	-40.83
$C_8Ti_6N_6$	133.69	-19.94	-30.89
$C_6Ti_7N_7$	127.74	-13.42	-16.05
$C_4Ti_8N_8$	121.87	-16.10	-25.16



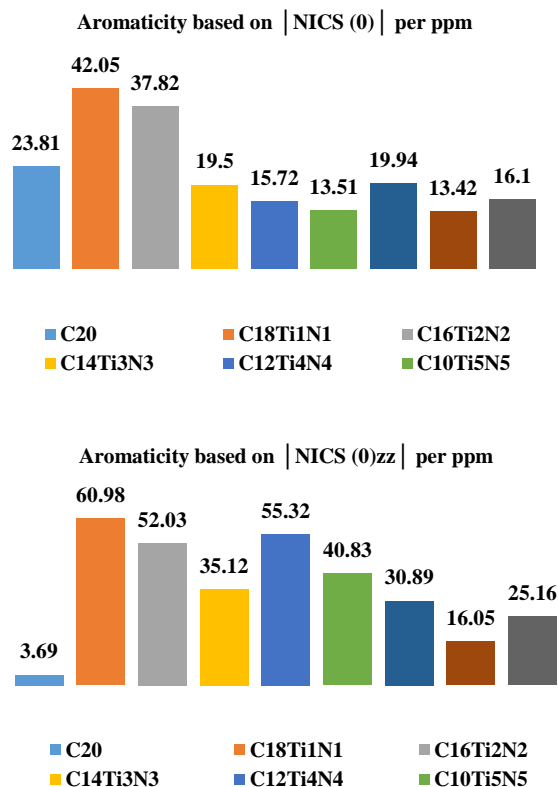
**Fig. 3.** The relationship between band gap and n, at B3LYP/AUG-cc-pVTZ.

The formations of these nanocages are quite complicated due to the possibility of high-spin states. Such possibilities arise due to insertion of Ti ( $^3F_2$ ) and N ( $^4S_{3/2}$ ) of atoms in  $C_{20}$ . The band gap values reveal different electronic charge-transfer possibilities within the considered molecules, while Ti—N units are increased in the fullerenes. The IE or IP value of  $C_{20}$ .

$_{2n}Ti_nN_n$  heterofullerenes is decreased with increasing n (Figure 4).



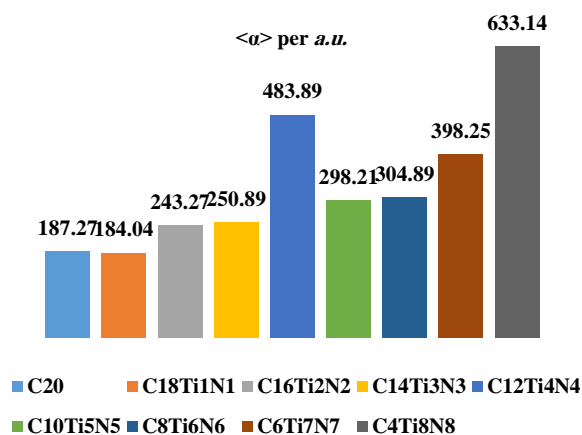
**Fig. 4.** The relationship between ionization potential and n. We are obtained isotropic parameter of -23.8 ppm for  $C_{20}$ , which indicates strong aromaticity of it *vs.* benzene (-8.5 ppm) (Table 7). The  $C_{20-2n}Ti_nN_n$  heterofullerenes show different NICS (0) from -42.05 to -13.42 ppm and they are aromatic. Furthermore, the studied heterofullerenes exhibit NICS (0)<sub>zz</sub> from -60.98 ppm for  $C_{18}Ti_1N_1$  to -16.05 ppm for  $C_6Ti_7N_7$  which imply strong ring current *vs.* benzene (-10.17 ppm). With increasing n, the delocalized  $\pi$ -electrons are shifted from more Ti heteroatoms to neighboring atoms (Figure 5).



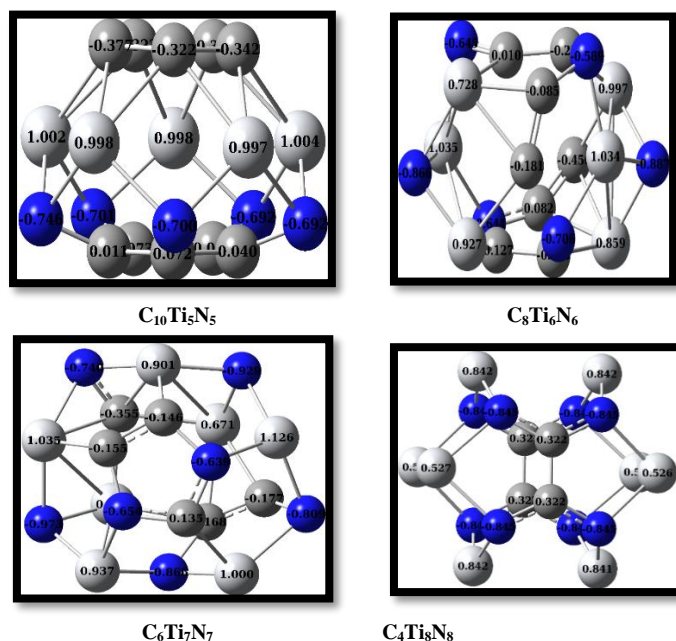
**Fig. 5.** The relationship between aromaticity and n.

