

# Structural Properties of Curcumin Molecule Using Density Functional Theory

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**Abstract—** The structural properties of curcumin (1,7-bis(4-hydroxy-3 methoxyphenyl)-1,6-heptadiene-3,5-dione) was studied with the density functional theory DFT correlation functional B3LYP method using various basis sets. The geometrical parameters which are studied in this research include the bond lengths and the bond angles, for the curcumin molecule in both ketone and enol form. These parameters calculated with the different basis sets. These basis sets are given similar results approximately so as a small molecule, except the experimental basis set (STO-3G).

The results showed that the double bonds are shorter than the single bonds; this is due to increase in negative charge density. As well, the presence an oxygen atom, which has two bonds and two lone pairs, leads to reduce size of the bond angles. Also from the results it can be found the structure approximately planer for the enol form, but it is non-planer for the ketone form.

**Index Terms—** curcumin, geometry optimization, DFT calculations.

## I. INTRODUCTION

Curcumin the active yellow pigment obtained from the dried rhizomes of *Curcuma longa* L., is a popular coloring spice and ingredient of many cosmetics and pharmaceuticals [1,2]. Curcumin has been generally associated with a large number of biological and cellular activities, including antioxidant, anti-inflammatory, anticarcinogenic and hypocholesterolemic properties [3,4]. In addition it is reported that curcumin is able to induce apoptosis in human cancer cells of different tissue origin, including B and T cells, colon, epidermis, prostate, breast and head [5,6]. Nowadays, curcumin is becoming more and more popular due to its profound effect on human health [7]. It is well known that curcumin can exist in at least two tautomeric forms; ketone and enol [8,9]. With structural formula (1,6-heptadiene-3,5-dione-1,7-bis(4-hydroxy-3-methoxyphenyl)-(1E,6E)) the curcumin structure contains a variety of functional groups including the  $\beta$ -diketo group, carbon-carbon double bonds and phenyl rings containing varying amounts of hydroxyl and methoxy substituents. Scheme 1 shows two tautomeric forms of curcumin [10,11]. Overall, the nature of many properties of curcumin remains unclear; so, it is important to investigate the structure and reactivity of this molecule. The present study demonstrates structural properties of curcumin by employing density functional theory (DFT) approach with many levels of basis sets and comparison with available experimental findings.

## II. THEORETICAL AND COMPUTATIONAL METHODS

All the calculations are performed with Gaussian 09 package of programs [12]. This work is based on the density functional theory (DFT) [13] approach to estimate the

structural properties of the curcumin by employing Beck's three parameters exact exchange functional (B3) combined with non-local gradient corrected correlation functional of Lee-Yang-Parr (LYP), denoted as B3LYP and many levels of theory.

According to B3LYP function, the exchange correlation energy is given by [14]:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA}) \quad (1)$$

Where the three parameters  $a_0 = 0.02$ ,  $a_x = 0.72$ , and  $a_c = 0.81$ . LDA, HF and GGA are the local density approximation, Hartree-Fock and generalized gradient approximation, respectively.

## III. RESULTS AND DISCUSSION

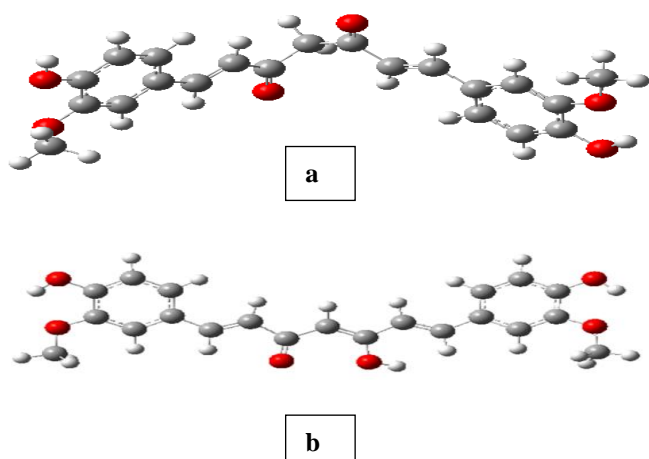
Present research concerns on studying structural properties of the curcumin molecule with different basis sets, and we will be using the 6-311+G(d,p) basis set for discussion. This is the basis set that gives satisfactory results for calculations.

The fully optimized structure of curcumin in both ketone and enol forms obtained at the B3LYP/6-311+G(d,p) level, are shown in Fig. 1. From the theoretical values obtained in this work, it has been found that the optimized bond lengths and angles for curcumin (enol form) molecule are in good agreement with the experimental values, but for other form has not been found experimental data. The results of geometrical parameters included the maximum and minimum values of bond lengths in (Angstrom) and bond angles in (degree), for both ketone and enol form, are declared in Tables I-IV. The computational levels of theory used in this work give a good result of length. As an example, the bonds C—C, C=C, C::C, C—O, C=O, C—H and O—H in Table I equals to (1.5338-1.4552), (1.3485-1.3474), (1.4114-1.3854), (1.4345-1.3562), (1.2212-1.2198), (1.0953-1.0826) and (0.9675-0.9633) Å, respectively, at 6-311+G(d,p) level.

