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Geometry and electronic properties of Vitamin C

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Abstract: Ascorbic acid (also known as Vitamin C) is a water soluble vitamin that is needed for the growth and repair of tissues in the body. Vitamin C protects against scurvy, heart disease, cancer, the common cold, and high blood pressure. Therefore, it is used as an antioxidant and dietary supplement. Vitamin C is naturally present in some fruits and vegetables and in some juices. In this study, the chemistry of vitamin C was explored. Geometry of ascorbic acid (AA) was optimized at DFT B3LYP/6-31+G(d,p). Geometrical parameters are tabulated and compared with experimental values. Natural atomic charges were also calculated. Unpaired electron radical anion of the ascorbate was confirmed by computation of the electron spin density at the same level. HOMO and LUMO molecular orbitals were calculated. Fukui functions were calculated and used to explore the reactivity of AA. Infra red and UV-VIS spectra of AA were measured and confirmed with the simulated spectra at B3LYP/6-31+G(d,p).

Keywords: *Ascorbic acid, DFT, Fukui functions, HOMO, HPLC.*

1. Introduction

Vitamins constitute a group of small molecular species that are important nutrients for animals and humans. In 1928, Albert Azent-Gyorgi and Charles Kingin isolated L-Ascorbic acid as a pure substance [1]. Most animals and human are not able to synthesize vitamin C, so that they should obtain it in their diets. Humans need a minimum of 60 mg/day of vitamin C for skin and teeth maintenance and to cure infection, and to prevent scurvy. AA (Figure 1) is an anti-oxidant and free radical scavenger, can be found found in fruits and vegetables, such as citrus fruits, melons, tomatoes, peppers, broccoli, green leafy and vegetables such as spinach, potatoes and papayas [2-7]. AA is vital for protein synthesis hence it helps the growth and repair of tissues in human body. It is necessary to form collagen (Fig.1S in Supplementary Material), an important skin proteins, ligaments, and blood vessels. Vitamin C is important for the wound healing, and for the repair and maintenance of cartilage, bones, teeth, blood vessels, gums and lipid metabolism [8-13].

Due to these importance and applications we are motivated to study this molecule. In the present

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study, we are going to explore the geometry, electronic/spectral properties and chemical reactivity of AA.

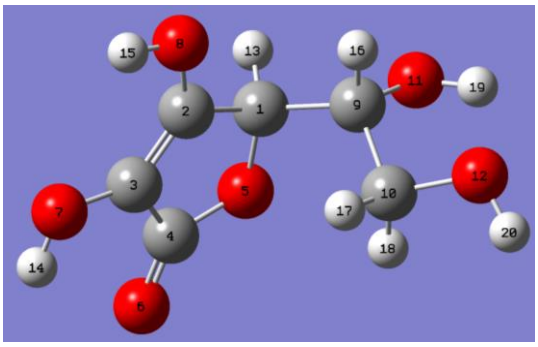


Figure 1. Structure of vitamin C.

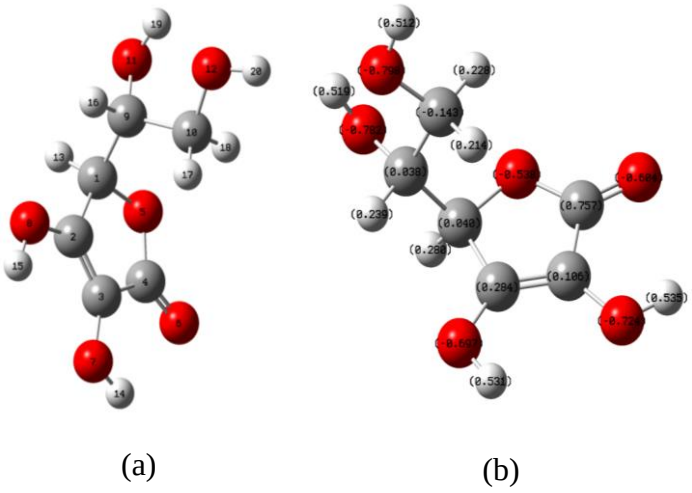
2. Computations and experimental details

All computations were done using G09 suit of programs [14]. Geometry optimized in the gas phase at DFT B3LYP/6-31+G(d,p) level of theory. A frequency job was performed on the optimized geometry to confirm a minimum energy structure. Fukui functions were calculated using DMol3 module [15,16] implemented in Material studio program [17]. UV-VIS spectra of AA were simulated using TD DFT method. Quantitative determination of vitamin C in juices was performed in De Montfort University, using Shimadzu Nexera SR with the settings; Flow rate A: 500 mL/min, maximum pressure: 6000 psi minimum pressure: 1 psi wavelength: 256 nm.

