Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 9 (2) 103-116: summer 2012
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

DFT Study and Comparison between B_6C_4Si and C_{16} Clusters as a Vitamin C Carrier

T. Ardalan[1], M. MonajJemi[1], H. Aghaie[2,*] and P. Ardalan[1]

[1] Ph. D. Student, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2] Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received October 2012; Accepted December 2012

ABSTRACT

In this study the chemical properties of B_6C_4Si and C_{16} Clusters connected vitamin C have been investigated using density functional theory (DFT). NMR parameters and HOMO- LUMO Gap energy are calculated by using density functional method (B3LYP) with 6-311G* basis set. Calculations show that HOMO- LUMO Gap energy of vitamin C decreases after connecting to B_6C_4Si or C_{16} cluster decreasing of HOMO- LUMO Gap energy, causes that vitamin C can act better as an electron donor and antioxidant. The NMR results show that vitamin C connects stronger to B_6C_4Si cluster in negative charges than positive charge. Thus by creating a negative field, vitamin C can be connected to the B_6C_4Si cluster and delivered easily by a positive filed. But for C_{16} cluster, the NMR results are quite different.

Keywords: DFT Study, NMR Parameters, Vitamin C, HOMO- LUMO Gap

INTRODUCTION

Since the end of last decade extensive research have been focused on group-IVA elemental clusters such as C_n , Si_n, Ge_n , Sn_n and Pb_n for both fundamental and technological reasons while very limited experimental and theoretical investigations performed on binary A_mB_n or ternary $A_lB_mC_n$ clusters (A, B, C= C, Si, and Ge) [1-5]. Over the past several years, various *ab initio* investigations have been performed on Si_mC_n binary microclusters, including the second-order Moller-Plesset (MP2) and coupled cluster singles and doubles (CCSD) calculations on Si_4C, [6] MP2 or higher-order perturbation (CASP2) on Si_2C_4, Si_3C_3 and Si_2C_4 [1,7]. MP2 and CCSD(T) on Si_3C_2 and CCSD(T) and tight-binding molecular dynamics studies on SiGe, Si_2Ge_2, and Si_2Ge_4 [8].

On the other hand vitamin C is considered the most important water-soluble antioxidant in extracellular fluids [9-12]. It is capable of neutralizing radical oxygen species (ROS) in the aqueous phase before lipid peroxidation is initiated. Vitamin C is an electron donor and therefore a reducing agent. All known physiological and biochemical actions of vitamin C are due to its action as an electron donor [13]. It donates two electrons from a double bond between the second and third carbons of the 6-carbon molecule. It is also called an antioxidant. It prevents organic compounds from

*Corresponding author: h.aghaie@srbiau.ac.ir

oxidation [14-17]. Due to the importance of vitamin C as an antioxidant in this study we used B_6C_4Si and C_{16} clusters as novel carriers for the vitamin C.

COMPUTATIONAL METHODS

The vitamin C, C_{16} and B_6C_4Si clusters were geometrically optimized using 6–311G* basis set with the Gaussian 03 by the B3LYP method (figs 1-4). Also HOMO–LUMO gap energy and NMR parameters were calculated using DFT method.

a) The isotropic value σ_{iso} of the shielding tensor which can be defined as: [18, 19]

$$\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$$

b) The anisotropy parameter ($\Delta\sigma$) can be defined as:

If $|\sigma_{11} - \sigma_{iso}| \geq |\sigma_{33} - \sigma_{iso}|$ $\Delta\sigma = \sigma_{11} - \frac{\sigma_{22} + \sigma_{33}}{2}$

If $|\sigma_{11} - \sigma_{iso}| \leq |\sigma_{33} - \sigma_{iso}|$ $\Delta\sigma = \sigma_{33} - \frac{\sigma_{22} + \sigma_{11}}{2}$

And

c) The asymmetry parameter (η) is given by:

If $|\sigma_{11} - \sigma_{iso}| \geq |\sigma_{33} - \sigma_{iso}|$ $\eta = \frac{\sigma_{22} - \sigma_{33}}{\delta}$

If $|\sigma_{11} - \sigma_{iso}| \leq |\sigma_{33} - \sigma_{iso}|$ $\eta = \frac{\sigma_{22} - \sigma_{11}}{\delta}$

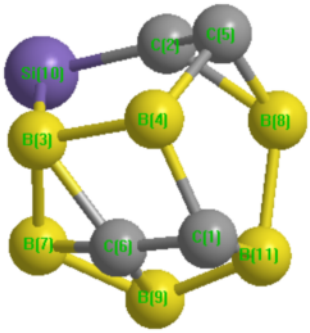


Fig. 1. The optimized structure of B_6C_4Si cluster.

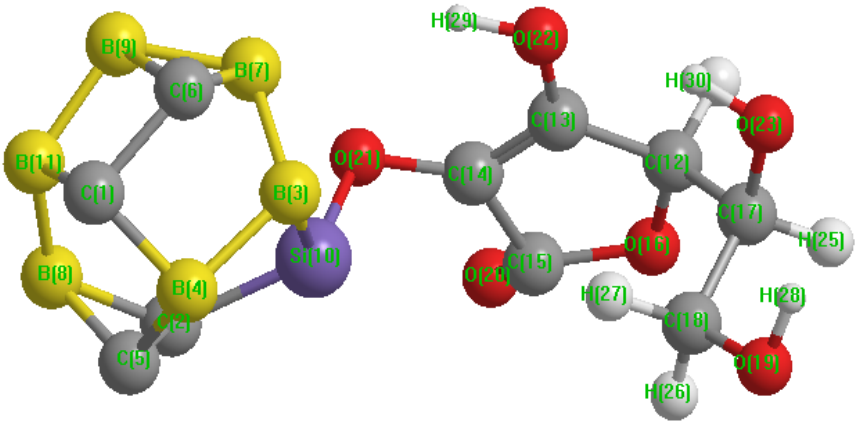


Fig. 2. The optimized structure of B_6C_4Si cluster inside vitamin C.

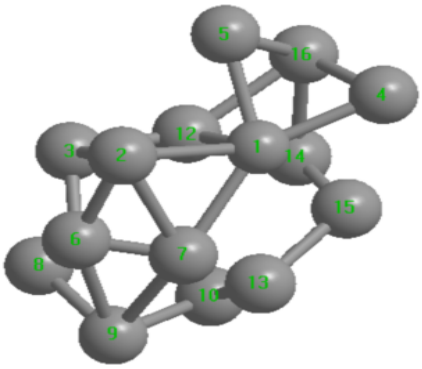


Fig. 3. The optimized structure of C_{16} cluster.

