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Spectroscopic, Electronic and Non-Linear Properties of 2-[3-Phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic Acide

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Abstract: In this study, 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide was optimized by using B3LYP/6-311G+(d,p) and HF/6-311G+(d,p) basis sets. Firstly, calculated IR data of compound were calculated in gas phase by using of 6-311G+(d,p) basis sets of B3LYP and HF methods and are multiplied with appropriate adjustment factors. Theoretical infrared spectrums are formed from the data obtained according to B3LYP and HF methods. Experimental IR values and theoretical values were compared. In the identification of calculated IR data was used the veda4f program. Also, ^{1}H-NMR and ^{13}C-NMR spectral data values were calculated according to the method of GIAO using the program package Gaussian G09W Software. Experimental and theoretical values were inserted into the graphic according to equitation of δexp=a+b. δ calc. The standard error values were found via SigmaPlot program with regression coefficient of a and b constants. Furthermore, molecular structure, HOMO and LUMO energy analysis, total static dipol moment (μ), the mean polarizability (<α>), the anisotropy of the polarizability (Δα), the mean first-order hyperpolarizability (<β>), electronegativity (χ), hardness (η), molecular electrostatic potential maps (MEP) and Mulliken charges of 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide molecule have been investigated by using B3LYP and HF levels with the 6-311G+(d,p) basis set.

Keywords: 1,2,4-Triazol-5-one, GIAO, Non-Linear Properties, Electronegativity HOMO and LUMO

Introduction

Triazole is an unsymmetrical heterocyclic organic compound having three nitrogen atoms in the five-membered ring. 1,2,4-Triazole and 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives are reported to possess a broad spectrum of biological activities such as antimicrobial, antifungal, antitumor, anti-HIV, antiviral, anticancer, anti-inflammatory, analgesic and antioxidant properties (Alkan et al., 2007; Hashem et al., 2007; Aytac et al., 2009; Bayrak et al., 2010; Gürsoy Kol and Yüksek, 2010; Güzeldemirci and Kucukbasmaci, 2010; Sancak et al., 2010; Beytur et al., 2019; Turhan Irak and Beytur, 2019). Also, several articles reporting the synthesis of some *N*-arylidenamino-4,5-dihydro-1*H*-1,2,4-triazol-5-one compounds and derivatives have been published (İkizler and Yüksek, 1994; Bahçeci et al., 2002; Yüksek et al., 2004; Yüksek et al., 2005; Yüksek et al., 2006; Turhan Irak and Gümüş, 2017).

In this paper, the optimized molecular structure, vibrational frequencies, spectroscopic parameters, atomic charges and frontier molecule orbitals (HOMO and LUMO) of the 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide have been calculated by using DFT/B3LYP and HF method with 6-311G+(d,p) basis set. All quantum chemical calculations were carried out by using Gaussian 09W (Frisch et al., 2009; Wolinski, Hilton & Pulay, 1990) program package and the GaussView molecular visualization program (Frisch, Nielson & Holder, 2003). The molecular structure and vibrational calculations of the molecule were computed by using Becke-3-Lee Yang Parr (B3LYP) (Becke, 1993; Lee et al.,1998) density functional method and Hatree-Fock with 6-311G+(d,p) basis set in ground state. IR absorption frequencies of analyzed molecule were calculated by two methods. Then, they were compared with experimental data (Çiftçi et al., 2018), which are shown to be accurate. The assignments of fundamental vibrational modes of the title molecule were performed

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on the basis of total energy distribution (TED) analysis by using VEDA 4f program (Jamroz, 2004). Furthermore, molecular structure, HOMO and LUMO energy analysis, total static dipol moment (μ), the mean polarizability (<α>), the anisotropy of the polarizability (Δα), the mean first-order hyperpolarizability (<β>), electronegativity (χ), hardness (η), molecular electrostatic potential maps (MEP) and Mulliken charges of titled compound have been investigated by using B3LYP and HF levels with the 6-311G+(d,p) basis set.