Even though the electronegativity difference is significant,  $\pi$ -delocalization effect on the ring perimeter is strengthened in  $C_{18}Ti_1N_1$  derivative, while such ring current is weakened in other

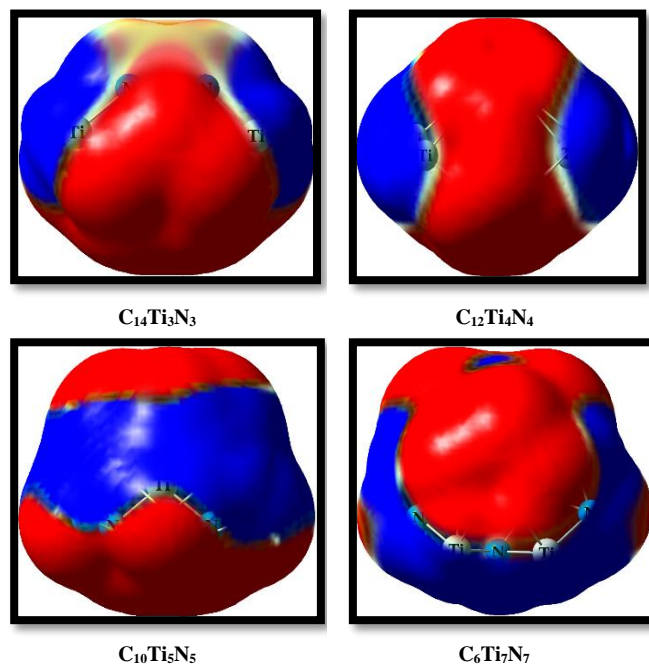
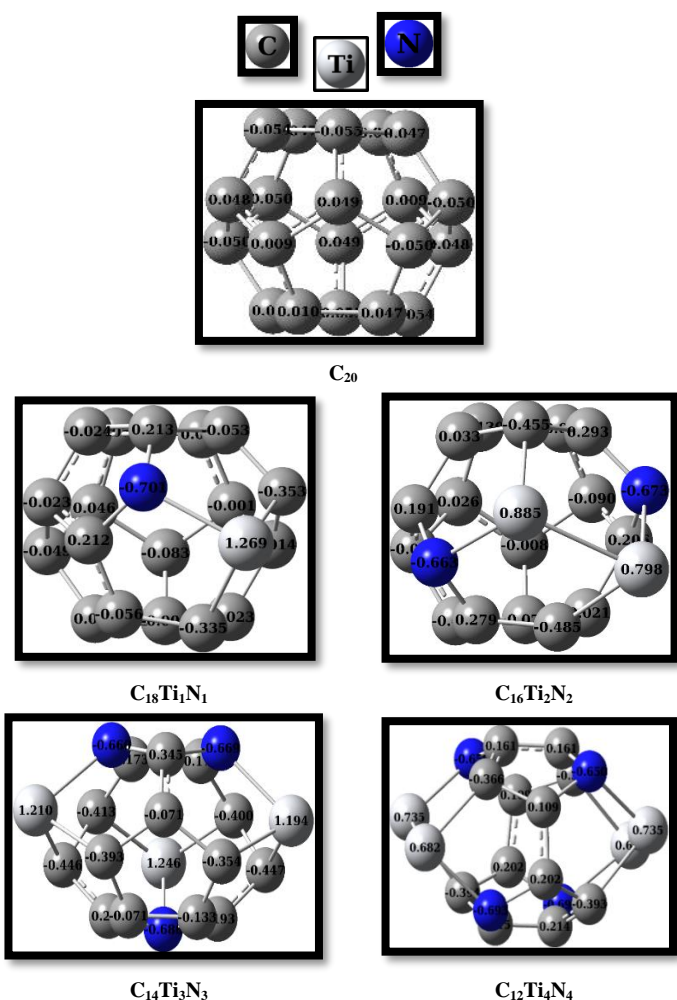
derivatives. Thus, the isotropic polarizability  $\langle\alpha\rangle$  is modified depending on  $n$  and dopant topology (Figure 6).



**Fig. 6.** The relationship between polarizability and  $n$ .  
**3.3. NBO charge, MEP, and hydrogen adsorption**  
 Obviously, the NBO charges of derivatives are not equivalent; so that the negative charge on N sites is changed from  $-0.973$  to  $-0.589e$  and the positive charge on Ti sites is improved from  $+0.527$  for  $C_4Ti_8N_8$  to  $+1.269$  for  $C_{18}Ti_1N_1$  (Figure 7).



**Fig. 7.** The NBO charge on atoms of C20 and heterofullerenes, at B3PW91/6-311++G\*\*.  
 Based on Froudakis's findings,  $C_{18}Ti_1N_1$  is as the suggested species for  $H_2$  storage [23]. The MEP is displayed though red—blue colors on Ti—N surfaces indicating their dispersed charges, correspondingly (Figure 8).