3. Results and Discussion

3.1 Geometry

Geometry of AA was optimized at B3LYP/6-31+G(d,p). Optimized geometry of AA showing atomic numeration (a) and natural atomic charge (b) are shown in Figure 2. Some geometrical parameters are given in Table 1. Experimentally measured geometrical parameters are shown in parentheses. Aliphatic C-C bond length is calculated to 1.506 Å for the ring and to 1.530 Å for the side chain. The experimental values are 1.493 and 1.521 Å for the ring and the side chain. C=C bond length is calculated to 1.341 Å and C=O 1.212 Å while the experimental value is 1.216 Å. Large discrepancies between computed and measured values are found in the O-H bond lengths ≈ 0.020 Å. Bond angles show good agreement between computed and measured values, for example angle C1-O5-C4 is 109.6 and 109.9 for computed and measured values. Dihedral angles confirm the planarity of the ring, for example C1-C2-C3-C4 is 0.7 º and O5-C1-C2-C3 is 1.1 º. Correlation between computed and measured geometrical parameters is displayed in Figure 3. Agreement between computed and measured geometrical parameters is easily observed in the figure.



(a) (b)

Figure 2. Optimized geometry of AA showing atomic numeration (a) and natural atomic charge (b).

3.2 Natural charges

Natural charges were computed and displayed in Figure 2. Negative charges (-0.538—0.798) are accommodated on oxygen atoms. Largest charge is on oxygen of the hydroxyl groups and smallest and smallest charge is on the ether oxygen. Positive charges are accommodated on carbon and hydrogen atoms. Largest positive charge (0.535) is on the hydrogen attached to oxygen of the hydroxyl group near to the carbonyl group. Weak intra molecular hydrogen bonds are formed between O7-H15 (2.724 Å) and O6-H14 (2.496 Å) and O12-H19 (2.270 Å).

Table 1. Computed and experimentally measured a (in parentheses) geometrical parameters of AA.

Bond	Bond length Å	Angle	(º)	Dihedral	(º)
R(1,2)	1.506 (1.493)	A(2,1,5)	103.8 (104.2)	D(5,1,2,3)	-1.1
R(1,5)	1.449 (1.444)	A(2,1,9)	115.1 (114.8)	D(5,1,2,8)	179.6
R(1,9)	1.532 (1.521)	A(2,1,13)	111.3 (110.5)	D(9,1,2,3)	-123.9
R(1,13)	1.095 (1.011)	A(5,1,9)	111.9	D(9,1,2,8)	56.9
R(2,3)	1.341	A(5,1,13)	107.2	D(13,1,2,3)	113.8
R(2,8)	1.348 (1.326)	A(9,1,13)	107.1	D(13,1,2,8)	-65.3
R(3,4)	1.463 (1.452)	A(1,2,3)	109.2 (109.5)	D(2,1,5,4)	1.1
R(3,7)	1.357 (1.361)	A(1,2,8)	119.5	D(9,1,5,4)	125.9
R(4,5)	1.366 (1.355)	A(3,2,8)	131.1	D(13,1,5,4)	-116.7
R(4,6)	1.212 (1.216)	A(2,3,4)	108.4 (107.8)	D(2,1,9,10)	71.3
R(7,14)	0.970 (0.929)	A(2,3,7)	128.4	D(2,1,9,11)	-165.7
R(8,15)	0.968 (0.949)	A(4,3,7)	123.0	D(2,1,9,16)	-48
R(9,10)	1.527 (1.521)	A(3,4,5)	108.7 (109.5)	D(5,1,9,10)	-46.9
R(9,11)	1.419 (1.427)	A(3,4,6)	126.9	D(5,1,9,11)	75.9
R(9,16)	1.1002	A(5,4,6)	124.3	D(5,1,9,16)	-166.4
R(10,12)	1.432 (1.431)	A(1,5,4)	109.6 (109.9)	D(13,1,9,10)	-164.2
R(10,17)	1.0971	A(3,7,14)	107.8	D(13,1,9,11)	-41.3
R(10,18)	1.0942	A(2,8,15)	109.8	D(13,1,9,16)	76.3
R(11,19)	0.967 (0.937)	A(1,9,10)	114 (112.7)	D(1,2,3,4)	0.7
R(12,20)	0.963 (0.945)	A(1,9,11)	107.0	D(1,2,3,7)	-179.2

[a] Exp. Ref [18].