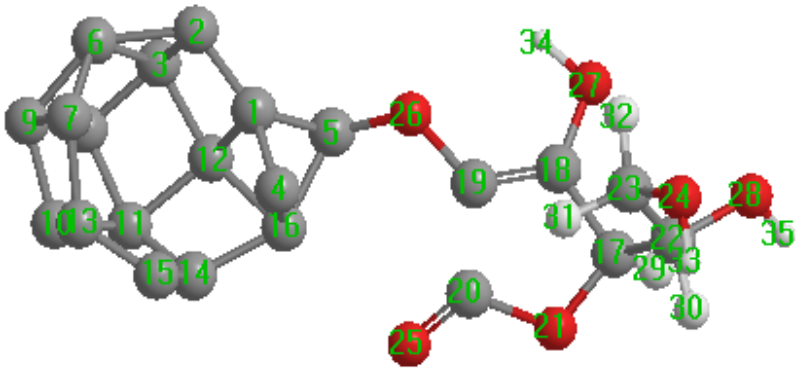


Fig. 4.The optimized structure of C_{16} cluster inside vitamin C.

RESULTS AND DISCUSSION

Calculation of NMR parameters

We studied B_6C_4Si and C_{16} structures as novel clusters for vitamin C carrier the NMR calculation on vitamin C before and after connection to B_6C_4Si or C_{16} cluster were performed in electric field of charges (Table 1-4).

The remarkable feature in these calculations is observed in calculations of η and δ for B_6C_4Si. We can see completely similar curves for η and δ (fig 5 d and e). This similarity exists after connecting B_6C_4Si cluster to vitamin C (fig 6 d and e). this similarity is not observed for C_{16} cluster (figs 7 d and e). Although for B_6C_4Si cluster the maximum and minimum points for all curves are around 0.4 and positive and negative areas show the completely different behavior. So we can find that most chemical shielding is around 0.4. There is a main different between σ_{aniso} and σ_{iso} curves. In a σ_{iso} curve minimum is around 0.4 but in σ_{aniso} curve maximum is around 0.4. This is also predictable and shows that these curves are very sensitive. We want to examine that what changes occur if the vitamin C connect to B_6C_4Si cluster and under what circumstances the vitamin C establishes a strong connection and in what situation the connection would be weak. The results show that vitamin C connects stronger to B_6C_4Si cluster in negative charges than positive charge. Thus by creating a negative field, vitamin C can be connected to the B_6C_4Si cluster and delivered easily by a positive filed.

For C_{16} cluster the maximum and minimum points for all curves are around 0.3 and positive and negative areas show completely different behavior. Figure 8 shows that after connecting to vitamin C the positive and negative regions are altered.

Table 1. List of calculation NMR Parameters for B_6C_4Si by B3LYP/6-311G* method.

Atom	σ_{iso} (ppm)	σ_{aniso} (ppm)	ΔE(J)	δ(ppm)	η	Δσ(ppm)	Dipole Moment(D)	Atomic Charge
C(1)	15.404	203.2859		-88.3601	-0.466230799	203.286		-0.215358
C(2)	-2.2178	141.5942		-81.9187	-0.793537983	141.5942		-0.321866
B(3)	52.835	133.0963		-39.7417	-2.426232396	133.0963		-0.175145
B(4)	104.4853	76.483		19.3555	6.162119294	76.48305		0.155613
C(5)	12.9332	133.6278		-77.8318	-1.187749737	133.62785		-0.130329
C(6)	65.8703	87.9347	-1549257658	-33.3222	-4.194257882	87.93465	1.1104	0.092395
B(7)	105.1492	72.6798		40.571	1.989181928	72.67985		-0.181616
B(8)	48.4045	90.9911		-24.2665	-3.489633857	90.9911		0.211138
B(9)	56.0825	99.8971		-11.4899	-5.965813454	99.8971		0.053974
Si(10)	308.6142	558.0335		-73.8824	-5.318868905	558.0335		0.501028
B(11)	68.2477	105.0258		-26.8745	-4.473657184	105.02585		0.010166

Table 2. List of calculation NMR Parameters for B_6C_4Si / vitamin C by B3LYP/6-311G* method.

Atom	σ_{iso} (ppm)	σ_{aniso} (ppm)	ΔE(J)	δ (ppm)	η	Δσ (ppm)	Dipole Moment(D)	Atomic Charge
C(1)	51.7685	127.4634		-63.0873	-0.653047444	127.4634		-0.211545
C(2)	-2.5195	313.2724		-135.1915	-0.417893876	313.2725		-0.372082
B(3)	45.8692	75.3988		-9.3024	-6.458258084	75.39875		-0.141152
B(4)	40.0682	71.1351		-23.6464	-3.383424115	71.1351		0.34487
C(5)	-58.3641	365.9541		-245.8767	1.221857134	-281.2689		-0.143581
C(6)	-25.182	312.2761		-179.9386	-0.563132091	312.2761		-0.085223
B(7)	21.531	131.4559		-117.0886	0.313053534	-207.9294		-0.066106
B(8)	17.5675	195.8474		-78.1012	-0.778123768	195.8474		0.156929
B(9)	43.0596	78.3748		-11.2975	-4.9979553	78.3747		0.041118
Si(10)	241.4842	202.8658		116.1229	0.99445329	202.8658		0.829306
B(11)	57.04	104.2714		-12.6414	-5.525376936	104.2714		0.00795
C(12)	104.2406	43.2761		79.6617	0.254915474	43.2761		0.187514
C(13)	25.4729	113.046		-51.6688	-1.527409191	113.046		0.194192
C(14)	56.7928	67.8508		-8.7491	-9.812437851	67.8508		0.121348
C(15)	10.6239	75.2396	-	-81.2274	0.104251767	-137.777	5.6394	0.396513
O(16)	121.3811	156.8511	3344427381	-60.4514	-4.286046312	156.8512		-0.296342
C(17)	105.1926	33.8447		86.6905	0.166581113	33.8447		0.141879
C(18)	118.813	45.5454		98.1639	0.111392274	45.54535		0.251546
O(19)	310.4372	36.2503		277.3162	0.151722474	36.25035		-0.165642
O(20)	-66.5163	541.3324		-322.0786	1.447516848	-383.3434		-0.319878
O(21)	202.8512	158.1074		116.1113	0.586290051	158.1074		-0.570839
O(22)	224.4761	121.2611		169.9778	0.165644572	121.2612		-0.133047
O(23)	290.335	69.8927		257.0295	0.077873551	69.8927		-0.167728
H(24)	27.1572	5.0029		24.2492	0.102296158	5.0029		0.255797
H(25)	28.1006	5.5426		24.9932	0.100811421	5.5426		0.234532
H(26)	28.5546	5.1436		23.555	0.278934409	5.14355		0.222904
H(27)	28.7463	8.2144		23.0642	0.255283079	8.21445		0.176376
H(28)	30.8951	13.7685		21.2429	0.476648668	13.7686		0.384019
H(29)	27.6404	12.4636		19.6492	0.390514627	12.46365		0.426796
H(30)	31.2802	16.39		21.7369	0.375403116	16.38995		0.397656

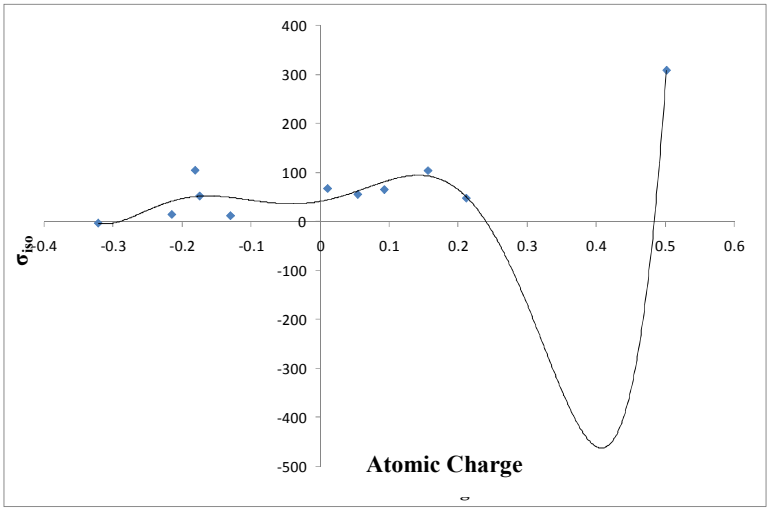
Table 3. List of calculation NMR Parameters for C_{16} by B3LYP/6-311G* method.

