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Theoretical Study of Fullerene C_{24} Isomers Using Semi-Empirical PM3 Method

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Abstract:

We present in this work a theoretical study of the fullerene C_{24} isomers in the gaseous phase. We have determined using the semi-empirical PM3 method the optimized geometry, electronic energy, thermodynamic quantities, vibration frequencies and infrared spectra. The study showed that the isomer D_{12h} has the lower total electronic energy and the most symmetric isomer D_{6d} has the smaller energy gap. It has been shown that among all C_{24} isomers, the D_{6d} isomer has the lowest energy gap and thus, its electrical conductivity is higher compared to the other isomers, unlike the D_{12h} isomer which has the larger energy gap, therefore it has the lower conductivity. Furthermore, the isomer D_{6h} has the greater infrared absorption intensity.

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Key Words: Fullerene C_{24} Isomers, Semi-Empirical PM3, Relative Stability, Theoretical IR Spectrum, Vibration Frequencies.

دراسة نظرية لمُتماكِبات الفوليرين C_{24} باستخدام طريقة PM3النصف تقريبية

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الملخص:

نقدم في هذا العمل دراسة نظرية لمُتماكِبات الفوليرين C_{24} في الطور الغازي. باستخدام الطريقة PM3 النصف تقريبية، جرى تقدير طاقة الاستقرار النسبي والهندسة المثلى والكميات الطّاقيّة والترموديناميكية وتواترات الاهتزاز وأطياف تحت الأحمر IR لجميع مُتماكباته. كما أظهرت الدراسة أنّ المتماكب D_{12h} هو الأخفض طاقةً، وبالتالي الأكثر استقراراً. والمتماكب D_{6d} الأكثر تناظراً ويملك أصغر فجوة طّاقيّة؛ وبذلك تكون ناقليته الكهربائية هي الأعلى من بين المتماكبات الأخرى على عكس المتماكب D_{12h} الذي يملك أكبر فجوةَ طّاقيّة وبالتالي أقل ناقليةَ، ويملك المُتماكب D_{6h} أكبرَ شدّةِ امتصاصٍ تحت الأحمر.

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الكلمات المفتاحية: متماكبات الفوليرين C_{24}، طريقة PM3 النصف تقريبية، الاستقرار الطّاقيّ النسبي، أطياف تحت الأحمر النّظريّة، تواترات الاهتزاز.

1. Introduction:

After the discovery of fullerene C_{60} in 1985[1], theoretical and experimental studies were carried out and dealt with the structures and stability of small fullerenes consisting of a number of atoms less than 60 carbon atoms, using the mass spectrometry method[2-15]. Fullerene C_{24}, one of the small fullerenes, was first recorded in1993[16], produced under experimental conditions from carbon vapor condensation. It has four isomers that were later studied, but the most common is the D_{6d} isomer that contains two hexagons with 12 pentagons between them [2,17,18]. At the theoretical level, in 1993[19], using the Hartree-Fock and second order Moller-Plesset perturbation theory (MP2), Jensen and Toftlund investigated the four isomers of C_{24} fullerene: cages (D_{6d},O_h), ring (D_{12h}) and sheet (D_{6h}). Their study showed that the D_{6h} isomer (Sheet) is the most stable, followed by D_{6d} isomer. Balevišius *etal.* (1997) [20], studied the chemical stability and electronic properties of D_{6d} isomer using the PM3 method implemented in MOPCA program[21]. In 2007[22], the geometrical parameters, total energy, heat of formation, energies of HOMO and LUMO orbitals, density of one electron states (DOS) are determined by using of semi-empirical quantum chemistry PM3 method for cubic polymerized structures of O_h isomer. The results of calculations allow assuming the existence of polymerized cubic crystal structure on the base of all considered small fullerenes. Recently, several studies[23-25], were concerned with C_{24} fullerene and its four isomers by studying their geometry, energy stability, spectra and interactions with other molecules. Using density functional theory DFT and coupled cluster calculations, the relative energies and infrared spectra determined the for four different types of C_{24} isomers. Among the four isomers, they found that the astronomical data are best approximated by the graphene(sheet) form of C_{24}, and the fact that this isomer is likely to be more abundant in space, given that now fullerene (C_{60}) has been detected in circumstellar and interstellar environments, it is quite possible that C_{24} fullerene would also be present in similar environments [24]. Very recently[26-28], the hydrogen storage properties of C_{24} fullerene were studied using the DFT. The study showed that C_{24} fullerene has a storage capacity ranging from 10-12 wt % H.