**Fig. 8.** Three-dimensional MEP of the selected derivatives, at B3PW91/6-311++G\*\*.

We are probed  $H_2$  adsorption on one to eight Ti and N-modified heterofullerenes using DFT simulations to introduce suitable systems for the storage of  $H_2$  molecules. We have not used number of the Ti and N heteroatoms more than eight in  $C_{20-2n}Ti_nN_n$  ( $n > 8$ ) because the optimized heterofullerenes with the molecular formula of  $C_{20-2n}Ti_nN_n$  ( $n > 8$ ) are collapsed to the segregated open cage structures. The mixed transition metal

(titanium) and the main element of the periodic table (nitrogen with more electronegative than boron element) have been chosen, because the results of previous studies displayed that the interaction between  $H_2$  molecules and Ti-decorated  $B_{38}$  and  $B_{40}$  fullerenes as the modified adsorbent materials are stronger than those of the other transition metals modified systems [13]. The hydrogen adsorption is designed by reaction of  $C_{20-2n}Ti_nN_n + 2H_2 \rightarrow C_{20-2n}Ti_nN_n \dots (H_2)_2$ . The overall trend of  $|E_{ads.}|$  (in kcal/mol) for two  $H_2$  molecules is arranged as  $C_4Ti_8N_8$   $| -33.20 | > C_6Ti_7N_7$   $| -31.04 | > C_8Ti_6N_6$   $| -29.41 | > C_{10}Ti_5N_5$   $| -27.54 | > C_{12}Ti_4N_4$   $| -25.72 | > C_{14}Ti_3N_3$   $| -23.22 | > C_{16}Ti_2N_2$   $| -21.08 | > C_{18}Ti_1N_1$   $| -18.9 |$  vs.  $C_{20}$  (+81.1). Next, the theoretical work needs to be supported more in its theoretical form. Thus, we are added  $n H_2$  to the titanium and nitrogen heteroatoms. Compared to  $1Ti/B_{38}/(H_2)_1$  complex with capacity of 2.56 wt% and  $|E_{ads.}|$  of 0.22 eV/ $H_2$ ; here  $C_{20-2n}Ti_nN_n$  systems show higher capacity. Each Ti—N unit can bind up to  $2H_2$  with  $|E_{ads.}|$  of 0.07 eV/ $H_2$ . For example, additional  $10H_2$  molecules can be absorbed to  $10H_2/C_{10}Ti_5N_5$  complex with capacity of 4.48 wt% and  $|E_{ads.}|$  of 0.37 eV/ $H_2$ . Hence, the net NBO positive charge of the Ti heteroatom is decreased from +1.269 to +0.6680 also, the net NBO negative charge of the nitrogen heteroatom is decreased from  $-0.701e$  to  $-0.232e$ .

### 3.4. Reactivity

Substituting of Ti—N units is led to various modifications of  $N$ ,  $\omega$ ,  $\mu$ ,  $\eta$ ,  $\chi$ ,  $S$ , and  $\Delta N_{max}$  (Table 8).

**Table 8.** The reactivity parameters (in eV), at M06-2X/6-311++G\*\*.

Species	$N$	$\omega$	$\mu$	$\eta$	$\chi$	$S$	$\Delta N_{max}$
$C_{20}$	3.73	4.53	-4.57	2.31	4.57	0.2 2	1.98
$C_{18}Ti_1N_1$	4.15	4.46	-4.28	2.06	4.28	0.2 4	2.08
$C_{16}Ti_2N_2$	4.55	4.32	-3.99	1.84	3.99	0.2 7	2.17
$C_{14}Ti_3N_3$	5.57	2.58	-3.01	1.76	3.01	0.2 8	1.71
$C_{12}Ti_4N_4$	5.65	7.01	-3.39	0.82	3.39	0.6 1	4.13
$C_{10}Ti_5N_5$	4.81	3.92	-3.75	1.80	3.75	0.2 8	2.09
$C_8Ti_6N_6$	5.59	2.93	-3.07	1.61	3.07	0.3 1	1.91
$C_6Ti_7N_7$	5.63	4.35	-3.23	1.20	3.23	0.4 2	2.69
$C_4Ti_8N_8$	5.85	3.54	-2.98	1.25	2.98	0.4 0	2.38

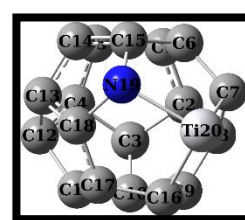
Regardless  $C_{10}Ti_5N_5$ ,  $N$  is increased nearly with increasing  $n$  (from 3.73 eV for  $C_{20}$  vs. 4.15 eV for  $C_{18}Ti_1N_1$  to 5.85 eV for  $C_4Ti_8N_8$ ). Moreover, three, and four substituted Ti—N unit structure is the least, and most electrophile species (2.58, and 7.01 eV for

$C_{14}Ti_3N_3$ , and  $C_{12}Ti_4N_4$ , respectively, vs. 4.53 eV for  $C_{20}$ ).  $C_{18}Ti_1N_1$  contains the minimum  $N$ ,  $S$ , and the maximum  $\chi$ ,  $\eta$ , and absolute  $\mu$  among eight analogues. In contrast,  $C_{12}Ti_4N_4$  includes the least  $\eta$  and the most  $\omega$ ,  $S$ , and  $\Delta N_{max}$ . Hence,  $C_{18}Ti_1N_1$ , and  $C_{12}Ti_4N_4$  are the least, and the most chemically reactive species, singly. The lowest and the highest positive  $\Delta N_{max}$  is demonstrated for  $C_{14}Ti_3N_3$  and  $C_{12}Ti_4N_4$  as the weakest and the strongest electron acceptor from other donors.

### 3.5. NBO analysis

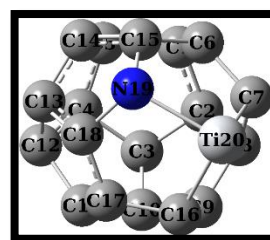
Here, we are focused on NBO analysis of  $Ti_1N_1C_{18}$  species (Tables 9 and 10).