Atom	σ_{iso} (ppm)	σ_{aniso} (ppm)	ΔE(J)	Δ (ppm)	η	Δσ (ppm)	Dipole Moment(D)	Atomic Charge
C(1)	144.5872	93.3762		-37.3666	-0.334055012	93.37615		-0.466909
C(2)	35.7451	325.6738		-292.024	0.486971628	-438.036		0.030961
C(3)	79.5391	292.1153		-212.695	0.831202658	-319.042		0.020178
C(4)	23.9893	204.9921		-260.08	0.050917795	-390.12		0.148009
C(5)	-118.524	419.7173		-466.681	0.199155269	-700.022		0.222305
C(6)	154.5825	349.5217		-185.146	-0.741458651	349.5217		-0.217261
C(7)	99.9966	175.213		-143.482	0.62820503	-215.222		0.402346
C(8)	86.0205	219.6147	-1591181.246	-113.832	-0.713812588	219.6147	0.7791	0.172774
C(9)	-239.227	580.4599		-418.436	0.849616059	-627.655		-0.060074
C(10)	34.9214	136.9272		-91.3025	0.999612278	-136.954		-0.096271
C(11)	-7.5029	150.9186		-80.8242	-0.755168625	150.9186		-0.395778
C(12)	134.3722	195.4777		-143.26	0.819322018	-214.891		-0.095303
C(13)	1.8131	183.4231		-83.964	-0.54363894	183.4231		0.10134
C(14)	57.0167	232.6991		-149.724	-0.963872763	232.6991		0.166453
C(15)	-49.1642	361.9883		-390.367	0.236402229	-585.551		-0.050202
C(16)	-31.3948	269.5492		-252.568	0.422981016	-378.851		0.117433

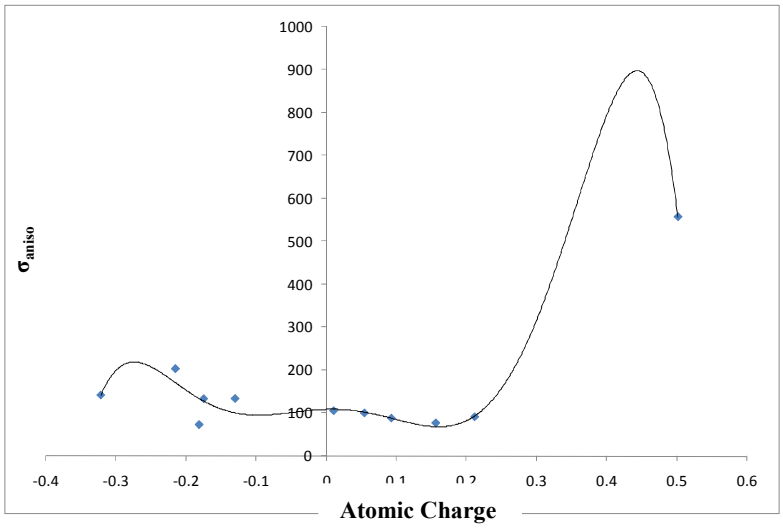
Table 4. List of calculation NMR Parameters for C_{16} /vitamin C by B3LYP/6-311G* method.

Atom	σ_{iso} (ppm)	σ_{aniso} (ppm)	ΔE(J)	Δ (ppm)	η	Δσ (ppm)	Dipole Moment(D)	Atomic Charge
C(1)	83.0791	124.7556	-3389066610	-59.8977	-0.611459205	124.7557	3.9941	-0.419824
C(2)	17.5169	314.4882		-151.6071	-0.848173997	314.4882		0.176006
C(3)	-8.4071	243.9314		-143.5676	-0.750169955	243.93145		-0.042687
C(4)	-120.9721	417.6694		-400.9731	0.690548817	-420.00155		0.179916
C(5)	6.081	114.3054		-96.5746	0.515161336	-153.98345		0.297922
C(6)	33.5337	147.8079		-34.6205	-1.090963447	147.80785		-0.088355
C(7)	12.4461	204.1295		-182.6148	0.422265337	-292.59135		0.141554
C(8)	11.742	151.8907		-110.3976	-1.295487402	151.89065		-0.017765
C(9)	-45.7468	293.0887		-213.5008	0.902768046	-297.06475		-0.0686
C(10)	-30.2892	120.726		-179.447	0.065814976	-223.73665		-0.097895
C(11)	44.6122	191.9118		-115.5461	-1.664923351	191.9118		0.108883
C(12)	153.6682	109.9127		89.24	0.622828328	109.9127		-0.036932
C(13)	28.005	55.3391		-19.0601	-3.00300628	55.3391		-0.025677
C(14)	21.0921	152.8095		-40.8595	-0.539169593	152.8095		-0.072851
C(15)	-75.2379	164.8101		-241.4911	0.221513754	-249.3798		0.137649
C(16)	-26.2074	213.0911		-142.8569	1.172305993	-174.9743		0.007632
C(17)	100.362	43.3451		79.7429	0.15476613	43.34515		-0.076323
C(18)	21.0423	133.2635		-73.529	-1.364091719	133.26355		0.301221
C(19)	32.917	93.6112		-38.2561	-2.089567415	93.61125		0.160405
C(20)	1.7726	121.227		-109.6795	0.457550408	-167.17815		0.522007
O(21)	62.6252	204.8119		-178.9042	-1.936888569	204.81195		-0.435309
C(22)	100.1009	22.7542		84.4828	0.190177172	22.75415		0.025979
C(23)	118.936	51.1741		95.317	0.137665894	51.17415		-0.058041
O(24)	275.1244	153.8505		204.8868	0.185020216	153.8505		-0.559429
O(25)	-254.7399	625.3822		-575.7099	0.890853362	-481.45495		-0.318766
O(26)	86.3413	131.586		0.4174	201.5421658	131.58595		-0.517916
O(27)	187.8892	134.081		113.0446	0.533435476	134.081		-0.57416
O(28)	251.2965	106.1611		210.1944	0.054378708	106.16115		-0.550953
H(29)	27.4432	4.665		25.042	0.067586455	4.66495		0.228107
H(30)	28.0884	4.866		24.6285	0.149249853	4.866		0.178602
H(31)	28.2509	7.8649		22.3644	0.291964014	7.8649		0.171712
H(32)	28.1733	5.6183		23.4359	0.244466822	5.61835		0.203087
H(33)	32.5386	14.1223		24.8772	0.237482514	14.12225		0.35415