In principle, the advanced quantum methods can be successfully applied to small and medium fullerenes, but their application to large fullerenes such as C_{240} or giant C_{6000} requires very advanced computers and the cost of computation is high if possible. For this reason it is important to test semi-empirical methods in the field of fullerenes; because the success of these methods in this field allows them to be applied to large and giant fullerenes at a reasonable computational cost. In this case it is possible to obtain at least a good qualitative characterization that allows the understanding and interpretation of the experimental results even if the quantitative characterization is imprecise. The C_{24} fullerene was chosen for two reasons. It is considered one of the small fullerenes for which there exist advanced and exact theoretical calculations that can be compared with the semi-empirical one. Furthermore, it has four isomers that the calculation must classify their energetic and spectral properties. In addition, we know from the scientific literature the important role played by semi-empirical methods in studying the properties of a very wide range of organic and metallic compounds, since semi-empirical methods are two to three times faster compared to ab initio or DFT methods in the calculations of the optimized geometry, electronic and spectroscopic properties [29]. Therefore, it is important to test these methods in the field of fullerenes in order to understand their applicability to large and big fullerenes, which is our goal in this work. Based on the above, in this study we propose a semi-empirical calculation of C_{24} fullerene isomers using the PM3 method.

2. Computational Methods

2.1. Semi-empirical methods

The calculations were made using semi-empirical PM3 method implemented in ORCA program package[30]. The semi-empirical methods are based on the Hartree–Fock equations[31,32,33]. These methods trait explicitly only the valence electrons, while the core electrons and the nuclei are treated as one effective fundamental potential. Furthermore, semi-empirical methods replace the three and four center

integrals by atomic parameters that can be obtained from empirical and experimental spectroscopic data[34,35]. The semi-empirical methods use the Slater Type Orbital(STO) which are more precise than the Gaussian one(GTO). Among the most important semi-empirical methods used are the MNDO, AM1 and PM3 methods. Last years, semi-empirical methods have developed and used greatly, especially to study the biological and large systems. Recent studies showed that the accuracy of modern semi-empirical methods may approach or sometimes exceed that of standard DFT methods[36-38]. Based on the MNDO and AM1 methods, Stewart developed the PM3 method by adding more parameters in order to obtain more accurate results compared to experimental ones. The PM3 method is also currently extremely popular for organic systems, and it is more accurate than AM1 for hydrogen bond angles[33,35].

2.2. ORCA and interface package

ORCA [39,40]is an ab initio quantum chemistry program package that contains modern electronic structure methods including density functional theory, many-body perturbation, coupled cluster, multi reference methods, and semi-empirical quantum chemistry methods. Its main field of application is larger molecules, transition metal complexes, and their spectroscopic properties. ORCA is developed in the research group of Frank Neese. The free version is available only for academic use at academic institutions. ORCA 5.0 is a major upgrade to the program. It features semi-empirical, Hartree-Fock, DFT, single- and multi reference(local) correlation methods, can compute a large array of molecular properties and is a fully integrated system for multilevel calculations including Quantum Mechanics(QM)/Molecular Mechanics (MM), and embedded crystals. And the compounds were built By using Chem Draw of Gabedit [41].

3. Results and discussion

In this work, we report the calculations of the electronic energy of the C_{24} fullerene isomers in order to determine their relative stability, the optimized geometry, some energy and thermodynamic quantities. Vibration frequencies and theoretical infrared spectra also determined.

3.1. Electronic energy

Table(1) shows the optimized energy of the C_{24} isomers on the surface potential energy(eV) by PM3 method.

Table(1): Total electronic energy (eV) of four isomers of C_{24}at PM3 method.

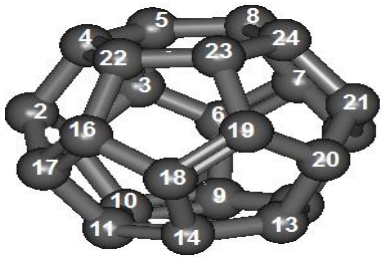
C24 Isomers	this work	Previous work			
	PM3	Sym.	Basis/theory	value	Ref.
D_{6d}	-2813.715	D_{6d}	6-31G(d)/B3LYP	-24862.744	[24]
			PM3	-2813.720	[20]
O_h	-2813.291	O_h	6-31G(d)/B3LYP	-24860.832	
			PM3	-2813	[22]
Ring(D_{12h})	-2818.504	D_{12h}	6-31G(d)/B3LYP	-24863.327	[24]
Sheet(D_{6h})	-2816.073	D_{6h}	6-31G(d)/B3LYP	-24863.978	

The electronic energies values for all four C_{24} isomers are presented in Table(1) at PM3 method. The energies of the four structures were calculated (-2813.715, -2813.291, -2818.504 and -2816.073 for D_{6d}, O_h, D_{12h} and D_{6h} isomer, respectively) and it was shown that the D_{12h} isomer has more stability. The corresponding values estimated at B3LYP complete basis set 6-31G(d)[24] are presented in the last columns. The trend of calculated electronic energies among the C_{24} isomers(D_{6d}, O_h) is in good agreement with the values at the PM3 method[20,22]. When comparing our calculations with previous theoretical calculations(6-31G(d)/B3LYP), we find that there is a difference in energy and it appeared clearly in the reference[24]. This is due to the accuracy of the quantum method used in the calculation as well as the basis set used. the PM3 method numerically computes the two- and three-center integrals using approximations parameters that can be taken from experiment or from special relationships. It does not take into account electronic correlation,

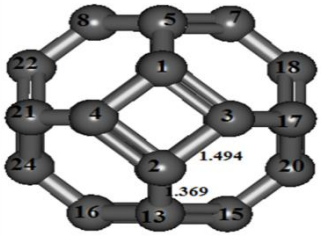
but generally gives the qualitative behavior of fullerenes. In contrast, in the DFT methods all integrals are calculated analytically using Gaussian basis set. Therefore, it is natural that there are large differences in energy between the two methods.