**Table 9.** The occupancy of the intramolecular bonds in  $Ti_1N_1C_{18}$ , at M06-2X/6-311++G\*\*.



Bond	Occup.	EDA (%)	EDB (%)
$\pi C3 = C10$	0.74318	43.41	56.59
$\sigma C7 - Ti20$	0.86892	47.47	52.53
$\sigma C8 - C9$	0.98876	49.88	50.12
$\sigma C15 - N19$	0.98465	40.01	59.99
$\sigma C18 - N19$	0.98498	40.16	59.84
LP(1) <sub>N19</sub>	0.72270		
LP(1) <sub>Ti20</sub>	0.73941		

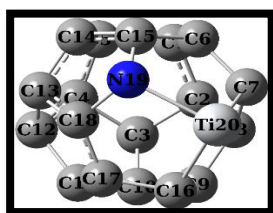
**Table 10.** The NBO, and hybridizations of the intramolecular bonds in  $Ti_1N_1C_{18}$ , at M06-2X/6-311++G\*\*.



Bond	NBO	s (%)	p (%)	d (%)
$\pi C3 = C10$	$0.6589 * sp^{99.99} d^{2.69}$ $+ 0.7523 * sp^{99.99} d^{1.30}$	0.07, 0.08	99.75, 99.81	0.18, 0.11
$\sigma C7 - Ti20$	$0.6890 * sp^{47.82} d^{0.01}$ $+ 0.7247 * sp^{0.10} d^{56.24}$	2.05, 1.74	97.93, 0.17	0.03, 98.07
$\sigma C8 - C9$	$0.7062 * sp^{2.00} d^{0.00}$ $+ 0.7080 * sp^{1.99} d^{0.00}$	33.28, 33.37	66.64, 66.55	0.08, 0.08
$\sigma C15 - N19$	$0.6325 * sp^{2.54} d^{0.00}$ $+ 0.7745 * sp^{2.10} d^{0.00}$	28.21, 32.19	71.67, 67.74	0.13, 0.07
$\sigma C18 - N19$	$0.6337 * sp^{2.53} d^{0.00}$ $+ 0.7736 * sp^{2.14} d^{0.00}$	28.29, 31.87	71.59, 68.07	0.13, 0.06
LP(1) <sub>N19</sub>	$sp^{99.99} d^{0.97}$	0.05	99.89	0.05
LP(1) <sub>Ti20</sub>	$sp^{0.08} d^{99.99}$	0.73	0.06	99.21

The first two columns show the type of orbital and occupancy between 0.98876 electrons for  $\sigma_{C8-C9}$  bonding orbital with  $sp^2$  hybrid vs. 0.72270, and 0.73941 electrons for  $LP(1)_{N19}$ ,  $LP(1)_{Ti20}$  lone pairs with  $sp^{99.99}d^{0.97}$ , and  $sp^{0.08}d^{99.99}$  hybrids, correspondingly. The  $sp^2$  hybrid on  $C_8$ , and  $C_9$  atoms of  $C_8-C_9$  sigma bond has 33.28, and 33.37% s, 66.64, and 66.55% p-character, respectively. Also, the  $sp^{99.99}d^{0.97}$  hybrid on lone pair of  $N_{19}$  has 0.05% s, 99.89% p, and 0.05% d-character. While, the  $sp^{0.08}d^{99.99}$  hybrid on lone pair of  $Ti_{20}$  has 0.73% s, 0.06% p, and 99.21% d-character. The occupancy of  $\sigma_{C7-Ti20}$ ,  $\sigma_{C15-N19}$ , and  $\sigma_{C18-N19}$  is 0.86892, 0.98465, and 0.98498 electrons, with  $0.6890*sp^{47.82}+0.7247*sp^{0.10}d^{56.24}$ ,  $0.6325*sp^{2.54}+0.7745*sp^{2.10}$ , and  $0.6337*sp^{2.53}+0.7736*sp^{2.14}$  hybrid, respectively. Evidently, hetero bonding orbitals of  $\sigma_{C7-Ti20}$ ,  $\sigma_{C15-N19}$ , and  $\sigma_{C18-N19}$  have 47.47%  $C_7$ , 40.01%  $C_{15}$ , 40.16%  $C_{18}$ , 52.53%  $Ti_{20}$ , 59.99%  $N_{19}$ , and 59.84%  $N_{19}$  characters in their corresponding hybrids, respectively. Therefore, titanium and nitrogen heteroatoms have the more percentage of NBOs and gives the more polarization coefficients (0.7247, 0.7745, and 0.7736) than the homo bonding bonds ( $C-C$  and/or  $C=C$ ) because typical titanium has low ability to form hybrid orbitals and prefers  $[Ar](4s^2)(3d^2)$  valence electronic configuration which leads to the divalent doublet ground state, and nitrogen has the higher electronegativity than carbon atom. The more important  $E^{(2)}$  of  $Ti_1N_1C_{18}$  is related to  $LP(1)_{N19} \rightarrow \pi^*_{C17=C18}$ ,  $\pi_{C8=C9} \rightarrow \sigma^*_{C7-Ti20}$ ,  $\pi_{C6=C15} \rightarrow \sigma^*_{C7-Ti20}$ ,  $\sigma_{C7-Ti20} \rightarrow \pi^*_{C8=C9}$  and  $LP(1)_{N19} \rightarrow \sigma^*_{C7-Ti20}$  orbital's and their corresponding energy is 10.03, 7.07, 6.58, 5.83, and 3.42 kcal/mol, correspondingly (Table 11).