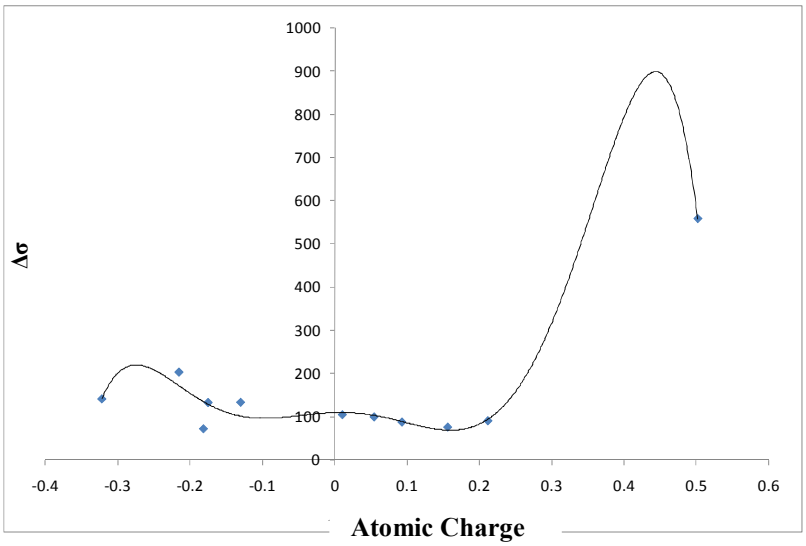
a


400
300
200
100
0
-100
-200
-300
-400
-500
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
σiso
Atomic Charge

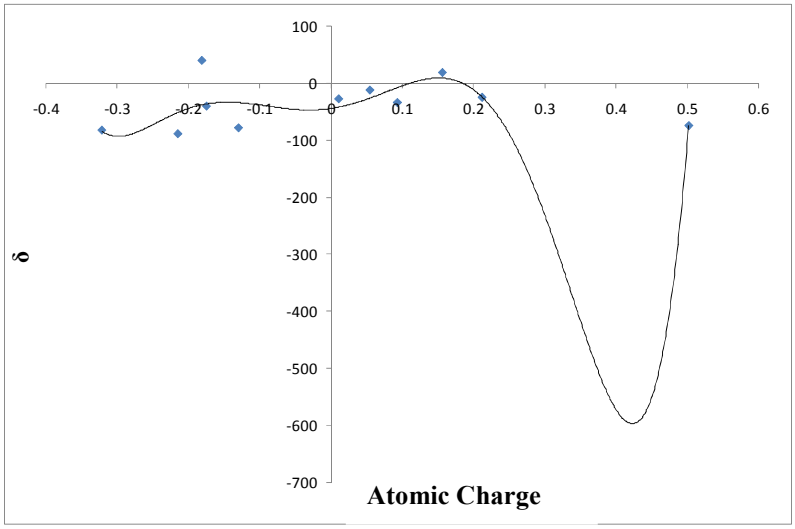
b


1000
900
800
700
600
500
400
300
200
100
0
-0.4
-0.3
-0.2
-0.1
0.3
0.4
0.5
0.6
σaniso
Atomic Charge

c


1000
900
800
700
600
500
400
300
200
100
0
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
Δσ
Atomic Charge

d



e

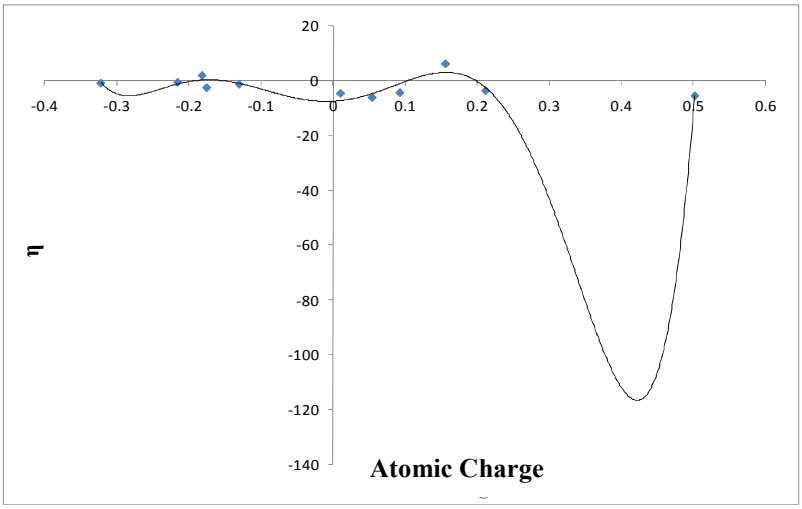
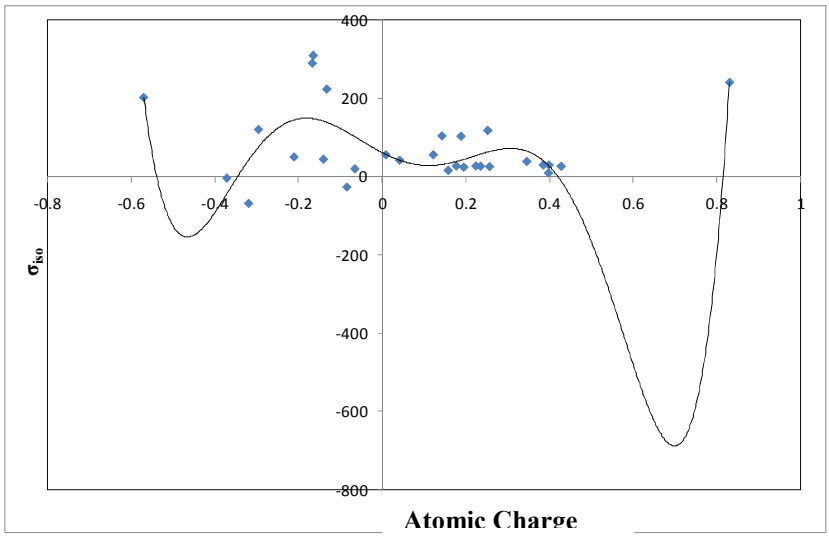
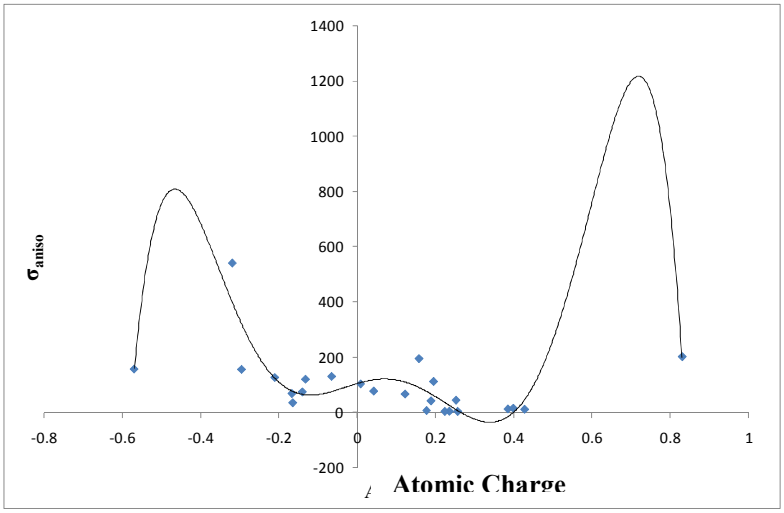


Fig. 5. Plot of a) σ_{iso}(ppm), b) σ_{aniso}(ppm), c) $\Delta\sigma$(ppm), d) δ(ppm) and e) η versus atomic charge for B_6C4Si cluster.