3.2. Optimized geometries of the C_{24} isomers

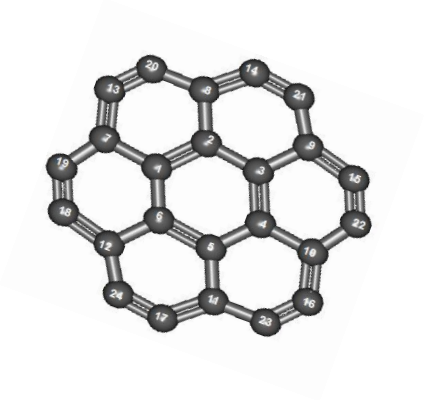
We present in the tables(2,3) of the most important bond lengths and angle values for C_{24} fullerene isomers calculated using PM3 method. We have used(R: Angstroms) to refer to the bond lengths and(A: Degrees) to refer to measurements of angles in the structure of the C_{24} fullerene isomers. the four shapes were obtained by using Chem Draw of Gabedit[41].



Cage(D_{6d})



Cage(O_h)



Sheet(D_{6h})

Ring(D_{12h})

Fig.1. The PM3 optimized geometry of the C_{24} isomers:

It is clear from fig.1 the difference between D_{6h} and $O_h$according to the distribution of adjacent hexagons in the fluorescent cage. The isomer D_{6h} consists of two hexagons, including 12 pentagons. Whereas, the O_h cage isomers consist of 6 quadrilaterals and 8 hexagons. As it can be seen from Figure (1), that the sheet isomer D_{6h} consists of hexagonal polygons connected to each other, as well as the carbon atoms connected to each other in a circular shape forming the ring isomer D_{12h}. The structure of the isomers of C_{24}fullerene was optimized by PM3 theory in Fig.1.

Table 2. Some bond lengths(R: Angstroms) and angles measurements(A: Degree) of two isomers(D_{6d}, O_h)of C24at PM3 method.

Cage D_{6d}			CageO_h		
This work		Previous work	This work		Previous work
PM3		B3LYP/6-31G(d) [24]	PM3		B3LYP/6-31G(d) [24]
R & A.	Value	Value	R & A.	Value	Value
R(19,18)	1.376	1.369	R(1,3)	1.494	1.492
R(19,20)	1.474	1.462	R(24,16)	1.369	1.375
R(19,23)	1.522	1.531	-	-	-
R(23,24)	1.423	1.423	-	-	-
A(16,22,23)	106.7	-	A(4,1,3)	89.9	-
A(22,23,19)	107.3	-	A(4,2,3)	89.9	-
A(19,18,14)	109.2	-	A(1,5,7)	119.9	-
A(17,16,18)	108.7	-	A(21,4,2)	119.9	-
A(22,4,5)	120	-	-	-	-
A(5,8,24)	119.9	-	-	-	-

It is clear from Table (2) that the cage isomer D_{6d} has four types of different bonds located between 1.376 (A°) and 1.522 (A°), where the average bond length of this isomer is 1.445 (A°). Whereas for the O_h cage isomer, it has only two types of bonds, 1.369 (A°) and 1.494 (A°). These calculated results have good agreement with previous investigation [24] on the D_{6d} in which its optimized structure is 1.423, 1.531, 1.462 Å, and 1.369 Å, respectively. For the O_h isomer, the carbon-carbon bond lengths of 1.375 and 1.492 Å have also been obtained at the same quantum method. When compared with the previous work [24] by the B3LYP/6-31G(d) method, the values were very close and sometimes equal, for cage D_{6d} and cage O_h. On the other hand, the measurements of the angles in the cage isomer D_{6d} fall within the range [106.7°-120.0°], as for the O_h cage isomer, these values fall within the range [119.9°-89.9°]. It is appropriate to note that the angles of pentagons deviate more or less than 108°(the measure of the angle in a regular pentagon). Likewise, we found that the angles of the hexagonal polygons deviate by an increase or decrease from the value 120° (the measure of the angle in a regular hexagon), where the angles values in the isomer D_{6d} were equal to the values of the angles of the regular hexagon and the value of the angle A(16,22,23) decreased = 106.7° than the angle of the regular pentagon by 1.3°, while the value of angle A(19,18,14)=109.2° increased by 1.2°, while O_h isomer the values of angles in the quadrilaterals and hexagons were almost equal to the values of the angles in the regular quadrilaterals and hexagons 120 ° and 90 ° respectively.

Table(3) Some bond lengths(R: Angstroms)and angles measurements(A: Degree) for the C_{24} isomers(D_{12h}, D_{6h}) using PM3 method.