As it turns out, the values of the bond lengths of the C—C bond is the longer than the other bonds in the molecule, and the single bonds C—C and C—O are longer than the double bonds C=C and C=O, respectively. However, the shorter distance in the double bonds may be due to the increases of the negative charge density of the atoms, so the attraction force is increase for the two atoms as it can be seen in C=C and C=O. Table I declares that the convergence between the bonds C—C and C—O comes from the convergence between their atomic numbers, and this reason explains the difference of C—H and O—H bonds. In addition, the neighboring atoms and bonds locations in the molecule also impact on the length of the bonds.

In Table II  $C-C=C$  and  $C-C=O$  angles obtained from 6-311+G(d,p) are (128.2391-121.0218) degree and (123.6414-120.6167) degree, respectively. These angles are larger than the other angles, such as  $C-C-C$  angle (115.7338-110.8125) degree, this because exist the double bond in the molecule. Where electron-electron repulsion of the bond pairs of the double bond is greater than repulsion between electrons of the single bond due to that the electrons of the double bond need for larger vacuum. Also the  $C-C=C$  angle is larger than the  $C-C=O$  angle, this because presence two lone pairs on oxygen. These trends are evident in Table III and IV for the enol form.

It is well known that specific intermolecular interactions plays a vital role in stabilize different conformations. Therefore, the presence of intermolecular hydrogen bonds between neighboring hydroxyl (OH) and methoxy (OCH<sub>3</sub>) groups has important implications regarding preferred molecular structures. In the present study, it has been found that the  $\beta$ -dicarbonyl moiety preferentially assumes the planar enol form stabilized by the strong intermolecular hydrogen bond; rather than the non-planar ketone form (see Fig. 1).



**Fig. 1: Optimized geometry for curcumin isomers (a-ketone form and b-enol form) at B3LYP/6-311+G(d,p) level.**

The bonds  $C-C$ ,  $C=C$ ,  $C:::C$ ,  $C-O$  and  $C=O$  in Table III obtained from 6-311+G(d,p) equals to (1.49-1.4576), (1.3632-1.3452), (1.4108-1.3864), (1.4241-1.3577) and (1.2278) Å, respectively, in a good agreement with experimental values (1.457-1.392), (1.403-1.348), (1.417-1.379), (1.440-1.316) and (1.312) Å, respectively [15]. Also Table IV illustrates the results of the bond angles of the enol form. The following angles,  $C-C=C$ ,  $C-C=O$  and  $C-O-C$  are (128.3918-120.2468), (123.9315-121.6569) and (118.7641-118.6064) degree, respectively. The experimental value for these angles are (128.3-120.7), (120.3) and (116.7) degree, respectively [15]. Other levels given approximately values of these parameters nearly to experimental results. All levels in this study gave similar results, this may be due to the molecule studied is one of the small systems which contains the atoms have small atomic number. STO-3G gave us approximately values different, this may be come from that level of theory is a small to describe the molecular system in compared with large basis sets, such as, 6-31G(d) and 6-31G(d,p) levels.

#### IV. CONCLUSIONS

Density functional method used in this study is found to be a powerful method for studying the structure properties of curcumin molecule, and B3LYP functional level is an efficient in this method to study the small molecules like curcumin molecule.

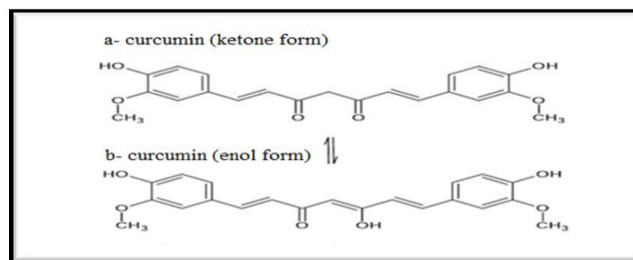
The results of the parameters of geometrical optimization of the enol form have been a good agreement with experimental data, while the experimental data of the other form has not been found.

The difference of atomic numbers for the conjugated atoms effects on the bond length between these atoms. In addition, the increase in negative charge density contributes in reduces bond length. The repulsion forces of the electrons directly effect on the size of the bond angle. However, the lone pairs play an important role in determining the size of the bond angle. Also the intermolecular hydrogen bonds between neighboring OH and OCH<sub>3</sub> groups, which have an important role in decide the preferred molecular structures. These conclusions help to interpret the geometrical optimization to study the other prosperities of the molecule.

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Scheme 1: Ketone and enol forms of curcumin.

Table I: The parameters for optimum bond lengths of ketone form.

