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Application of the quantum chemical descriptor to the quantitative structure-activity of the ascorbic acid molecule: DFT and MP2 survey

H. EL Ouafy[1], T. EL Ouafy*[2], M. Oubenali[1], M. Mbarki[1], A. EL Haimouti[3], M. Echajia[1]

[1]*Laboratory of Organic and Analytical Chemistry, Sultan Moulay Slimane University, Faculty of Science and Technology, Beni Mellal, Morocco*

[2] *Laboratory of Organic and Analytical Chemistry, Sultan Moulay Slimane University, Polydisciplinary Faculty, Khouribga, Morocco*

[3] *Laboratory of Chemistry, Modeling and Environmental Sciences, Sultan Moulay Slimane University, Polydisciplinary Faculty, Khouribga, Morocco*

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Abstract

In this work, we used B3LYP / 6-311G (d, p) to determine the chemical descriptor, the ionization potential (I), the electron affinity (A), the chemical potential (μ), the chemical hardness (η). Nonlinear optical descriptors (NLO) such as dipole moment (μ), polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ), 3D maps of HOMO and LUMO orbitals, lengths and Bond angles of ascorbic acid are also determined by both DFT and MP2 (The Møller-Plesset theory of order 2 perturbation). Both DFT and MP2 methods yielded almost the same value of dipole moment. The DFT and MP2 methods gave slightly different values for polarization, hyperpolarizability and second hyperpolarization because of the number of variables taken into consideration in the calculations by each method. The negative and positive regions of ascorbic acid were determined by molecular electrostatic potential.

Keywords: Ascorbic acid, descriptors chemical, HOMO, LUMO, DFT, MP2.

*Corresponding author.
E-mail address: tarikelouafy@gmail.com

1. Introduction

Vitamin C (Ascorbic acid) (**Fig 1**) is a water-soluble vitamin that is widely found in fruits, vegetables and other raw food products, such as juices and sports drinks, this acid is necessary for the synthesis of many biological processes and must be ingested daily through pharmaceutical products. Vitamin C deficiency causes scurvy, an insidious but deadly disease. Ascorbic acid (AA) is one of the interesting and well-known acids in nature which is synthesized from D-glucose or D-galactose [1]. A recommended daily intake of AA is about 70–90 mg. Inadequate intake will result in the symptoms of scurvy, gingival bleeding, and so on; excess AA intake will also lead to urinary stones, diarrhea and stomach convulsion [2]. Due to the importance of AA in the life cycle, its determination in aqueous solution is very important. Generally, AA is used in the pharmaceutical, chemical, cosmetic and food industries because of its bioactivity and as an antioxidant [3,4]. The lack of ascorbic acid leads to scurvy [5,6]. Ascorbic acid is known to increase accessibility. Vitamin C has been shown to kill HIV-positive cells and help people with HIV by boosting the immune system [7]. Vitamin C is an antioxidant that has received a lot of attention in the prevention and treatment of cancer, including its use of vitamin C supplements [8-12], physical and chemical properties of ascorbic acid (**Table 1**), vitamin C belongs to the sugar group with 6 atoms and is a derivative of D-Glucose. It is composed of a ketone function, a lactone cycle, an enediol function, and two alcohol functions: one primary and the other secondary. AA has two forms optical: levorotatory and dextrorotatory, but only the levorotatory form, natural form (ascorbic acid) is biologically active [13]. Vitamin C can be extracted from nature or created by the synthetic route from D-Glucose. Vitamin C functions as a vital electron donor [14]. Antioxidants are key components in the prevention of oxidative damage to proteins and DNA [15]. Oxidative damage is associated with the development of both mild and severe health conditions including cancer, diabetes, cardiovascular disease, arthritis, and cataracts [16]. Summarizes the techniques used to determine vitamin C in a variety of samples [17,18]. Infrared and UV-Visible techniques have been used to quantify and characterize biological samples [19]. The structure and spectroscopic properties of ascorbic acid (vitamin C) are of great chemical, biochemical and pharmacological importance because the human body cannot produce vitamin C by itself [20]. Besides, a complete vibrational characterization of ascorbic acid is very important to know the degree of decomposition of it and to quantify vitamin C in food and pharmaceutical products [21].