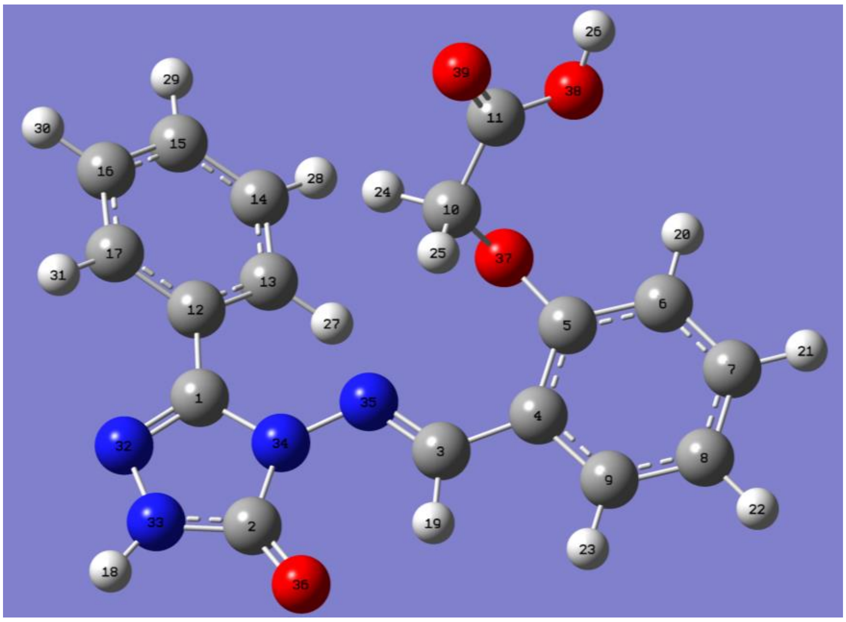

Figure 1. The optimized molecular structure (Gaussview Appearance) of 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide with DFT/B3LYP 6-311G+(d,p) level.

Method

The molecular structure of the title compound in the ground state is computed by performing both the density functional theory (DFT) and Hartree-Fock (HF) (Becke, 1993; Lee, 1998) at 6-311G+(d,p) level. Density functionals for all studies reported in this paper have been in the following form

$$E_{XC} = (1-a_0)E_X^{LSDA} + a_0 E_X^{HF} + a_X \Delta E_X^{B88} + a_C E_C^{LYP} + (1-a_C)E_C^{VWN}$$

where the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke’s exchange functional correction, the gradient corrected correlation functional of Lee, Yang and Parr, and the local correlation functional of Vosko, Wilk and Nusair (Vosko et al., 1980). The theoretical geometric structure of the title compound is given in Figure 1. Molecular geometry is restricted and the optimized geometrical parameters of the title compound in this study are carried out by using Gaussian 09W program package (Frisch et al., 2009) and the visualization parts were done with GaussView program (Dennington et al., 2009) on personal computer employing 6-311G+(d,p) basis set. Additionally, harmonic vibrational frequencies for the title compound are calculated with these selected methods and then scaled by 0.9516 and 0.9905, respectively (Avcı and Atalay, 2008) and these results were compared with the experimental data (Çiftçi et al., 2018).

Results and Discussion

Analysis of vibrational modes

In spectroscopic field, the vibrational spectra of substituted benzene derivatives have been greatly investigated by various spectroscopic, since the single substitution can have a tendency to put greater changes in vibrational wavenumbers of benzene (Tereci et al., 2012; Pir et al., 2013). In other words, molecular system of benzene is greatly affected by the nature of substituents. The number of potentially active fundamentals of non-linear molecule which have N atoms is equal to (3N-6) apart from three translational and three rotational degrees of freedom. The title molecule contains 39 atoms and 111 normal vibration modes have C1 symmetry (Table 1).