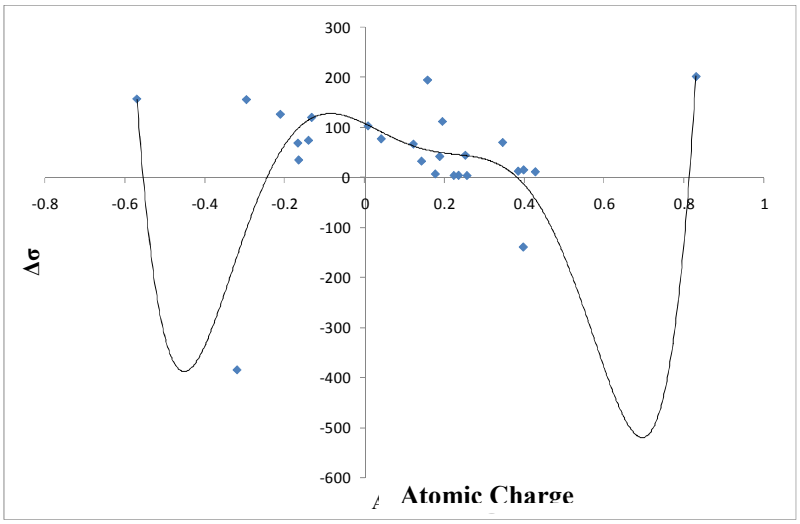
a



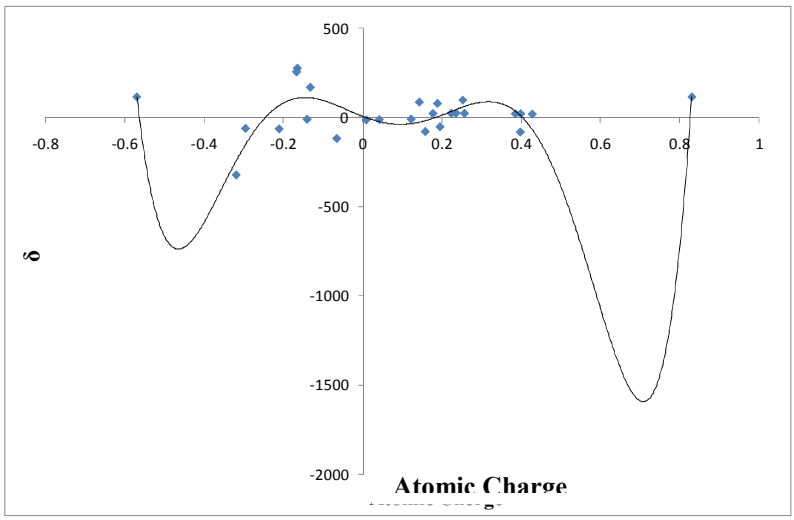
b


1400
1200
1000
800
600
400
200
0
-200
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
σaniso
Atomic Charge

c


300
200
100
0
-100
-200
-300
-400
-500
-600
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
Δσ
Atomic Charge

d


500
0
-500
-1000
-1500
-2000
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
δ
Atomic Charge