**Table 11.** The  $E^{(2)}$  of the intramolecular bonds in  $Ti_1N_1C_{18}$ , at M06-2X/6-311++G\*\*.



Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$ (kcal/mol)
$\pi_{C8=C9}$	$\sigma^*_{C7-Ti20}$	7.07
$\pi_{C6=C15}$	$LP^*(2)_{Ti20}$	0.30
$\pi_{C6=C15}$	$\sigma^*_{C7-Ti20}$	6.58
$\sigma_{C7-Ti20}$	$\pi^*_{C8=C9}$	5.83
$\sigma_{C7-Ti20}$	$\sigma^*_{C9-C16}$	0.26
$LP(1)_{N19}$	$\sigma^*_{C7-Ti20}$	3.42
$LP(1)_{N19}$	$\pi^*_{C17=C18}$	10.03

These interactions is resulted from the electron donating of the bonding orbitals to the electron accepting anti-bonding orbitals, indicating higher CT is happened in these orbitals, compared to lower CT from  $\pi_{C6=C15}$  to  $LP^*(2)_{Ti20}$ , and from  $\sigma_{C7-Ti20}$  to  $\sigma^*_{C9-C16}$  with  $E^{(2)}$  of 0.30, and 0.26 kcal/mol, respectively.

#### 4. Conclusions

Substituent effects of  $Ti-N$  units on geometry,  $\Delta E_{HOMO-LUMO}$ , ionization potential, aromaticity, NBO charge of  $C_{20}$  derivatives are accessed, at DFT. The vibrational frequency calculations imply exclusive of  $C_4Ti_8N_8$  species, reminders are real minima and none of analogous collapse to open deformed cage. The  $\Delta E_{HOMO-LUMO}$  of 1.79, 2.06, and 1.80 eV proposes the  $C_{18}Ti_1N_1$  as the most kinetic stable and the weakest conductive structure. Also, the  $\Delta E_{HOMO-LUMO}$  of 0.98, 0.82, and 0.97 eV suggests the  $C_{12}Ti_4N_4$  with four separated  $Ti-N$  units via 4  $C=C$  bonds as the least kinetic stable and the strongest conductive system. The calculated IE (IP) of 162.07 kcal/mol, NICS (0) of -42.05 ppm and NICS (0)<sub>ZZ</sub> of -60.98 ppm display  $C_{18}Ti_1N_1$  that in which one  $Ti-N$  unit is replaced to two neighboring carbon atoms, as the most thermodynamic stable and the most aromatic nanocage. The most and the least charge on Ti of  $C_{18}Ti_1N_1$  (+1.269) and  $C_4Ti_8N_8$  (+0.527), also the least and the most  $|E_{ads.}|$  of -18.9 and -33.20 kcal/mol, leads to increasing and decreasing capacity of  $C_{18}Ti_1N_1$  and  $C_4Ti_8N_8$  for hydrogen storage, respectively. Furthermore, in going from  $C_{18}Ti_1N_1$  to  $C_4Ti_8N_8$ , as n increases both nucleophilicity index ( $N$ ), and chemical potential ( $\mu$ ) increase with  $C_{18}Ti_1N_1$  and  $C_4Ti_8N_8$  turning out as the least and most nucleophilic species, respectively, while electronegativity ( $\chi$ ) decreases. The MEP maps qualitatively verify the nucleophilicity strength. The NBO analysis of  $C_{18}Ti_1N_1$  points out higher ICT including  $LP(1)_N \rightarrow \pi^*_{C=C}$ ,  $\pi_{C=C} \rightarrow \sigma^*_{C-Ti}$ ,  $\pi_{C=C} \rightarrow \sigma^*_{C-Ti}$ ,  $\sigma_{C-Ti} \rightarrow \pi^*_{C=C}$  and  $LP(1)_N \rightarrow \sigma^*_{C-Ti}$  orbitals.

#### Acknowledgements

Authors state that no fund is used in this research.

#### References

- [1] (a) M. Koohi, H. Bastami, Structure, stability, MEP, NICS, reactivity, and NBO of Si-Ge nanocages evolved from  $C_{20}$  fullerene at DFT. Monatshefte für Chemie – Chem. Mont. 151 (2020) 693. (b) M. Koohi, M. Ghavami, B. N. Haerizade, H. Zandi, M. Z. Kassae, Cyclacenes and short zigzag nanotubes with alternating Ge-C bonds: theoretical impacts of Ge on the ground state, strain, and band gap. J. Phys. Org. Chem. 27 (2014) 735. (c) M. T. Baei, M. Koohi, M. Shariati, Characterization of  $C_{20}$  fullerene and its isolated  $C_{20-n}Ge_n$  derivatives (n = 1-5) by alternating germanium atom(s) in equatorial position: A DFT survey.