Bond (Å)	STO-3G	3-21G(d)	6-31G	6-31G(d)	6-31G(d,p)	6-311G	6-311+G(d,p)
C—C	1.5776 1.487	1.5472 1.4557	1.5343 1.456	1.5355 1.4554	1.5352 1.4552	1.5299 1.456	1.5338 1.4552
C=C	1.3569 1.3562	1.3482 1.3478	1.3559 1.3547	1.3515 1.3504	1.3511 1.35	1.3523 1.3511	1.3485 1.3474
C:::C	1.4166 1.3851	1.4152 1.3801	1.4178 1.3872	1.414 1.3865	1.4139 1.3864	1.4166 1.3851	1.4114 1.3854
C—O	1.4685 1.3800	1.4789 1.3748	1.4681 1.378	1.431 1.3567	1.4315 1.3558	1.4685 1.3801	1.4345 1.3562
C=O	1.2529 1.2506	1.2476 1.2412	1.2545 1.2513	1.2262 1.2246	1.2264 1.2246	1.2529 1.2506	1.2212 1.2198
C—H	1.0920 1.0799	1.0966 1.0816	1.0963 1.0832	1.0981 1.0849	1.0974 1.0843	1.0921 1.0807	1.0953 1.0826
O—H	0.9764 0.9717	0.9998 0.9921	0.9813 0.9763	0.9741 0.9703	0.9706 0.9666	0.9764 0.9717	0.9675 0.9633

Table II: The parameters for optimum bond angles of ketone form.

Bond angle (deg)	STO-3G	3-21G(d)	6-31G	6-31G(d)	6-31G(d,p)	6-311G	6-311+G(d,p)
C—C=C	127.803 120.9695	128.0154 119.6613	128.1705 121.1864	128.4374 120.6306	128.4474 120.5487	128.2729 121.3702	128.2391 121.0218
C—C—C	114.6179 110.8495	116.3167 111.1041	116.5985 110.9541	115.8603 110.3042	115.9173 110.4114	116.7938 111.0292	115.7338 110.8125
C—C=O	123.3251 122.0512	123.9713 120.9822	123.525 120.172	123.5792 120.5656	123.5677 120.5641	123.3389 119.9867	123.6414 120.6167
C—O—C	112.3831 111.9752	118.1602 117.2543	118.9862 118.8669	118.208 116.0288	118.2056 116.0603	119.1049 119.0523	118.6446 116.4905
C—O—H	103.2302 102.8406	109.9943 106.1632	111.4998 109.2463	108.8428 107.0267	109.0374 107.1452	119.1049 119.0523	109.7184 107.9782

Table III: The parameters for optimum bond lengths of enol form.

Bonds (Å)	STO-3G	3-21G(d)	6-31G	6-31G(d)	6-31G(d,p)	6-311G	6-311+G(d,p)
C—C	1.5299 1.4864	1.4896 1.4587	1.4838 1.4585	1.4696 1.4591	1.4898 1.459	1.4828 1.4576	1.49 1.4576
C=C	1.3786 1.3545	1.3573 1.3448	1.3647 1.3518	1.3643 1.3481	1.3641 1.3476	1.3615 1.3483	1.3632 1.3452
C:::C	1.4405 1.3996	1.4152 1.3807	1.3518 1.3881	1.4135 1.3873	1.4133 1.3872	1.4159 1.3861	1.4108 1.3864
C—O	1.4694 1.4037	1.4587 1.375	1.4519 1.3797	1.4206 1.3556	1.421 1.3546	1.4529 1.3817	1.4241 1.3577
C=O	1.2718	1.2511	1.2609	1.2331	1.2331	1.2596	1.2278
C—H	1.1103 1.0961	1.0962 1.0816	1.0958 1.0833	1.0974 1.0849	1.0968 1.0843	1.0916 1.08	1.0946 1.0826
O—H	1.0371 1.0259	0.9996 0.9943	0.9812 0.9779	0.9739 0.9706	0.9704 0.9672	0.9762 0.9731	0.9673 0.9634

Table IV: The parameters for optimum bond angles of enol form.

Bond angle (deg)	STO-3G	3-21G(d)	6-31G	6-31G(d)	6-31G(d,p)	6-311G	6-311+G(d,p)
C—C=C	127.803 120.9695	128.4536 119.5139	128.2775 120.9433	128.5336 120.5463	128.5385 120.4519	128.4147 121.1427	128.3918 120.2468
C—C=O	123.3251 122.0512	124.6425 120.7642	124.0505 120.9074	123.7718 121.4685	123.7973 121.4401	123.9015 120.94	123.9315 121.6569
C—O—C	112.3831 111.9752	118.2144 118.0454	118.9674 118.774	118.319 118.1675	118.3135 118.1649	119.2158 119.0098	118.7641 118.6064
C—O—H	103.2302 102.8406	109.4282 106.0558	111.3421 109.0203	108.4492 106.8445	108.5436 106.9607	111.6141 109.3031	109.5183 107.8289