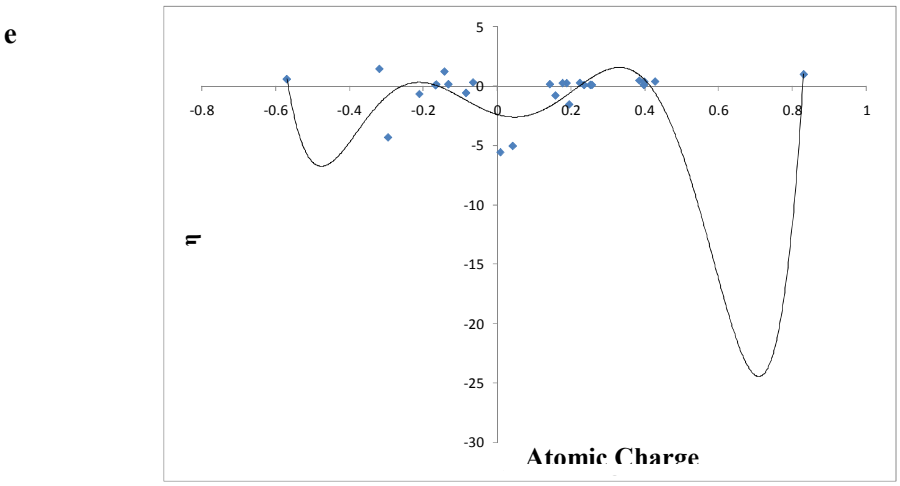
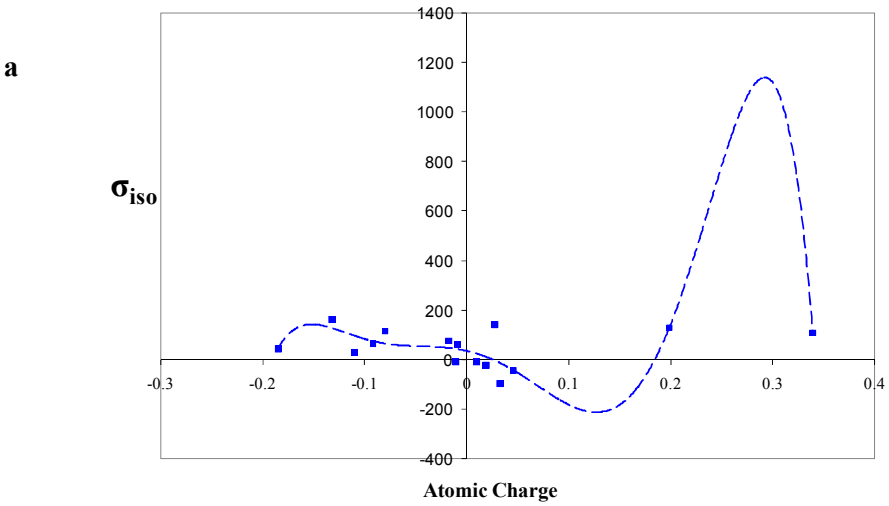
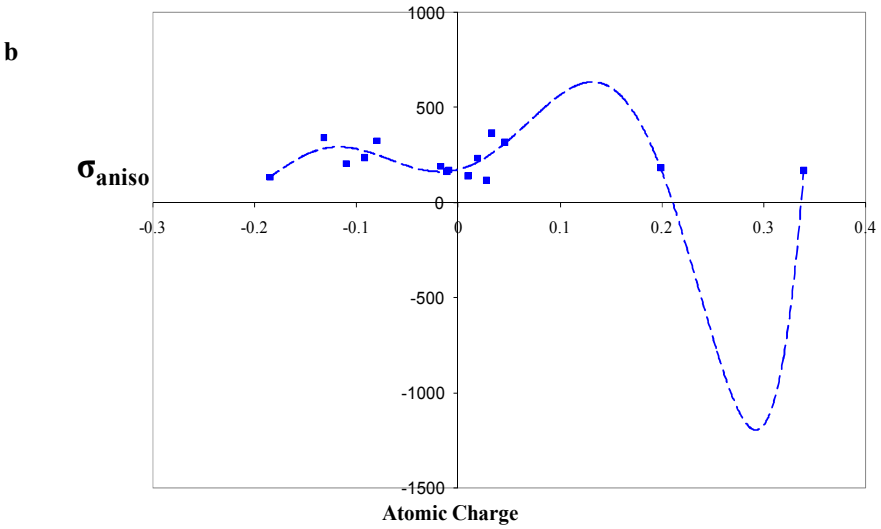
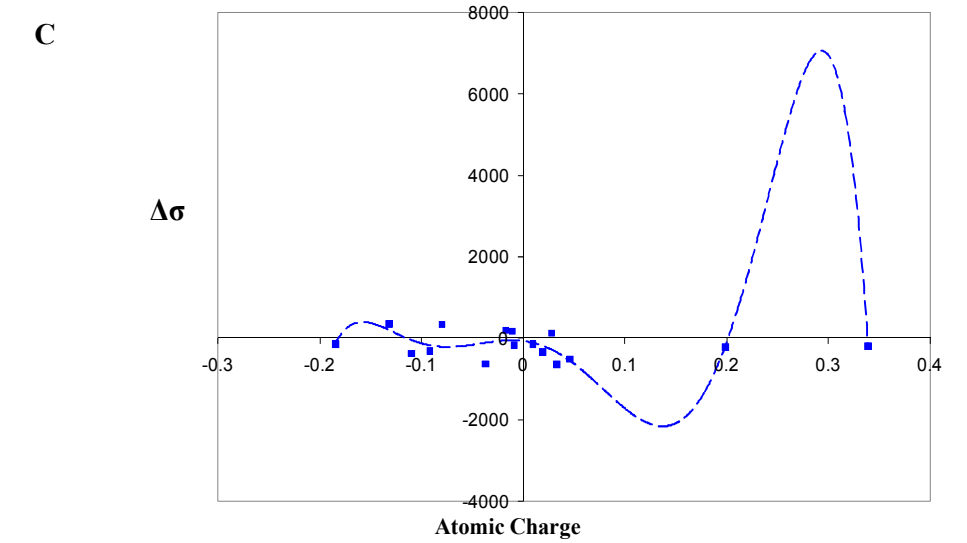
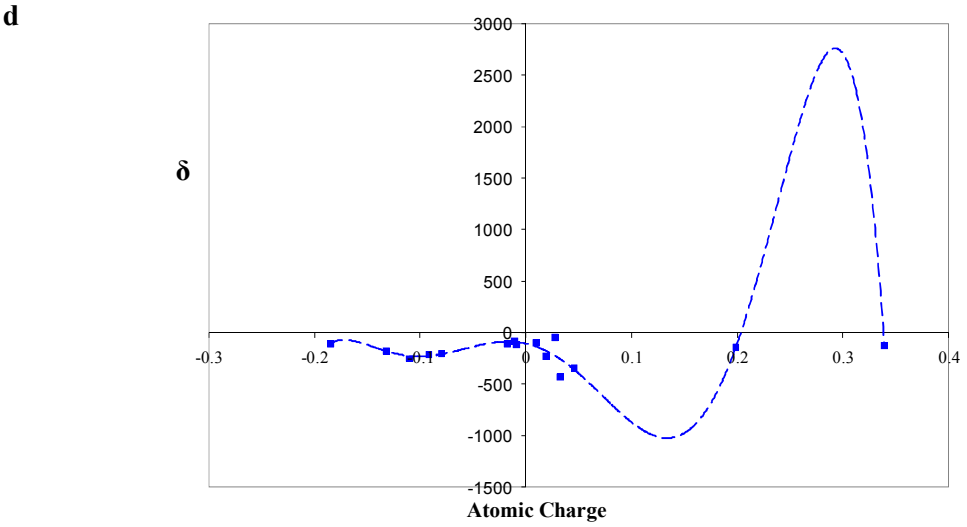


Fig. 6. Plot of a) σ_{iso}(ppm), b) σ_{aniso} (ppm), c) $\Delta\sigma$(ppm), d) δ(ppm) and e) η versus atomic charge for B_6C_4Si cluster beside vitamin C.