Ring D_{12h}			Sheet D_{6h}		
This work		Previous work	This work		Previous work
PM3		HF/DZP [19]	PM3		HF/DZP [19]
R & A.	Value	Value	R & A.	Value	Value
R(13,2)	1.203	1.197	R(21,9)	1.381	1.391
R(1,13)	1.362	1.385	R(9,3)	1.462	1.456
-	-	-	R(3,2)	1.451	1.447
-	-	-	R(17,24)	1.234	1.210
A(13,2,14)	164.9		A(21,9,3)	112.5	112.6
-	-	-	A(3,2,8)	119.9	120.0
-	-	-	A(4,3,9)	120.0	-
			A(24,21,9)	127.4	127.4
-	-	-	A(14,8,20)	134.8	-

It is clear from Table(3) that the isomer D_{12h} has only two types of bonds are 1.203(A°) and 1.362(A°). while the sheet isomer D_{6h} has four different types of bonds, their lengths range from 1.234(A°) to 1.462(A°). On the other hand, the D_{12h} isomer has values of its angles[164.9°-165.0°] and the D_{6h} isomer whose angle measures are within the domain[134.8°-112.5°]. In D_{6h} isomer, the values of the angles were deviated by an increase and decrease from the values of the angles in the regular hexagon. These calculated results(bond lengths and angles) have good agreement with previous investigation [19]. We conclude that the increase and decrease in the values in the PM3 method is due to the difference in the geometric structure of the isomers. In short, molecular geometry determines all the physic-chemical properties of matter.

3.3. The energetic and thermodynamic quantities of C_{24} isomers

In the tables (4,5,6,7) we presented the PM3 energies E_{HOMO}, E_{LUMO}, E_{Gap}, ionization potential, electronic affinity, electronegativity, electronic chemical potential, electronic hardness, electronic electrophilicity, thermal energy, entropy, enthalpy and Gibbs free energy.

3.3.1. HOMO and LUMO energies and energy gap

Table (4) we report the PM3 energy values of the highest E_{HOMO} molecular orbital and the lowest E_{LUMO} unoccupied molecular orbital, and the energy difference between them E_{Gap}.

Table (4) Comparison of E_{HOMO}, E_{LUMO} and E_{Gap} values(in eV) of four isomers of C_{24} at PM3 method with their counterpart calculated with previous work.

Sym.	E_{Homo}	E_{Lumo}	Energy gap		
	This work	This work	This work	Previous work [20,22]	Previous work [24]
D_{6d}	-9.384	-3.222	6.162	6.160	1.825
O_h	-9.570	-2.511	7.059	7.059	2.522
Ring D_{12h}	-9.038	-1.535	7.508	-	1.881
Sheet D_{6h}	-9.280	-2.127	7.153	-	3.425

Table(4) summarized the energy of HOMO and LUMO and E_g values as obtained from PM3 results. The O_h isomer, in absolute terms, has the largest values of $E_{HOMO}$and the ring isomer D_{12h} has the smallest values of E_{LUMO}, while we noticed that the smallest values of the energy gap E_{Gap} in the isomer D_{6d} was(6.162eV). When comparing our values with previous works[24], the energy gap was larger, because the PM3 method does not take into account the electronic bonding, it depends on the Hartree-Focke equations and makes an approximate calculation. Whereas, the DFT method calculate all integrals fairly accurately. we note that the energy gap values of the two isomers(D_{6d}, O_h) are equal in value with the reference [20,22]. The reason for this is that we use the same method PM3and this confirms the correctness of our calculations. Thus, the D_{6d} isomer is considered to be the most electrically conductive of the other isomers. On the other hand, the ring isomer D_{12h} has the largest value of the energy gap by a difference of (1.364 eV) than D_{6d} isomer; Thus, it ranks last in electrical conductivity compared to these isomers. The value of the energy gap indicates whether the materials are conductors, semiconductors, or insulators. The energy gap is defined as the amount of energy needed for an electron to move from the valence band. to the conduction band. The value of gap energy, in electron volts, is zero or very small in the conductors, bigger than 3 in the insulating materials, and it is considered relatively large, and between 0.1 to 3 in the semiconductors [42]. It is clear from the energy gap values presented in Table (4) that PM3 method is considered C_{24} fullerene isomers in our work as insulators. On the other hand, results of the work [24] showed that the C_{24} semiconducting fullerene isomers, except the D_{6h}isomer, were considered dielectric materials and had an energy gap of 3.425eV. The large difference in E_g between PM3 and DFT is explained by the fact that the DFT method computes all integrals fairly accurately, while PM3 does an approximation.

3.3.2. Ionization potential, Electronic Affinity, Electronegativity, and Electronic chemical potential

In Table(5) we presented the values of ionization potential(I), electronic affinity(A), electronegativity(χ), and electronic chemical potential(μ) for C_{24} isomers by PM3 method.

Table (5): Values of the ionization potential, electronic affinity, electronegativity and electronic chemical potential(in eV) of four isomers of C_{24} at PM3 method.

Sym.	**I**		A		**χ**	**μ**
	This work	Previous work	This work	Previous work	This work	This work
	PM3	**B3LYP/6-31G(d)[24]**	PM3	تجريبي [43]	PM3	PM3
D_{6d}	9.38	7.36	3.22	2.90	6.303	-6.3035
O_h	9.57	7.54	2.51	-	6.0405	-6.0405
D_{12h}	9.03	-	1.35	-	5.2872	-5.2872
D_{6h}	9.28	8.00	2.12	-	5.7036	-5.7036

We Table(5) show that:

• the value of the largest ionization potential is for the O_h isomer. This means that the energy required to remove an electron from it, is greater than the energy required to remove an electron from the remaining isomers.