In this work, we were interested in the study of the structural and spectroscopic properties of ascorbic acid. We used DFT and MP2 methods to calculate the thermochemical descriptors (the optimization of the geometries, the lengths and the bond angles of the molecules, the energies and the densities of the frontier molecular orbitals HOMO and LUMO, the electronic chemical potential, electronegativity, chemical hardness, overall softness, overall electrophilic index, overall nucleophilic index, nonlinear

magnetic optical properties). The MP2 level has been used with the DFT method, whose usefulness for the description of molecular physical and chemical properties [22-26].

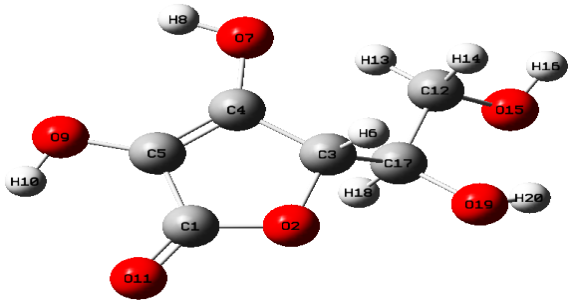


Fig. 1. Chemical structure of ascorbic acid.

Table 1. Physical and chemical properties of ascorbic acid.

Aspect	Molecular weight	Density	Boiling point	Solubility in water	Dissociation constant	Rotating power	Log (P)
Solid white	176.124 g/mol	1.65 g/cm^3 à 293K	464K	333.0 g/L à 293K	pka_1=4.1 pka_2=11,8	[αD]=+21° dans l'eau	-1.85

2. Computational method

All calculations were made using the GAUSSIAN 09 software package [27]. The function B3LYP was used to optimize the geometry and the determination of energies with lengths and angles of the bonds of the molecule of ascorbic acid by two methods DFT and MP2 and to calculate the harmonic vibrations frequencies using the basic set 6–311G (d, p). For all the optimized structures, we calculated the harmonic vibration frequencies of the corresponding links to determine the stationary points on the surface of the potential energy. The HOMO and LUMO orbital distribution were determined using the theoretical level B3LYP / 6–311G (d, p) for optimizing the structure of the compounds. Atomic partial charges were also calculated for the two structures from the potential electrostatic surface (ESP) according to the Merz-Singh-Kollman to the same level theory. Optimization of the structure, UV-vis, IR and vibrational simulation spectra of ascorbic acid and ascorbic acid molecules was carried out using the theory of functional density (DFT). All these calculations were performed using the Becke hybrid exchange and the Lee-Yang-Parr correlation function, B3LYP [28].

3. Results and discussion

3.1. UV-visible and infrared vibration spectra of the ascorbic acid molecule

The calculations of the functional density theory depend on the configuration interaction time with a single excitation (TD-DFT) of the orbital molecular geometry in the gas show that the visible absorption

maxima of ascorbic acid correspond to the electronic transition from HOMO to LUMO. The UV-visible spectrum **Fig 2** allows a chemist in his laboratory: to identify an unknown compound; check the purity of a known product by the absence of bands; monitor a reaction by studying the appearance or disappearance of reagents, intermediates or species and measure a mixture according to the intensity of the peaks or integration curves. Today, spectroscopy has a wide range of research applications.

Theoretical harmonic frequencies (cm^{-1}) and infrared intensities for ascorbic acid with B3LYP Methods using a basic set 6-311G (d, p). The spectra calculated for ascorbic acid are requested in **Fig 3**. Fourier Transform Infrared spectroscopy is based on the absorption of infrared radiation through the sample. It identifies the recognized chemical functions thanks to the detection of vibrations characteristic of chemical bonds. This technique allows a qualitative characterization from its spectral and quantitative signature allowing the dosage of a substance at very low contents [29].