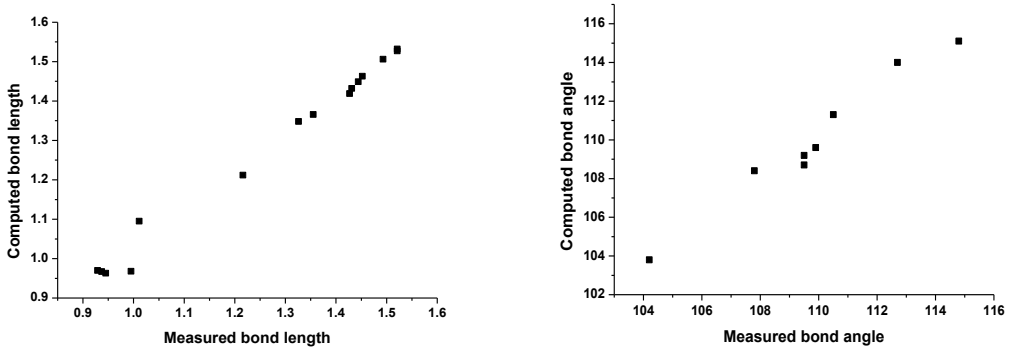


Figure 3 Correlation between computed and measured geometry.

3.3 Molecular orbitals

Study of the molecular orbitals and their properties such as energy are essential for chemists. Frontier electron density theory has been used to predict the most reactive position in π-electron systems [18]. The energy of the highest occupied and lowest unoccupied molecular orbitals indicates the chemical activity of the molecule [19,20]. As seen from Figure 4, in the highest occupied molecular orbital, HOMO, electrons are mainly delocalized on the C=C and hydroxyl groups. In the first excited state electron density will go into the lowest unoccupied molecular orbital, LUMO, the electron density will mainly be delocalized on the C-C and hydroxyl group as shown in Figure 4.

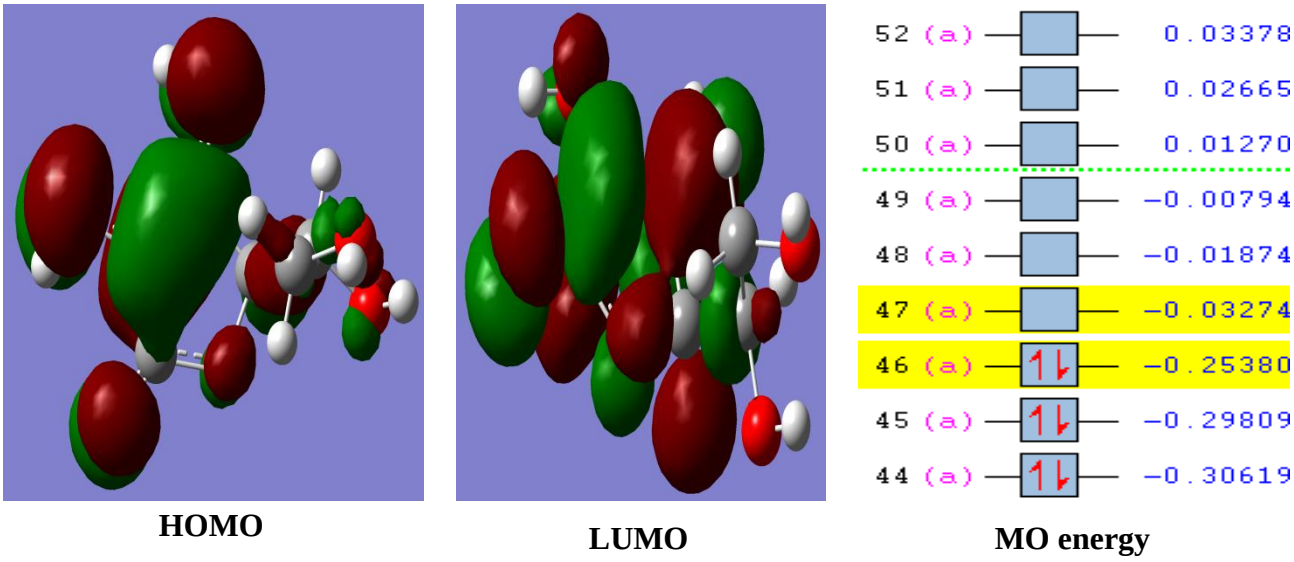


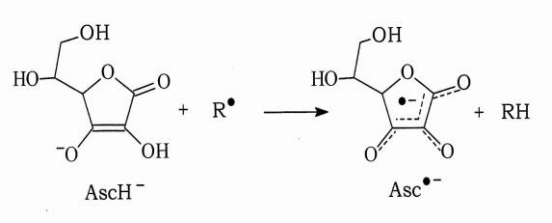
Figure 4. HOMO and LUMO molecular orbitals and energies of vacant and filled molecular orbitals.