• D_{6d} isomer has the highest value for electronic affinity, while the D_{12h} isomer has the lowest value for electronic affinity. When comparing the values of the electronic affinity for the D_{6d} isomer with the previous experimental work[43], we found that the values are very close, and this indicates the validity of our results.

• According to the absolute value, the largest value of the electronegativity and the electronic chemical potential is for D_{6d} isomer, that is, the ability of D_{6d} isomer to draw the electronic cloud is bigger, while the smallest value for the electronegativity and the chemical potential is for the more stable D_{12h} isomer. This shows that the four isomers have the same number of carbon atoms(24 atoms), but they different in the geometric location(molecular geometry) of these atoms, and this explains the difference in physical properties. In short, molecular geometry determines all the physic-chemical properties of matter.

3.3.3. Hardness, softness, electrophilicity, electric dipole moment and Electric Polarizability

Table(6) shows values of hardness (η), softness(S), electrophilicity(ω) and electric dipole moment(μ) for each of the C_{24} fullerene isomers using PM3 method.

Table(6) Values of the hardness, electrophilicity(eV), electric dipole moment(Debye) and Electric Polarizability(a.u) of C_{24} isomers using PM3 method.

Sym.	η	S	ω	μ	α_{iso}	
	This work	This work	This work	This work	This work	Previous work
	PM3	**PM3**	**PM3**	**PM3**	**PM3**	B3LYP/6-31+G(d)**[**44**]**
D_{6d}	3.081	0.162	6.447	0.00402	255.550	215
O_h	3.529	0.141	5.812	0.00025	245.104	-
D_{12h}	3.751	0.133	3.725	0.00015	529.397	-
D_{6h}	3.576	0.139	4.547	0.00002	307.477	-

We conclude from Table(6) that D_{12h} isomer has the largest values of electronic hardness, the smallest values of electrophilicity and the smallest values of softness. In contrast to D_{6d}isomer based on the above, we find that the D_{6d} isomer shows more resistance to changing the electronic distribution than the other isomers studied in this work. It is also noted from Table(6) that the D_{6h} isomer is more symmetric; because of the small value of the dipole moment compared to other isomers. Next is D_{12h} isomer in terms of symmetry, followed by O_h , D_{6d} isomers, respectively. The electric dipole moment is a vector quantity; it is equal to the vector sum of electric dipole moments of the bonds of molecule. When structure of molecule is perfectly symmetrical, electric dipole moment of the molecule is equal to zero due to the cancellation of the electric dipole moments of each other, and value of electric dipole moment of the molecule increases as it moves away from symmetry. Although the Electric Polarization is difficult to calculate theoretically and difficult to measure experimentally, D_{12h}isomer had the biggest value of polarization, meaning that the electronic cloud of the ring is greatly affected by the applied electric field. When compared with the previous work [44], by the B3LYP/6-31+G(d) method, the difference in the values was clear, meaning that our values of the PM3 method are bigger than the values of the previous work for the D_{6d} cage. Polarizability describe the response of a system in an applied electric field. They determine not only the strength of molecular interactions (e.g., long-range intermolecular induction, dispersion forces) as well as the cross sections of different scattering and collision processes but also the nonlinear optical properties of the system. The isotropic polarizability <α> is calculated as the mean value as given in the following equation:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

3.3.4. Thermal energy, Entropy, Enthalpy and Gibbs free energy.

In Table(7) we report the PM3 values of heat energy(U), entropy(S), enthalpy(H) and Gibbs free energy(G).

Table (7) Values of heat energy(U), entropy, enthalpy and Gibbs free energy for C_{24} isomers by PM3 method.

Sym.	U(a.u.)	H(a.u.)	S(kcal/mol)	G(a.u.)
D_{6d}	-103.2461	-103.2451	26.95	-103.2881
O_h	-103.2245	-103.2235	24.74	-103.2630
D_{12h}	-103.4242	-103.4233	40.48	-103.4878
D_{6h}	-103.3306	-103.3297	33.22	-103.3826

We conclude from Table(7) that the values of the inner energy, entropy and Gibbs free energy for the studied isomers follow the same order of energy stability. This is because it results from the total electronic energy values, as is evident in the following relationships:

$$\mathrm{U} = E_{el} + \mathrm{E}_{\mathrm{ZPE}} + E_{\mathrm{vib}} + E_{\mathrm{rot}} + E_{\mathrm{trans}}$$

Where:

E_{el}: is the electronic energy
$\mathrm{E}_{\mathrm{ZPE}}$: is the zero point energy
E_{vib}: is the vibrational energy
E_{rot}: is the rotational thermal energy
E_{trans}: is the translational thermal energy

$$\mathrm{H} = \mathrm{U} + k_B \cdot \mathrm{T}$$

$$G = H - T \cdot S$$

3.4. Frequencies of vibration and infrared spectra

We list, in order, in Table(8) and Fig(2) the PM3 vibrational frequencies and infrared spectra of C_{24} fullerene isomers.