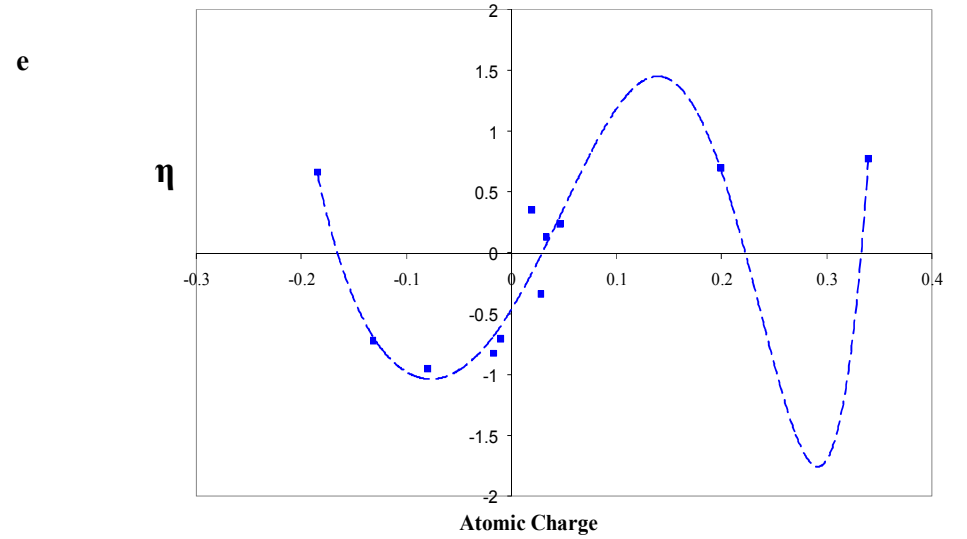
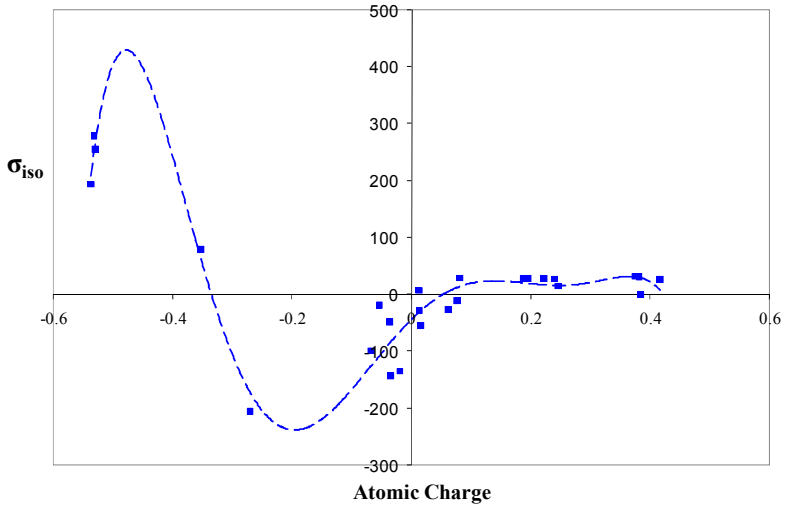
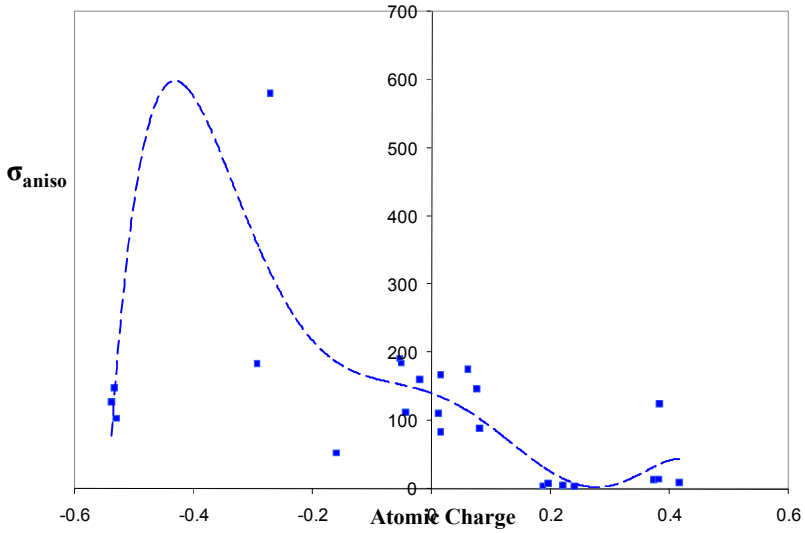


Fig. 7. Plot of a) σ_{iso} b) σ_{aniso} c) $\Delta\sigma$ d) δ and e) η versus atomic charge for C16 cluster.

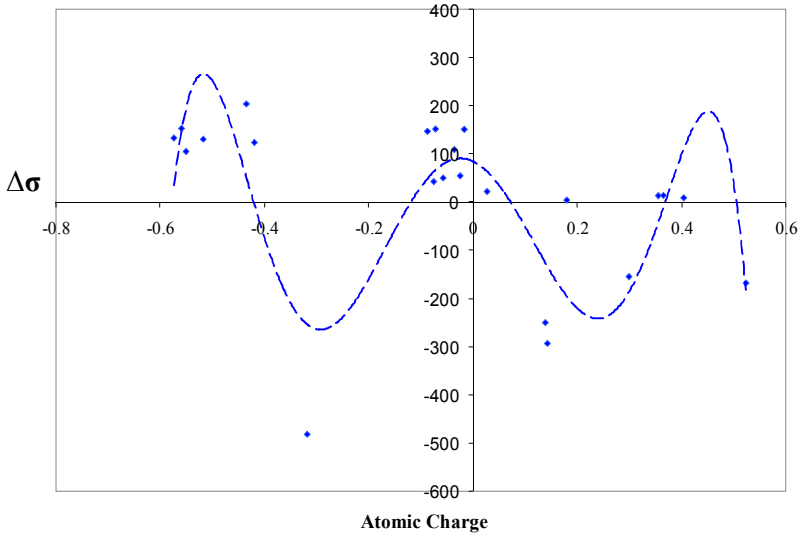
a


σiso
500
400
300
200
100
0
-100
-200
-300
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
Atomic Charge

b


σaniso
700
600
500
400
300
200
100
0
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
Atomic Charge

c


Δσ
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
Atomic Charge

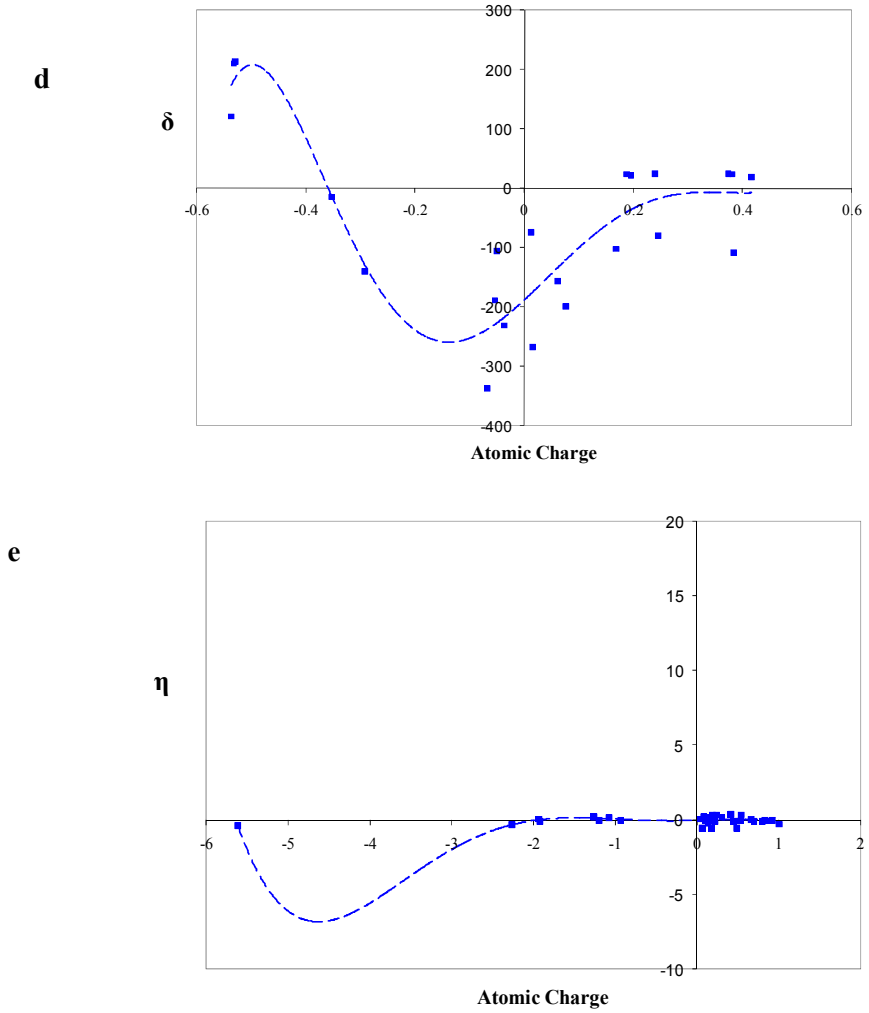


Fig. 8. Plot of a) σ_{iso} b) σ_{aniso} c) $\Delta\sigma$ d) δ and e) η versus atomic charge for C_{16} cluster beside vitamin C.