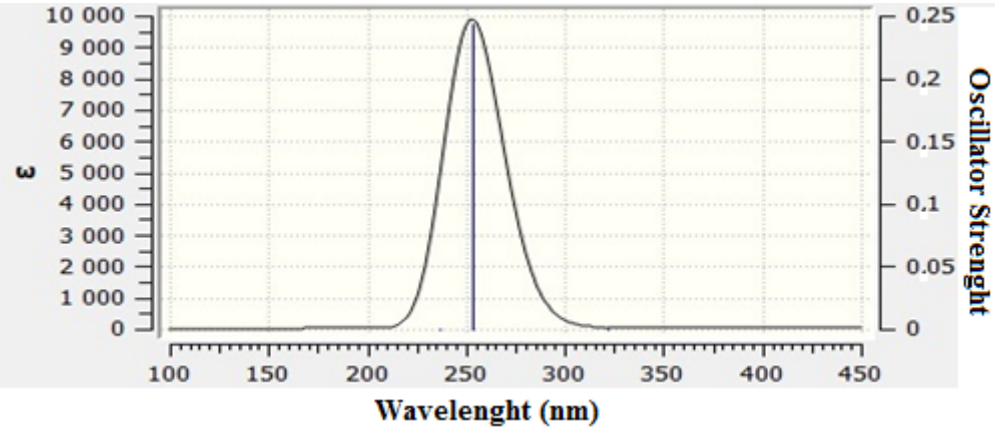


Fig 2. UV-visible spectra of ascorbic acid

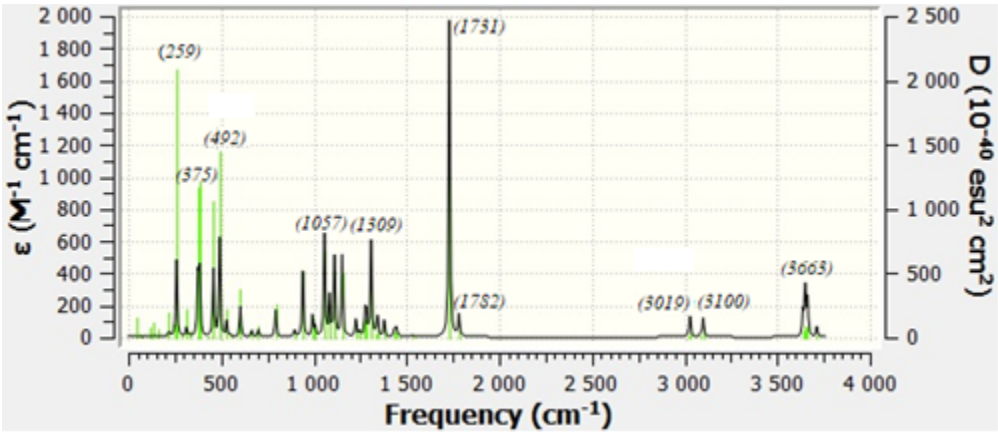
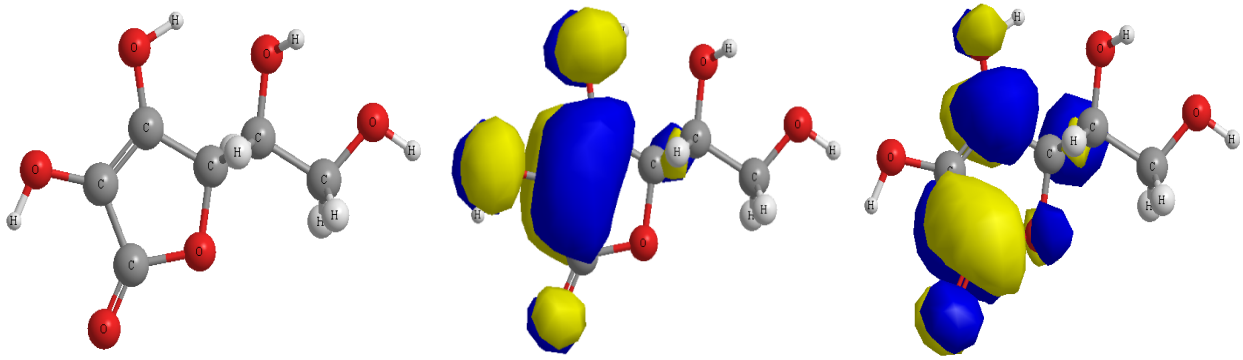