3.4 Chemical reactivity

The density of electrons on an atom is an important property that contains all the information about the molecular systems. The local philicity contains information about the global electrophilicity and Fukui function represents chemical reactivity and selectivity [21]. In a molecular system, the atomic site, which possesses highest condensed Fukui function, favors the higher reactivity. Table 1S in Supplementary Material shows the condensed Fukui functions and local philicity as calculated based on Mullikin and Hirchfeld calculated charges. From the results of Table 1S, the reactivity order for the radical attack was found on and ranked as O6 > C2 > O7 > O8. This is in agreement with unpaired electron being resides on the oxygen atoms. This also confirmed with the computation of the electron spin density that shown in Figure 5 which support this argument. For nucleophilic attack, the order of reactivity could be ranked as O6 > C2 > C4 > O5. On the other hand, for electrophilic attack, the reactivity order could be ranked as O7 > O8 > C3 > C2 >O6. This is also confirmed by the pictures of the HOMO and LUMO in Figure 4.

3.5 Chemical reactivity

Vitamin C is a highly effective antioxidant. It can absorb free oxygen radicals. Vitamin C can protect biological molecules in the body, such as proteins, lipids, carbohydrates, and nucleic acids (DNA and RNA) from damage by free radicals according to:



Evidence of free radical ascorbate ion was confirmed by calculating the electron spin density (Figure 5). The ascorbate radical is usually observed as a simple doublet species by EPR as shown in Figure 6 [22].

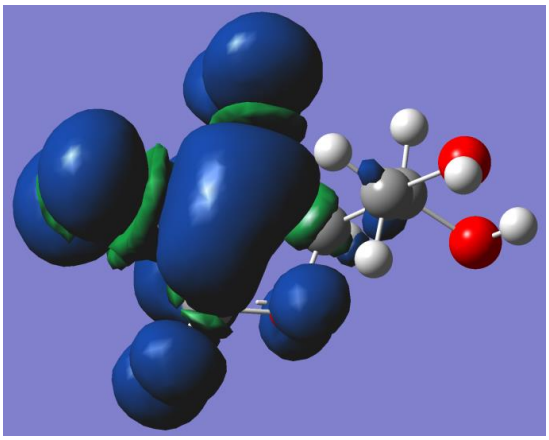


Figure 5. Electron spin density of ascorbate radical anion.

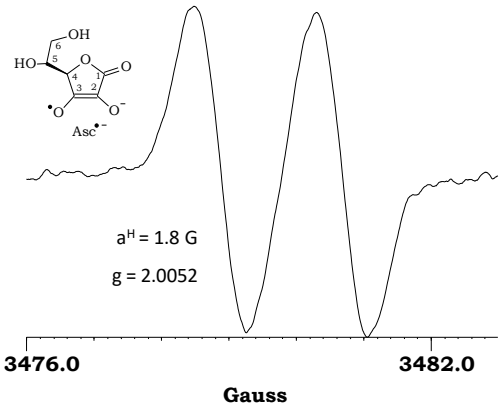


Figure 6. EPR spectrum of AA.

3.6 Spectral characteristics

UV-VIS spectra of AA was simulated using TD DFT method (Fig. 3S in Supplementary Material) and compared with the experimentally measured UV-VIS spectra in water [23] as shown in Fig. 3S.

The UV-VIS Spectra of AA in Water shows absorption around λ=265-253. The simulated spectra shows 234 nm in the gas phase. Discrepancy is due to the effect of high polarity of the water solvent.

IR spectra of AA in the gas phase was simulated at B3LYP/6-31+G(d,p) and displayed in Fig. 4S in Supplementary Material. Comparing this simulated spectrum with that measured in nujol shown in Fig. 4S (taken from NIST) indicates the agreement between computed and measured one.

3.7 HPLC determination of AA fruit juice

Standard solutions 10-50 ppm were prepared and scanned in the HPLC. Table 2S in the Supplementary Material shows the area and height as a function of retention time for the prepared standard solutions. Data is graphed in Fig. 5S in Supplementary Material. Juice samples were measured and given in Table 3S in Supplementary Material. Overall, it was the orange juice that had the highest concentration of ascorbic acid.

4. Conclusion

In this study, the chemistry of vitamin C was explored. Geometry of ascorbic acid (AA) was optimized at DFT B3LYP/6-31+G(d,p). electronic properties of AA such as, HOMO and LUMO molecular orbitals and Fukui functions were calculated. Fukui functions were calculated to explore the reactivity of AA. The reactivity order for the radical attack was found on and ranked as O6 > C2 > O7 > O8. For nucleophilic attack, the order of reactivity could be ranked as O6 > C2 > C4 > O5. On the other hand, for electrophilic attack, the reactivity order could be ranked as O7 > O8 > C3 > C2 >O6. Natural charges were computed. Negative charges (-0.538—0.798) were found to accommodate on oxygen atoms. Positive charges are accommodated on carbon and hydrogen atoms. Largest positive charge (0.535) is on the hydrogen attached to oxygen of the hydroxyl group near to the carbonyl group. Weak intra molecular hydrogen bonds are formed between O7-H15 (2.724 Å) and O6-H14 (2.496 Å) and O12-H19 (2.270 Å). Simulated UV-VIS and IR spectra are used to confirm the measured spectra.

Acknowledgments

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