- Heteroatom Chem. 29 (2018) e21410. (d) S. Soleimani Amiri, M. Koochi, B. Mirza, Characterizations of B, and N heteroatoms as substitutional doping on structure, stability, and aromaticity of novel heterofullerenes evolved from the smallest fullerene cage C<sub>20</sub>: A density functional theory perspective. *J. Phys. Org. Chem.* 29 (2016) 514. (e) M. Koochi, S. Soleimani Amiri, B. N. Haerizade, Substituent effect on structure, stability and aromaticity of novel B<sub>n</sub>N<sub>m</sub>C<sub>20-(n+m)</sub> heterofullerenes. *J. Phys. Org. Chem.* 30 (2017) e3682. (f) M. Koochi, S. Soleimani-Amiri, M. Shariati, Novel X- and Y-substituted heterofullerenes X<sub>4</sub>Y<sub>4</sub>C<sub>12</sub> developed from the nanocage C<sub>20</sub>, where X = B, Al, Ga, Si and Y = N, P, As, Ge: a comparative investigation on their structural, stability, and electronic properties at DFT. *Struct. Chem.* 29(3) (2018) 909. (g) M. Koochi, M. Shariati, S. Soleimani Amiri, A comparative study on the Ge<sub>6</sub>C<sub>14</sub> heterofullerene nanocages: a density functional survey. *J. Phys. Org. Chem.* 30 (2017) e3678.
- [2] (a) M. Z. Kassaee, F. Boazar, M. Koochi, Heteroatom impacts on structure, stability and aromaticity of X<sub>n</sub>C<sub>20-n</sub> fullerenes: A theoretical prediction, *J. Mol. Struct. (Theochem, Comput. Theor. Chem.)* 940 (2010) 19. (b) M. T. Baei, M. Koochi, M. Shariati, Structure, stability, and electronic properties of AIP nanocages evolved from the world's smallest caged fullerene C<sub>20</sub>: A computational study at DFT, *J. Mol. Struct.* 1159 (2018) 118. (c) M. Koochi, M. Z. Kassaee, M. Ghavami, B. N. Haerizade, A. A. Ahmadi, C<sub>20-n</sub>Ge<sub>n</sub> heterofullerenes (n = 5 - 10) on focus: A density functional perspective, *Monatsh. Chem.* 146 (2015) 1409. (d) M. Koochi, S. Soleimani Amiri, M. Shariati, Silicon impacts on structure, stability and aromaticity of C<sub>20-n</sub>Si<sub>n</sub> heterofullerenes (n = 1 - 10): A density functional perspective, *J. Mol. Struct.* 1127 (2017) 522.
- [3] (a) E. Vessally, S. A. Siadati, A. Hosseinian, L. Edjlali, Selective sensing of ozone and the chemically active gaseous species of the troposphere by using the C<sub>20</sub> fullerene and graphene segment, *Talanta* 162 (2017) 505. (b) E. Vessally, S. Soleimani-Amiri, A. Hosseinian, L. Edjlali, A. Bekhradnia, The Hartree-Fock exchange effect on the CO adsorption by the boron nitride nanocage, *Physica E* 87 (2017) 308. (c) L. Safari, E. Vessally, A. Bekhradnia, A. Hosseinian, L. Edjlali, A DFT study on the sensitivity of two-dimensional BN nanosheet to nerve agents cyclosarin and tabun, *Thin Solid Films* 623 (2017) 157. (d) S. A. Siadati, E. Vessally, A. Hosseinian, L. Edjlali, Possibility of sensing, adsorbing, and destructing the Tabun-2D-skeletal (Tabun nerve agent) by C<sub>20</sub> fullerene and its boron and nitrogen doped derivatives, *Synthetic. Met.* 220 (2016) 606. (e) E. Vessally, S. Soleimani-Amiri, A. Hosseinian, L. Edjlali, A. Bekhradnia, A comparative computational study on the BN ring doped nanographenes, *Appl. Surf. Sci.* 396 (2017) 740.
- [4] (a) E. Vessally, F. Behmagham, B. Massoumi, A. Hosseinian, L. Edjlali, Carbon nanocone as an electronic sensor for HCl gas: Quantum chemical analysis, *Vacuum* 134 (2016) 40. (b) S. Bashiri, E. Vessally, A. Bekhradnia, A. Hosseinian, L. Edjlali, Utility of extrinsic [60] fullerenes as work function type sensors for amphetamine drug detection: DFT studies, *Vacuum* 136 (2017) 156. (c) F. Behmagham, E. Vessally, B. Massoumi, A. Hosseinian, L. Edjlali, A computational study on the SO<sub>2</sub> adsorption by the pristine, Al, and Si doped BN nanosheets, *Superlattices Microstruct.* 100 (2016) 350.
- [5] Q. Feng, Y. Li, N. Wang, Y. Hao, J. Chang, Z. Wang, X. Zhang, Z. Zhang, L. Wang, A Biomimetic Nanogenerator of Reactive Nitrogen Species Based on Battlefield Transfer Strategy for Enhanced Immunotherapy, *Small* 16 (2020) e2002138.
- [6] L. He, J. Liu, Y. Liu, B. Cui, B. Hu, M. Wang, Z. Peng, Titanium dioxide encapsulated carbon-nitride nanosheets derived from MXene and melamine-cyanuric acid composite as a multifunctional electrocatalyst for hydrogen and oxygen evolution reaction and oxygen reduction reaction, *Appl. Cat. B: Env.* 248 (2019) 366.
- [7] (a) E. Vessally, M. D. Esrafil, R. Nurazar, P. Nematollahi, A. Bekhradnia, A DFT study on electronic and optical properties of aspirin-functionalized B<sub>12</sub>N<sub>12</sub> fullerene-like nanocluster, *Struct. Chem.* 28 (2017) 735. (b) E. Vessally, E. Ahmadi, S. Alibabaei, M. D. Esrafil, A. Hosseinian, Adsorption and decomposition of formaldehyde on the B<sub>12</sub>N<sub>12</sub> nanostructure: a density functional theory study, *Monatsh. Chem.* 148 (2017) 1727. (c) K. Nejati, A. Hosseinian, E. Vessally, A. Bekhradnia, L. Edjlali, A theoretical study on the electronic sensitivity of the pristine and Al-doped B<sub>24</sub>N<sub>24</sub> nanoclusters to F<sub>2</sub>CO and Cl<sub>2</sub>CO gases, *Struct. Chem.* 28 (2017) 1919.
- [8] (a) M. Bertau, F. Wahl, A. Weiler, K. Scheumann, J. Worth, M. Keller, H. Prinzbach, From Pagodanes to Dodecahedranes - Search for a Serviceable Access to the Parent (C<sub>20</sub>H<sub>20</sub>) Hydrocarbon, *Tetrahedron* 53 (1997) 10029. (b) H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J. Worth, L. T. Scott, M. D. Gelmont, D. Olevano, B. V. Issendorff, Gas-Phase Production and Photoelectron Spectroscopy of the Smallest Fullerene, C<sub>20</sub>, *Nature* 407 (2000) 60.
- [9] S. Soleimani-Amiri, M. Koochi, Z. Azizi, Characterization of nonsegregated C<sub>17</sub>Si<sub>3</sub> heterofullerene isomers using density functional theory method, *J. Chin. Chem. Soc.* 65 (2018) 1453.
- [10] (a) J. M. Campanera, C. Bo, J. M. Poblet, General Rule for the Stabilization of Fullerene Cages Encapsulating Trimetallic Nitride Templates, *Angew. Chem., Int. Ed.* 44 (2005) 7230. (b) J. C. Gonzalez, S. Mondal, F. Ocayo, R. Guajardo-Maturana, A. Muñoz-Castro, Nature of C<sub>60</sub> and C<sub>70</sub> fullerene encapsulation in a porphyrin- and metalloporphyrin-based cage: Insights from dispersion-corrected density functional theory calculations, *Int. J. Quantum Chem.* 120 (2019) e26080. (c) F. A. Shakib, M. R. Momeni, Density functional investigation of metal encapsulated X@C<sub>12</sub>Si<sub>8</sub> heterofullerene (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>), *Physica B* 406 (2011) 1471.
- [11] (a) S. A. Siadati, E. Vessally, A. Hosseinian, L. Edjlali, Possibility of sensing, adsorbing, and destructing the Tabun-2D-skeletal (Tabun nerve agent) by C<sub>20</sub> fullerene and its boron and nitrogen doped derivatives. *Synthetic Met* 220 (2016) 606. (b) E. Vessally, S. A. Siadati, A. Hosseinian, L. Edjlali, Selective sensing of