Table (8) Vibration frequencies of the C_{24} fullerene isomers by PM3 method.

Sym.	Wave number (cm^{-1})	IR intensities (km/mol)
D_{6d}	863.318	5.218
	921.591	18.572
	1011.230	100.070
	1375.050	4.875
	1622.880	5.218
O_h	964.010	100.070
	1246.30	27.818
D_{12h}	505.100	81.704
	2420.890	100.000
D_{6h}	947.770	89.744
	1192.510	41.416
	1805.370	7.519
	2134.850	99.806

The C_{24}fullerene has 66 harmonic vibration modes (3N-6)=66. We notice from Table(8) in the infrared spectrum of C_{24} fullerene isomers that the D_{6d} isomer has five modes of vibration, and $O_h$isomer has two modes of vibration, while the D_{12h} isomer has two modes vibration, while the D_{6h} isomer has four modes. We note that intensity of absorption with respect to strongest peak follows the behavior of frequency as it increases with increasing frequency for most of the isomers. Table(8) also shows the increase in the value of the frequency corresponding to the biggest peak when moving successively between the four isomers.

We note that the intensity of absorption with respect to the largest peak follows the behavior of the frequency as it increases with increasing frequency for the isomers (D_{12h}, D_{6h}). We also note that the largest absorption intensity belongs to D_{12h} isomer. This can be explained by the fact that the vibration pattern responsible for this peak accompanies a big change in the dipole moment during the vibration process, and this allows for a bigger absorption potential that leads to a bigger absorption intensity. These vibrational modes have been presented in Figure 2.

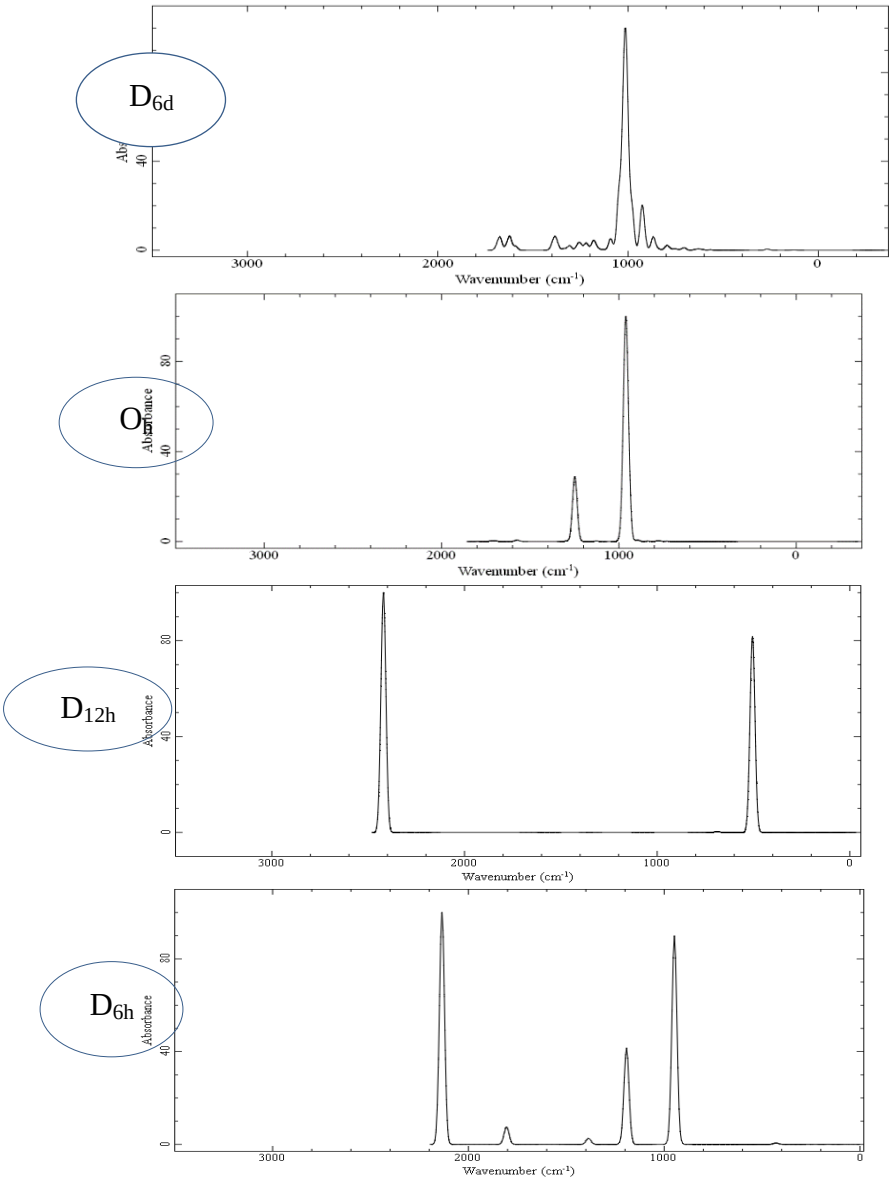


Figure 2. Infrared spectra of four isomers of C_{24}at PM3 method.