Experimentally (Çiftçi et al., 2018), the investigated titled compound, as expected the IR spectra data, the N-H stretching vibration at 3179 cm^{-1} and two C=O peak at 1708 cm^{-1} range was observed. In addition, C=N stretching vibration at 1597 cm^{-1} and COO stretching vibrations at 1229 cm^{-1} are occurred. Theoretically and experimentally (Çiftçi et al., 2018), the calculated vibrational frequencies for the 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide are summarized in Table 1. Furthermore the experimental IR (Çiftçi et al., 2018) and simulated spectra by using B3LYP/6-311G+(d,p) and HF/6-311G+(d,p) levels of the titled compound under investigation are given in Figure 2.

Table 1. The calculated frequencies values of the titled compound

Selected Vibrational Types	**Experim.**	**Scaled DFT**	**Scaled HF**
δ $O_{37}C_{5}C_{6}$ (23)	423	439	447
τ $C_{1}C_{13}C_{17}C_{12}$ (21)	484	502	507
δ $C_{12}O_{37}C_{5}$ (12), τ $C_{5}C_{6}C_{7}C_{8}$ (32), τ $O_{37}C_{4}C_{6}C_{5}$ (10), τ $H_{20}C_{6}C_{7}C_{8}$ (12)	544	572	582
δ $O_{39}C_{11}O_{38}$ (34), δ $O_{37}C_{5}C_{6}$ (10), δ $C_{11}C_{10}O_{37}$ (20)	576	587	602
δ $C_{15}C_{14}C_{13}$ (30), δ $O_{36}C_{2}N_{33}$ (18)	596	614	623
τ $O_{36}N_{33}N_{34}C_{2}$ (73)	678	714	734
τ $H_{27}C_{13}C_{14}C_{15}$ (39), τ $N_{32}N_{34}C_{12}C_{1}$ (10), τ $C_{1}C_{13}C_{17}C_{12}$ (19)	758	760	787
τ $H_{20}C_{6}C_{7}C_{8}$ (36)	802	831	859
δ $C_{5}C_{6}C_{7}$ (38), δ $C_{4}C_{3}N_{35}$ (11)	839	877	899
δ $H_{27}C_{13}C_{14}$ (23), τ $H_{27}C_{13}C_{14}C_{15}$ (35), τ $H_{31}C_{17}C_{16}C_{15}$ (28)	880	913	948
τ $H_{19}C_{3}N_{35}N_{34}$ (79)	943	980	1013
ν $O_{37}C_{10}$ (40)	1028	1039	1061
ν $C_{14}C_{13}$ (24), δ $H_{24}C_{13}C_{14}$ (22), ν $N_{33}N_{32}$ (14)	1066	1079	1082
$O_{37}C_{5}$ (25), $C_{10}C_{11}$ (10), δ $H_{26}O_{38}C_{11}$ (41)	1111	1141	1106
δ $H_{24}C_{10}O_{37}$ (12), ν $O_{37}C_{5}$ (19)	1168	1199	1201
δ $H_{24}C_{10}O_{37}$ (51)	1229	1267	1265
δ $H_{19}C_{3}N_{35}$ (18), δ $H_{18}N_{33}N_{32}$ (40)	1354	1367	1405
δ $H_{20}C_{6}C_{7}$ (11), δ $H_{27}C_{13}C_{14}$ (11)	1423	1434	1457
ν $N_{32}C_{1}$ (29), ν $C_{14}C_{13}$ (12)	1488	1542	1588
ν $N_{32}C_{1}$ (40), ν $C_{5}C_{6}$ (12)	1597	1602	1704
ν $O_{39}C_{11}$ (86), ν $O_{36}C_{2}$ (74), ν $N_{33}C_{2}$ (11)	1708	1753	1805
ν $C_{10}H_{24}$ (99)	2791	2973	2935
ν $C_{10}H_{24}$ (99)	2916	3016	2982
ν $C_{3}H_{27}$ (77)	2936	3068	3013
ν $C_{13}H_{27}$ (53)	3011	3089	3036
ν $C_{17}H_{31}$ (83)	3076	3102	3048
ν $N_{33}H_{18}$ (100)	3179	3558	3556
ν $O_{38}H_{26}$ (100)	3208	3632	3722