- ozone and the chemically active gaseous species of the troposphere by using the C<sub>20</sub> fullerene and graphene segment. *Talanta* 162 (2017) 505. (c) E. Vessally, S. Soleimani-Amiri, A. Hosseinian, L. Edjlali, A. Bekhradnia, The Hartree-Fock exchange effect on the CO adsorption by the boron nitride nanocage. *Physica E* 87 (2017) 308. (d) K. Nejati, A. Hosseinian, E. Vessally, A. Bekhradnia, L. Edjlali, A comparative DFT study on the interaction of cathinone drug with BN nanotubes, nanocages, and nanosheets. *Appl. Surf. Sci.* 422 (2017) 763. (e) A. Hosseinian, E. Vessally, A. Bekhradnia, K. Nejati, G. Rahimpour, Benzoylthalamine drug interaction with the AlN nanosheet, nanotube and nanocage: Density functional theory studies. *Thin Solid Films* 640 (2017) 93.
- [12] P. W. Dunk, N. K. Kaiser, M. Mulet-Gas, A. Rodríguez-Fortea, J. M. Poblet, H. Shinohara, C. L. Hendrickson, A. G. Marshall, H. W. Kroto, The Smallest Stable Fullerene, M@C<sub>28</sub> (M = Ti, Zr, U): Stabilization and Growth from Carbon Vapor, *J. Am. Chem. Soc.* 134 (2012) 9380.
- [13] H. Dong, T. Hou, S.-T. Lee, Y. Li, New Ti-decorated B<sub>40</sub> fullerene as a promising hydrogen storage material, *Sci. Reports* 5 (2015) 9952.
- [14] (a) A. Hassanpour, P. Delir Kheirollahi Nezhad, A. Hosseinian, A. G. Ebadi, S. Ahmadi, S. Ebrahimiasl, Characterization of IR spectroscopy, APT charge, ESP maps and AIM analysis of C<sub>20</sub> and its C<sub>20-n</sub>Al<sub>n</sub> heterofullerene analogous (n = 1 - 5) using DFT, *J. Phys. Org. Chem.* 34 (7) (2021) e4198. (b) K. Nejati, A. Hosseinian, L. Edjlali, E. Vessally, The effect of structural curvature on the cell voltage of BN nanotube based Na-ion batteries, *J. Mol. Liq.* 229 (2017) 167. (c) L. Safari, E. Vessally, A. Bekhradnia, A. Hosseinian, L. Edjlali, A DFT study on the sensitivity of two-dimensional BN nanosheet to nerve agents cyclosarin and tabun. *Thin Solid Films*, 623 (2017) 157. (d) A. Hassanpour, L. Youseftabar-Miri, P. Delir Kheirollahi Nezhad, S. Ahmadi, S. Ebrahimiasl, Kinetic stability, and NBO analysis of the C<sub>20-n</sub>Al<sub>n</sub> nanocages (n = 1 - 5) using DFT investigation, *J. Mol. Struct.* 1233 (2021) 130079. (e) A. Hassanpour, S. Yasar, A. G. Ebadi, S. Ebrahimiasl, S. Ahmadi, Thermodynamic stability, structural and electronic properties for the C<sub>20-n</sub>Al<sub>n</sub> heterofullerenes (n = 1 - 5): A DFT study, *J. Mol. Model.* (2021) DOI: 10.1007/s00894-021-04727-y.
- [15] P. Liu, H. Zhang, X. Cheng, Y. Tang, Ti-decorated B<sub>38</sub> fullerene: A high capacity hydrogen storage material, *Int. J. Hydrogen Energy* 41 (2016) 19123.
- [16] (a) A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* 38 (1988) 3098. (b) A. D. J. Becke, Density-functional thermochemistry. III. The role of exact exchange, *Chem. Phys.* 98 (1993) 5648. (c) C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785. (d) A. D. Becke, Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing, *J. Chem. Phys.* 104 (1996) 1040.
- [17] (a) M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, General atomic and molecular electronic structure system, *J. Comput. Chem.*, 14 (11) (1993) 1347. (b) A. L. Sobolewski, W. Domcke, *Ab Initio* Investigation of the Structure and Spectroscopy of Hydronium-Water Clusters, *J. Phys. Chem. A* 106 (2002) 4158.
- [18] (a) W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio* Molecular Orbital Theory, John Wiley & Sons, New York (1986). (b) J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic structure Methods*, Gaussian, Inc., Pittsburgh, PA (1996).
- [19] (a) F. Weinhold, E. D. Glendening, NBO 7.0 Program Manual Natural Bond Orbital Analysis Programs. *J. Comput. Chem.* 33 (2012) 2363. (b) E. D. Glendening, C. R. Landis, F. Weinhold, Natural bond orbital methods. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 2 (2012) 1.
- [20] (a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, Nucleus-independent chemical shifts (NICS): a simple and efficient aromaticity probe. *J. Am. Chem. Soc.* 118 (1996) 6317. (b) P. v. R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin, O. L. Malkina, An evolution of the aromaticity of inorganic rings: refined evidence from magnetic properties. *J. Am. Chem. Soc.* 119 (1997) 12669. (c) P. v. R. Schleyer, M. Manoharan, Z. Wang, B. Kiran, H. Jiao, R. Puchta, N. J. R. van Eikema Hommes, Dissected nucleus-independent chemical shift analysis of p-aromaticity and antiaromaticity. *Org. Lett.* 3(16) (2001) 2465.
- [21] (a) L. R. Domingo, E. Chamorro, P. Pérez, Understanding the Reactivity of Captodative Ethylenes in Polar Cycloaddition Reactions. A Theoretical Study. *J. Org. Chem.* 73 (2008) 4615. (b) R. G. Parr, L. Szentpaly, S. Liu, Electrophilicity Index. *J. Am. Chem. Soc.* 121 (1999) 1922. (c) R. G. Pearson Absolute electronegativity and hardness: applications to organic chemistry. *J. Org. Chem.* 54 (1989) 1423. (d) P. K. Chattaraj, S. Giri, Stability, Reactivity, and Aromaticity of Compounds of a Multivalent Superatom. *J. Phys. Chem. A* 111 (2007) 11116. (e) J. Padmanabhan, R. Parthasarathi, V. Subramanian, P. K. Chattaraj, Electrophilicity-Based Charge Transfer Descriptor. *J. Phys. Chem. A* 111 (2007) 1358.
- [22] (a) R. C. Haddon, L. T. Scott,  $\pi$ -Orbital Conjugation and Rehybridization in Bridged Annulenes and Deformed Molecules in General:  $\pi$ -Orbital Axis Vector Analysis. *Pure Appl. Chem.* 58 (1986) 137. (b) R. C. Haddon, Chemistry of the fullerenes: The manifestation of strain in a class of continuous aromatic molecules. *Science* 261 (1993) 1545. (c) T. Lin, W.-D. Zhang, J. Huang, C. He, A DFT Study of the Amination of Fullerenes and Carbon Nanotubes: Reactivity and Curvature. *J. Phys. Chem. B* 109 (2005) 13755. (d) H. Prinzbach, A. Weller, P. Landenberger, F. Wahl, J. Worth, L. T. Scott, M. Gelmont, D. Olevano, B. Issendorff, Gas-Phase Production and Photoelectron Spectroscopy of the Smallest Fullerene, C<sub>20</sub>. *Nature* 407 (2000) 60. (e) Z. Chen, T. Heine, H. Jiao, A. Hirsch, W. Thiel, P. v. R.