4. Conclusion:

In this paper, a theoretical study of the four C_{24} isomers of fullerene was carried out using PM3 method. The optimized geometry of the four isomers is determined with respect to the convenable symmetry group. Also, the and relative stability energies, energy gap, some quantities of energies, thermodynamics, vibration frequencies and theoretical infrared absorption spectra were calculated. The study showed that the PM3 method provided good results when studying the geometry of the four C_{24} molecules, while the results were acceptable for the rest of the properties compared to other theoretical methods. The study also showed that the ring isomer(D_{12h}) is the most stable among the four isomers studied, followed by the sheet isomer(D_{6h}) and then the cages (D_{6d}, O_h), while the highest adsorption intensity was for the sheet isomers(D_{6h}).

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5. References:

1. Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., & Smalley, R. E. (1985). C60: Buckminsterfullerene. nature, 318(6042), 162-163.
2. Kroto, H. W. (1987). The stability of the fullerenes Cn, With n=24, 28, 32, 36, 50, 60, and 70. Nature, 329, p529.
3. Feyereisen, M., Gutowski, M., Simons, J., & Almlöf, J. (1992). Relative stabilities of fullerene, cumulene, and polyacetylene structures for C n: n= 18–60. The Journal of chemical physics, 96(4), 2926-2932.
4. T. Guo, M. D., Diener, Y., Chai, A. J., Alford, R. E., Haufler, S. M., & McClure, T. & et al. (1992). Uranium Stabilization of C28 - A Tetravalent Fullerene. Science, 257, P161
5. Raghavachari, K., Zhang, B., Pople, J. A., Johnson, B. G., & Gill, P. M. W. (1994). Isomers of C24. Density functional studies including gradient corrections. Chemical physics letters, 220(6), 385-390.
6. Jones, R. O., & Seifert, G. (1997). Structure and bonding in carbon clusters C14 to C24: chains, rings, bowls, plates, and cages. Physical review letters, 79(3), 443.
7. Piskoti, C., Yarger, J., & Zettle, A. (1998). C36, a new carbon solid. Nature,393, pp: 771-4.
8. Mishra, R. K., Lin, Y.,& Lee, S.(1999) Growth mechanism of C28 (Td) fullerene: energetics and transition-state structures analysis, , Chem. Phys. Letts., 313, p437
9. Chen, Z., Jiao, H., Bühl, M., Hirsch, A., & Thiel, W. (2001). Theoretical investigation into structures and magnetic properties of smaller fullerenes and their heteroanalogues. Theoretical Chemistry Accounts, 106(5), 352-363.
10. Paulus, B. (2003). Electronic and structural properties of the cage-like molecules C20 to C36. Physical Chemistry Chemical Physics, 5(16), 3364-3367.
11. Chang, Y. F., Zhang, J. P., Sun, H., Hong, B., An, Z., & Wang, R. S. (2005). Geometry and stability of fullerene cages: C24 to C70. International journal of quantum chemistry, 105(2), 142-147.
12. An, W., Shao, N., Bulusu, S., & Zeng, X. C. (2008). Ab initio calculation of carbon clusters. II. Relative stabilities of fullerene and nonfullerene C 24. The Journal of chemical physics, 128(8), 084301.
13. Sun, G., Nicklaus, M.C., & Xie, R. (2005). Structure, Stability, and NMR properties of lower fullerenes C38-C50 and Azafullerene C44N6. J. Phys. Chem. A, 109, P 4617.
14. Pattanayak, J., Kar, T., & Scheiner, S. (2004). Substitution Patterns in Mono BN-Fullerenes: Cn (n = 20, 24, 28, 32, 36 and 40. J. Phys. Chem. A., 108, P 7681.
15. Talanov, V. M., Fedorova, N. V., & Gusarov, V. V. (2010). Symmetrical Features of the Structure of C24 and C48 Fullerenes. Glass Physics and Chemistry, 36(3), 358-368.
16. Von Helden, G. V., Hsu, M. T., Gotts, N. G., Kemper, P. R., & Bowers, M. T. (1993). Do small fullerenes exist only on the computer? Experimental results on C=/− 20 and C+/− 24. Chemical physics letters, 204(1-2), 15-22.
17. Kent, P. R. C., Towler, M. D., Needs, R. J., & Rajagopal, G. (2000). Carbon clusters near the crossover to fullerene stability. Physical Review B, 62(23), 15394.
18. Martin, J. M., El-Yazal, J., & François, J. P. (1996). On the structure and vibrational frequencies of C24. Chemical physics letters, 255(1-3), 7-14.
19. Jensen, F., & Toftlund, H. (1993). Structure and stability of C24 and B12N12 isomers. Chemical physics letters, 201(1-4), 89-96
20. Balevišius, L. M., Stumbrys, E., & Tamulis, A. (1997). Conformations and electronic structure of fullerene C24 and C26 molecules. Fullerenes, Nanotubes, and Carbon Nanostructures, 5(1), 85-96.
21. Stewart, J. J. (1990). MOPAC manual. Constraints, 3(2).
22. Popov, A. P., & Bazhin, I. V. (2007). Cubic polymerized structures of small fullerenes C 20, C 24, C 28, C 32. In Hydrogen Materials Science and Chemistry of Carbon Nanomaterials (pp. 713-719). Springer, Dordrecht.