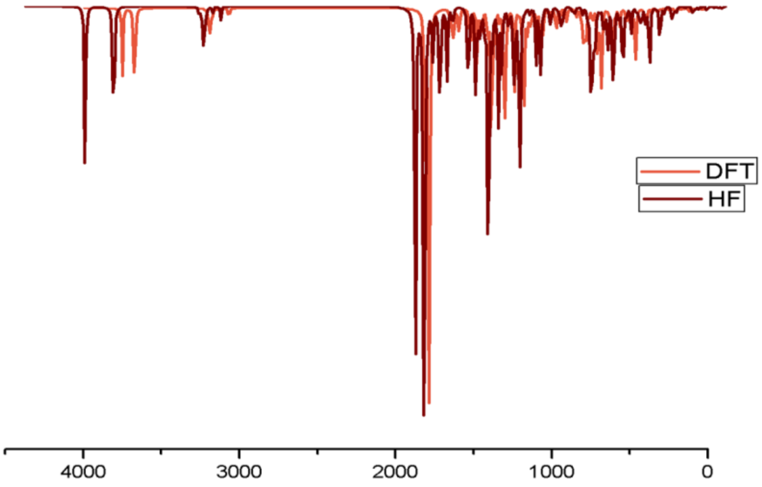

Figure 2. IR spectra simulated with DFT/B3LYP/6-311G+(d,p) and HF/6-311G+(d,p) levels of the titled compound

NMR spectral analysis

the isotropic chemical shift analysis allows us to identify relative ionic species and to calculate reliable magnetic properties in nuclear magnetic resonance (NMR) spectroscopy which provide the accurate predictions of molecular geometries, (Wade, 2006; Rani, et al., 2010; Subramanian et al., 2010). For this purpose, the optimized molecular geometry of the 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide was obtained by using B3LYP and HF methods with 6-311G+(d,p) basis level in DMSO solvent. By considering the optimized molecular geometry of the titled compound. The ^{1}H and ^{13}C NMR chemical shift values were calculated at the same level by using Gauge-Independent Atomic Orbital method (Table 2). Theoretically and experimentally values (Çiftçi et al., 2018) were plotted according to δ exp=a. δ calc.+ b, Eq. a and b constants regression coefficients with a standard error values were found using the SigmaPlot program. The correlation graphics are given Figure 3 and the linear correlation data of the titled compound by considering the results are given in Table 2. Therefore the (R^2) values (DFT/HF) for ^{1}H NMR (DMSO) and ^{13}C NMR (DMSO) chemical shifts in different solvents has been found as 0.2228 and 0.98849 for the 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide (Figure 3). In our study, the ^{1}H-NMR spectrum of the titled compound was observed belong to H181 proton peak at 12.38 ppm because acidic show feature (Yüksek, 1992; Yüksek et al., 2005; Yüksek et al., 2006, Çiftçi et al., 2018). H19 protons were observed at 10.01 ppm. Therotically, DMSO solvent these values for the mentioned proton atoms were found as 8.05/7.15 and 10.54/9.53 ppm, respectively. In Table 2, the biggest ^{13}C chemical shift value of the molecule are observed at 170.38 ppm for the C11 carbon atom double bounded to the oxygen in carbonyl group (Anderson et al., 2004). DMSO solvent the calculated ppm values (DFT/HF) for C11 carbon atom were theoretically found as 179.70/163.08 ppm. Additionaly, due to the electronegative property of nitrogen atoms in molecule, the experimental NMR chemical shift values for C1 and C2 carbon atom the bounded to nitrogen atoms in 1,2,4–triazol ring and C3 carbon atom with sp^{2} hybride are observed at 145.16, 151.83 and 152.17 ppm, respectively.