Schleyer, Theoretical Studies on the Smallest Fullerene: From Monomer to Oligomers and Solid States. Chem. Eur. J. 10 (2004) 963. (f) A. Hirsch, Z. Chen, H. Jiao, Spherical Aromaticity in  $I_h$  Symmetrical Fullerenes: The  $2(N+1)^2$  Rule. Angew. Chem. Int. Ed. 39 (2000) 3915–3917. (g) M. N. Huda, A. K. Ray, Evolution of SiC nanocluster from carbon fullerene, a density functional theoretic study. Chem. Phys. Lett. 457 (2008) 124. (h) R. W. Alder, M. E. Blake, J. M. Oliva, Diaminocarbenes; Calculation of Barriers to Rotation about C<sub>carbene</sub>-N Bonds, Barriers to Dimerization, Proton Affinities and <sup>13</sup>C NMR Shifts. J. Phys. Chem. A 103 (1999) 11200.

- [23] (a) G. E. Froudakis, Why alkali-metal-doped carbon nanotubes possess high hydrogen uptake, Nano. Lett. 1 (2001) 531. (b) A. Mavrandonakis, G. E. Froudakis, M. Schnell, M. Muhlhauser, From pure carbon to silicon carbon nanotubes: an *ab initio* study, Nano. Lett. 3 (2003) 1481. (c) G. Mpourmpakis, G. E. Froudakis, G. P. Lithoxoos, J. Samios, SiC nanotubes: a novel material for hydrogen storage, Nano. Lett. 6 (2006) 158