Fig 3. Infrared spectrum of vitamin C by the B3LYP method

3.2. Quantum chemical calculation

Quantum chemical calculations were performed using the functional density theory (DFT) with a basic set 6-31G (d, p) implemented in the Gaussian 09 software package [30,31]. The molecular orbital boundary (HOMO and LUMO) is very important for describing chemical reactivity. The HOMO

containing electrons represents the capacity (E_{HOMO}) to donate an electron, while LUMO does not electrons, as electron acceptors represent the ability (E_{LUMO}) to obtain an electron. The energy gap between these orbitals determines by optimization. The quantum chemical parameters have been calculated according to [32,33] and presented in table 2 and the optimized molecule structure of ascorbic acid is shown in **Fig 4**. The electrostatic potential is considered predictive of chemical reactivity because the negative potential regions are expected to be sites of protonation and nucleophilic attack, while the positive potential regions may indicate electrophilic sites. **Fig 5** shows the molecular electrostatic potential (MEP) and the electrostatic potential of the potential Maps. It can be seen that electrostatic potentials on the surface of the molecules are represented by different colors. The red parts indicate the regions of negative electrostatic potential, the blue sites represent the regions of positive electrostatic potential and the parts of green color represent the regions of zero potential. Also, the negative (red) regions of MEP are linked to electrophilic reactivity and positive (blue) to nucleophilic reactivity.



Optimized molecular structure *HOMO* *LUMO*

Fig 4. Optimized molecular structures, HOMO and LUMO of ascorbic acid

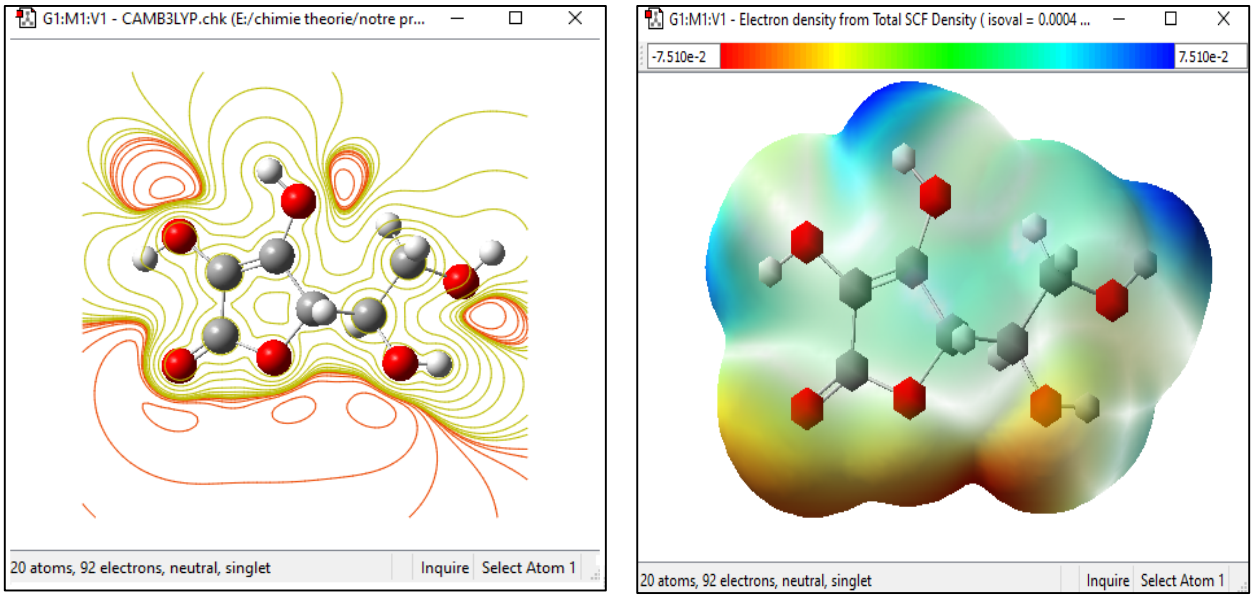


Fig 5. Contour electrostatic potential and electrostatic potential maps around the molecule of ascorbic acid