Table 2. The calculated and experimental ^{1}H and ^{13}C NMR isotropic chemical shifts of the titled compound

	Experiment.	**DFT/631d/DMSO**	**Diff./DMSO**	**HF/631d/DMSO**	**Diff/DMSO**
C1	145,16	153,48	-8,32	143,66	1,50
C2	151,83	155,64	-3,81	144,63	7,20
C3	152,17	158,19	-6,02	149,49	2,68
C4	122,19	132,27	-10,08	116,63	5,56
C5	157,78	165,80	-8,02	150,23	7,55
C6	121,89	130,72	-8,83	116,79	5,10
C7	130,53	137,77	-7,24	128,76	1,77
C8	113,43	130,09	-16,66	116,97	-3,54
C9	133,55	141,78	-8,23	131,50	2,05
C10	65,36	73,69	-8,33	52,62	12,74
C11	170,38	179,70	-9,32	163,08	7,30
C12	126,30	132,98	-6,68	119,42	6,88
C13	127,19	133,01	-5,82	123,99	3,20
C14	128,48	133,44	-4,96	121,29	7,19
C15	128,97	135,74	-6,77	126,46	2,51
C16	126,30	132,83	-6,53	120,21	6,09
C17	128,48	134,80	-6,32	126,34	2,14
H18	12,38	8,05	4,33	7,15	5,23
H19	10,01	10,54	-0,53	9,53	0,48
H20	7,56	7,88	-0,32	7,45	0,11
H21	7,49	7,68	-0,19	7,48	0,01
H22	7,53	7,57	-0,04	7,18	0,35
H23	7,06	7,85	-0,79	7,61	-0,55
H24	4,88	3,95	0,93	2,92	1,96
H25	4,88	4,19	0,69	3,01	1,87
H26	13,15	6,60	6,55	5,68	7,47
H27	7,85	8,26	-0,41	7,91	-0,06
H28	7,55	7,85	-0,30	7,45	0,10
H29	7,54	7,72	-0,18	7,61	-0,07
H30	7,07	7,68	-0,61	7,48	-0,41
H31	7,91	8,56	-0,65	8,00	-0,09

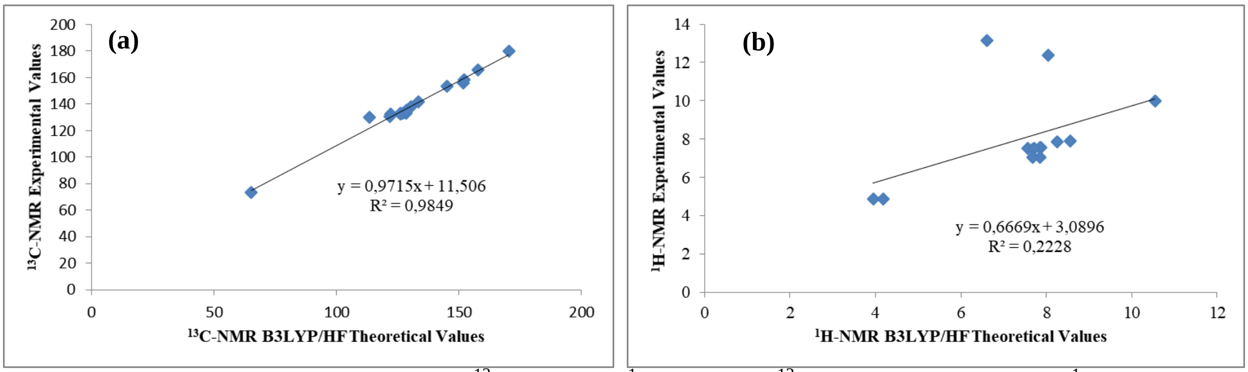

Figure 3. The correlation graphics for ^{13}C-NMR (a), ^{1}H-NMR (b), ^{13}C-NMR (DMSO) (c) and ^{1}H-NMR (DMSO) (d), chemical shifts of the titled compound

Frontier molecular orbital analysis

The energies of two important molecular orbitals of the title molecule; the second highest and highest occupied MO's (HOMO), the lowest and the second lowest unoccupied MO's (LUMO) were calculated by using DFT/B3LYP and HF methods with 6-311G+(d,p) level and are presented in Table 3. The energy gap of the title molecule was calculated at DFT/B3LYP and HF level, which reveals the chemical reactivity and proves the occurrence of eventual charge transfer. The HOMO is located almost over the carbon atoms, oxygen atoms and also slightly delocalized in hydrogen atom and the LUMO is mainly delocalized in carbon atoms of benzene ring. The energy gap (energy difference between HOMO and LUMO orbital) is a critical parameter in determining molecular electrical transport properties (Fukui, 1982). The HOMO-LUMO energy gap of the title molecule is found to 4.272/2.752 eV. obtained at DFT/HF method with 6-311G+(d,p) basis set.