Table 5. HOMO, LUMO and HOMO- LUMO Gap energies.

	Vitamin C	**B_6C_4Si cluster beside vitamin C**	**C_{16} cluster beside vitamin C**
HOMO energy (eV)	-0.26814	-0.21210	-0.23359
LUMO energy(eV)	-0.09013	-0.12834	-0.18401
HOMO-LUMO gap energy(eV)	0.17801	0.08376	0.04958

Calculation of HOMO, LUMO and HOMO- LUMO Gap Energies

Table 5 shows the values of HOMO, LUMO and HOMO–LUMO Gap energies for vitamin C and vitamin C beside B_6C_4Si or C_{16} cluster using B3LYP method and 6-311G* basis set. Table 5 demonstrates that HOMO energy of vitamin C increases and HOMO–LUMO Gap energy decreases after connecting to B_6C_4Si or C_{16} cluster.

Vitamin C is an electron donor (reducing agent or antioxidant), and probably all of its biochemical and molecular functions can be accounted for by this function [20-23]. Also by decreasing of HOMO-LUMO Gap energy for vitamin C beside B_6C_4Si or C_{16} cluster, vitamin C can act better as an electron donor and antioxidant.

CONCLUSION

The chemical properties of B_6C_4Si and C_{16} Clusters as vitamin C carriers have been investigated using DFT method. NMR parameters, HOMO, LUMO and HOMO-LUMO Gap energies are calculated. The results of HOMO–LUMO Gap calculation show that HOMO- LUMO Gap energy of vitamin C decreases after connecting to B_6C_4Si or C_{16} cluster and by decreasing of HOMO- LUMO Gap energy, vitamin C can act better as an electron donor and antioxidant. The calculation of NMR parameters shows that vitamin C connects stronger to B_6C_4Si cluster in negative charges than positive charge. Thus by creating a negative field vitamin C can be connected to the B_6C_4Si cluster and delivered easily by using a positive filed but for C_{16} cluster, the NMR results are quite different.

REFERENCES

[1] M. Monajjemi, M. Baei, F. Mollaamin (2008).Quantum mechanics study of hydrogen chemisorptions on nanocluster vanadium surface. Russian J. Inorg. Chem., 53, 1430-1437.

[2] M. Monajjemi, S. Ketabi, R. Ghiasi, K. Zare, H. Passdar, M. Karimkhani, L. Saedi (2004). Theoretical study of interaction between adenine and M+(M = Li, Na, K, Rb, Cs) and M^{2+} (M = Mg, Ca, Sr, Ba). Inter. Elect. J. Molec. Design, 3, 789-801.

[3] M. Monajjemi, V. Lee, M. Khaleghian, B. Honarparvar, F. Mollaamin F (2010). Theoretical Description of Electromagnetic Nonbonded Interactions of Radical, Cationic, and Anionic NH2BHNBHNH2 Inside of the B18N18 Nanoring., J. Phys. Chem. C., 114, 15315-15330

[4] C. Maiti, L. Bera, S. Maikap, S. Ray, N. Chakrabarti (2000). Growth of Silicon Germanium Alloy Layers. Def. Sci. J., 50, 299-315.

[5] G. Froudakis, A. Zdetsis, M. Mühlhäuser, B. Engels, S. Peyerimhoff (1994). A comparative *ab initio* study of the Si2C4, Si3C3, and Si4C2 clusters. J. Chem. Phys., 101, 6790-6799.

[6] M. Monajjemi M, V. Lee, M. Khaleghian, B. Honarparvar, F. Mollaamin (2010). Theoretical Description of Electromagnetic Nonbonded Interactions of Radical,Cationic, and Anionic NH2BHNBHNH2 Inside of the B18N18 Nanoring. J. Phys. Chem. C., 114, 15315-15330.

[7] G. Froudakis, M. Muhlhauser, A. Zdetsis (1995). Theoretical study of the Si3C2 cluster. Chem. Phys. Lett., 233, 619-626.

[8] M. Monajjemi, H. Chegini, F. Mollaamin, P. Farahani (2011). Theoretical Studies of Solvent Effect on Normal Mode Analysis and Thermodynamic Properties of Zigzag (50) Carbon Nanotube. Fullerenes, Nanotubes, Carbon Nanostructures. 19, 469-482.

[9] N. C. Cook, S. Samman (1996). Flavonoids Chemistry, metabolism, cardioprotective effects, and dietary sources, Nutritional Biochem., 7, 66-76.

[10] S. Kaviarasan, G. H Naik, R. Gangabhagirathi, C. V. Anuradha, K. I. Priyadarsini (2007). In vitro studies on antiradical and antioxidant activities of fenugreek (Trigonella foenum graecum) seeds, Food Chemistry., 103, 31-37.

[11] E. J. Lien, S. Ren, H. H. Bui, R. Wang (1999). Quantitative structure activity analysis of phenolic antioxidants, Free Rad Bio Med,, 26, 285-294.

[12] R. L, Prior, G. Cao (2000). Antioxidant phytochemicals in fruits and vegetables. Diet and health implications", Hort Sci., 35, 588-592.

[13] S. Englard, S. Seifter (1986). "The biochemical functions of ascorbic acid. Annual review of Nutrition", 6, 365–406.

[14] D. Prockop, K. Kivirikko, "Collagens: molecular biology, diseases, and potential for therapy (1995). Annual Review of Biochemistry, 64, 403–434.

[15] C. Rebouche (1991). Ascorbic acid and carnitine biosynthesis", American Journal

of Clinical Nutrition., 54(Suppl.), S1147–S1152.

[16] M. Levine (1991). Ascorbic acid and in situ kinetics: a new approach to vitamin requirements, American Journal of Clinical Nutrition,, 54(Suppl.), S1157–S1162.

[17] B. Eipper (1993). Peptidylglycine alpha amidating monooxygenase: a multifunctional protein with catalytic, processing, and routing domains, Protein Science., 2, 489– 496.

[18] D. Becke (1988). Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. Sect. A., 38, 3098-3100.

[19] C. Lee, W. Yang, R. Parr (1988). Development of the Colle-Salvetti correlation-energy formula into into a functional of the electron density, Phys. Rev. B., 37, 785- 789.

[20] T. Zakharian (2005). A Fullerene-Paclitaxel Chemotherapeutic: Synthesis, Characterization and Study of Biological Activity in Tissue Culture, J Am Chem Soc., 127, 12508-12509.

[21] Z. Liu, Nano Res (2009) Carbon Nanotubes in Biology and Medicine: In vitro and in vivo Detection, Imaging and Drug Delivery., 2, 85-120.

[22] Z. Liu, J Mater Chem (2011). Single-walled Carbon Nanotubes in Biomedical Imaging., 21, 586-598.

[23] W. Yang, Angew Chem Int Ed (2010) Carbon nanomaterials in biosensors: should you use nanotubes or grapheme, 49, 2114-2138.