The following quantum descriptors have been calculated from the optimized structure obtained:

Ionization potential: $I = -E_{HOMO}$

Electronic affinity: $A = -E_{LUMO}$

Absolute electronegativity : $\chi = \frac{I+A}{2}$

Overall hardness: $\eta = I - A$

Overall softness: $\sigma = \frac{1}{\eta} = \frac{1}{E_{LUMO}-E_{HOMO}}$

Electronic chemical potential: $\mu = -\frac{(I+A)}{2}$

Maximum charge transfer: $\Delta Nmax = -\frac{\mu}{\eta}$

Overall electrophilicity: $\omega = \frac{\mu^2}{2\eta}$

Overall nucleophilia N: $N = E_{HOMO} - E_{HOMO(TCE)}$ with $E_{HOMO(TCE)}$ = -9.3686 eV calculated by DFT/B3LYP 6-311G (d, p).

In order to highlight the electrophilic / nucleophilic character of salicylic acid, we calculated: the ionization potential I, the electronic affinity A, the electronic chemical potential μ, the absolute electronegativity χ, the overall hardness η, the overall softness σ, the overall electrophilicity index ω, the index of overall nucleophilic N and the maximum charge transfer ΔN_{max} (**Table 2**). The maximum charge proportion that phenol can acquire from its environment is ΔN_{max} = 0.692 eV).

Table 2. Quantum theoretical parameters of molecules calculated using B3LYP / 6-311G (d, p).

Parameters	E_{LUMO} (ev)	E_{HOMO} (ev)	ΔE (eV)	I (eV)	A (eV)	μ (eV)
Ascorbic acid	-1.668	-10.340	8.672	10.340	1.668	-6.004

Parameters	χ (eV)	η (eV)	σ (ev^{-1})	ω (eV)	N (eV)	ΔN_{max}(eV)
Ascorbic acid	6.004	8.672	0.115	2.078	-0.971	0.692

3.3. Nonlinear optical proprieties

The dipole moment (μ), the polarizability (α), the first hyperpolarizability (β) and the second hyperpolarizability (γ) are calculated using a basic set of DFT and MP2 on the basis of the B3LYP 6-311G approach (d, p). The complete equations to calculate the amplitude of the total static dipole moment (μ), the polarizability (α), the first hyperpolarizability (β) and the second hyperpolarizability (γ), using the components x, y, z of 09W The Gaussian output is as follows [34]:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

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

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

$$< \gamma > = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2 [\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{xxzz}])$$

The results for the dipole moment, linear polarizability, first hyperpolarizability and second hyperpolarizability of ascorbic acid are tabulated in **Table 3**. The dipole moment of the molecule is again calculated using DFT / MP2 and Method B3LYP with basic set 6-311G (d, p). Dipole moment reflects the distribution of molecular charges and is given as a three-dimensional vector. Consequently, it can be utilized as a descriptor to represent the charge movement through the molecule as a function of the negative and positive charge centers. Dipole moments are necessarily determined for neutral molecules. For charged molecules, its values depend on the orientation and the choice of the origin of the molecular. The value of the dipole moment and the first polarizability calculated by the DFT method is greater than that calculated by the MP2 method. The polarizability calculated by the two methods is almost the same. The second hyperpolarizability obtained by the DFT method is lower than that found by the MP2 method. The difference sometimes in the values calculated by the two methods is explained by the MP2 method is an Ab initio method based on the calculation of the wave function which depends on 4N variables (three spatial coordinates and the fourth of spin) and energies of molecular orbitals. While the density functional theory (DFT) goes beyond reducing the number of variables by replacing the wave function with a function which is the electronic density ρ (x, y, z) which does not depend on 3 variables only.