23. Manna, D., & Martin, J. M. (2016). What are the ground state structures of C20 and C24? An explicitly correlated ab initio approach. The Journal of Physical Chemistry A, 120(1), 153-160.
24. Wang, Z., Zhang, J., & Cao, Z. (2010). Theoretical studies on electronic structures and thermal stabilities of C24O isomers derived from C24. Journal of Molecular Structure: THEOCHEM, 949(1-3), 88-90.
25. Sadjadi, S., Kwok, S., Cataldo, F., García-Hernández, D. A., & Manchado, A. (2020). A theoretical investigation of the possible detection of C24 in space. Fullerenes, Nanotubes and Carbon Nanostructures, 28(8), 637-641.
26. Zhang, Y., & Cheng, X. (2018). Hydrogen storage property of alkali and alkaline-earth metal atoms decorated C24 fullerene: A DFT study. Chemical Physics, 505, 26-33.
27. Ahangari, M. G., & Mashhadzadeh, A. H. (2020). Density functional theory based molecular dynamics study on hydrogen storage capacity of C24, B12N12, Al12 N12, Be12O12, Mg12O12, and Zn12O12 nanocages. International Journal of Hydrogen Energy, 45(11), 6745-6756.
28. Sathe, R. Y., Bae, H., Lee, H., & Kumar, T. D. (2020). Hydrogen storage capacity of low-lying isomer of C24 functionalized with Ti. International Journal of Hydrogen Energy, 45(16), 9936-9945.
29. Zheng, G., Irle, S., & Morokuma, K. (2005). Performance of the DFTB method in comparison to DFT and semiempirical methods for geometries and energies of C20–C86 fullerene isomers. Chemical physics letters, 412(1-3), 210-216.
30. Brehm, M. ORCA 5.0.1 Molecular Dynamics Module.
31. Pracht, P., & Bannwarth, C. (2022). Fast Screening of Minimum Energy Crossing Points with Semiempirical Tight-Binding Methods. Journal of Chemical Theory and Computation.
32. [32] Thiel, W. (2000). Semiempirical methods. Modern methods and algorithms of quantum chemistry, 261-283.
33. [33] Young, D. (2004). Computational chemistry: a practical guide for applying techniques to real world problems. John Wiley & Sons.
34. Stewart, J. J. (2007). Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements. Journal of Molecular modeling, 13(12), 1173-1213.
35. Kayi, H.(2009). PARAMETERIZATION OF THE AM1* SEMIEMPIRICAL MOLECULAR ORBITAL METHOD FOR THE FIRST-ROW TRANSITION METALS AND OTHER ELEMENTS. Doctora Thesis, aus Bursa, Türkei,PP 1-211
36. Dral, P. O., Wu, X., Spörkel, L., Koslowski, A., Weber, W., Steiger, R., ... & Thiel, W. (2016). Semiempirical quantum-chemical orthogonalization-corrected methods: theory, implementation, and parameters. Journal of chemical theory and computation, 12(3), 1082-1096.
37. Wu, X., Koslowski, A., & Thiel, W. (2016). Semiempirical Quantum Chemistry. Electronic Structure Calculations on Graphics Processing Units: From Quantum Chemistry to Condensed Matter Physics, 239-253.
38. Pérez-Tabero, S., Fernández, B., Cabaleiro-Lago, E. M., Martínez-Núñez, E., & Vázquez, S. A. (2021). New Approach for Correcting Noncovalent Interactions in Semiempirical Quantum Mechanical Methods: The Importance of Multiple-Orientation Sampling. Journal of chemical theory and computation, 17(9), 5556-5567.

39. Neese, F. (2012). The ORCA program system. Wiley Interdisciplinary Reviews: Computational Molecular Science, 2(1), 73-78.
40. Neese, F. (2022). Software update: The ORCA program system—Version 5.0. Wiley Interdisciplinary Reviews: Computational Molecular Science, 12(5), e1606.
41. Allouche, A.R. (2011). Gabedit-Agraphical user interface for computational chemistry softwares, Journal of Computational Chemistry, 32, 174-82.
42. Üngördü, A., & Tezer, N. (2017). The solvent (water) and metal effects on HOMO-LUMO gaps ofguanine base pair: A computational study, J. Mol Graph Model, 74, 265–72.
43. EXPT S. Yang, K. I. Taylor, M. I. Craycraft, I. Conceico, C. I. Pettiette, O.Cheshnovsky, and R. E. Smalley, Chern. Phys. Lett. 144,431 (1988).
44. Kosar, N., Tahir, H., Ayub, K., & Mahmood, T. (2021). DFT studies of single and multiple alkali metals doped C24 fullerene for electronics and nonlinear optical applications. Journal of Molecular Graphics and Modelling, 105, 107867.