3.4. Bond length and angle properties

In this article, we will deepen our studies on selective bond lengths (Å) and angles (degrees). The MP2 level was used with the DFT method, the utility of which to describe molecular physical and chemical properties. The optimized geometric parameters and the inputs used to determine the link lengths and angles, the results of which are also presented in **Tables 4** and **5**, respectively as experimental results available for comparison. The common atoms in the structure of this product are identified using an arbitrary numbering scheme (**Fig 1**) of ascorbic acid. The following points should be noted in these tables.

Table 3. Electric dipole moments (Debye) by two methods DFT and MP2 of ascorbic acid calculated using B3LYP / 6-311G (d, p).

	Parameters	DFT	MP2
Dipole moment (Debye)	μ_x	-3.6036	2.5616
	μ_y	4.7698	5.7829
	μ_z	-2.7505	0.4081
	μ	6.5804	6.3380
Polarizability (Debye)	α_{xx}	-61.9652	-62.4680
	α_{yy}	-64.6397	-74.8058
	α_{zz}	-71.6882	-69.1164
	α	-66.097	-68.796
First Hyperpolarizability (Debye)	β_{xxx}	-13.4147	58.3383
	β_{xyy}	-22.1922	18.4977
	β_{xzz}	-12.5307	-4.5175
	β_{yyy}	24.3380	38.0690
	β_{xxy}	53.5859	36.8807
	β_{yzz}	-0.1785	-1.7011
	β_{zzz}	8.8682	1.2866
	β_{xxz}	-12.1862	3.7043
	β_{yyz}	-5.101	-3.8618
	β	91.828	73.293
Second Hyperpolarizability (Debye)	γ_{xxxx}	-1374.9588	-1488.9545
	γ_{yyyy}	-505.6580	-613.5822
	γ_{zzzz}	-209.4471	-157.1024
	γ_{xxyy}	-302.0504	-432.1492
	γ_{yyzz}	-133.0042	-140.9240
	γ_{xxzz}	-333.9064	-341.5835
	γ	-725.597	-845.309

First, the common bond lengths are almost identical (**Table 4**) for the molecule, which has variations. The DFT and MP2 results for ascorbic acid were very similar and in good condition following the experimental structure. So, the geometrical product study showed a good agreement between the theoretical and experimental results.

Table 4. Bond lengths (Å) of ascorbic acid. (The experimental values of the first are extracted from the crystal structure [35].

bond lengths (Å)	DFT	MP2	Exp
C_1=O_{11}	1.228	1.209	1.216
C_1-O_2	1.400	1.362	1.355
C_5=C_4	1.339	1.344	1.338
C_4-O_7	1.372	1.354	1.326
C_3-O_{17}	1.525	1.523	1.521
C_{17}-O_{19}	1.447	1.413	1.427
C_{12}-O_{15}	1.461	1.429	1.431
C_5-O_9	1.379	1.353	1.361

Table 5. Angles (º) of ascorbic acid. *(*The experimental values of the former are extracted from the crystal structure [35].

Angles (θº)	DFT	MP2	Exp
O_{11}-C_1-C_5	127.1	125.9	129.1
O_9-C_5-C_4	126.3	129.3	127.5
C_1-O_2-C_3	109.2	109.1	109.1
C_3-C_{17}-O_{19}	111.2	106.1	111.7
C_{17}-C_{12}-O_{15}	103.6	104.7	108.1
C_4-C_3-O_2	102.6	104.8	104.1

Conclusion

The B3LYP / 6-311G (d, p) computation level seems to be adequate for optimization of the geometry of the molecule. HOMO, LUMO and energy gaps describe the possible charge, the transfer interactions taking place in the molecule and determination of the theoretical molecular structures of ascorbic acid by the DFT and MP2 methods. Linear polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) the values of the molecule studied have been calculated. The molecular electrostatic potential determined the properties and the activity of the ascorbic acid. The ascorbic acid molecule can acquire a maximum charge of 0.692 eV from its environment.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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