Table 3. The calculated HOMO-LUMO energies of the titled compound (3) according to DFT/B3LYP/6–31G(d) and HF/B3LYP/6–31G(d) levels

Electronic properties	**B3LYP**	**HF**
I; Ionization Potential (eV)	6.145	8.430
A; Electron Affinity (eV)	1.873	5.679
η; Chemical Hardness (eV)	2.136	1.376
S; Molecular Softness (eV)	1.068	0.689
χ; Electronegativity (eV)	4.009	7.05
Total Energy (a.u.)	-1497	-1492
ΔE; Energy Gap (eV)	4.272	2.752

Mulliken's atomic charges

The Mulliken atomic charges at the HF/6-311G+(d,p) and B3LYP/6-311G+(d,p) level of 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide in gas phase are given in Table 4 (Mulliken, 1955). The electronegative N32, N33, N34, N35, O36, O37, O38 and O39 atoms of the titled compound have negative atomic charge values. The Mulliken atomic charges (B3LYP/HF) of the mentioned atoms were calculated as -0,18358/-0,06376, -0,18470/-0,38072, -0,18497/-0,19111, 0,04705/-0,03712, -0,36908/-0,49686, 0,07053/0,05755, -0,18642/-0,30668 and -0,26420/-0,36914a.u., respectively. The C2, C3, C4, C6, C13 and C16 carbon atoms bounded to the mentioned electronegative atoms in the molecule under study have positive atomic charge values. The values of the positive charges of the mentioned carbon atoms were found as 0,54508/0,77855, 0,13796/0,47904, 0,88901/1,20224, 0,03142/0,20002, 0,58601/0,74340 and 0,02243/0,47360 a.u., respectively. Therefore the C1 atom surrounded with two electronegative N32 and N34 atoms. In the titled compound the atomic charges of all hydrogen atoms have positive values.

Table 4. Mulliken atomic charges of the titled compound

	B3LYP	**HF**		**B3LYP**	**HF**		**B3LYP**	**HF**
1C	-0,08604	-0,04616	**14C**	-0,02262	-0,34609	**27H**	0,31520	0,17005
2C	0,54508	0,77855	**15C**	-0,21346	-0,25993	**28H**	0,13673	0,14209
3C	0,13796	0,47904	**16C**	-0,52235	-0,22423	**29H**	0,12864	0,14123
4C	0,88901	1,20224	**17C**	-0,45032	-0,00277	**30H**	0,13096	0,14147
5C	-0,47927	-1,03838	**18H**	0,33533	0,37704	**31H**	0,14235	0,15549
6C	-0,20818	-0,30140	**19H**	0,17444	0,20726	**32N**	-0,18358	-0,06376
7C	-0,23333	-0,32372	**20H**	0,14732	0,16557	**33N**	-0,18470	-0,38072
8C	-0,20602	-0,38056	**21H**	0,13554	0,14630	**34N**	-0,18497	-0,19111
9C	-0,60935	-0,47661	**22H**	0,13182	0,14150	**35N**	0,04705	-0,03712
10C	-0,54042	-0,41960	**23H**	0,13945	0,14896	**36O**	-0,36908	-0,49686
11C	0,03142	0,20002	**24H**	0,22609	0,24619	**37O**	0,07053	0,05755
12C	0,58601	0,74340	**25H**	0,19323	0,19155	**38O**	-0,18642	-0,30668
13C	0,02243	-0,47360	**26H**	0,27772	0,30292	**39O**	-0,26420	-0,36914

Nonlinear Optic Properties

The materials having nonlinear activity possess a nonlinear response to the electric fields associated with the light of a laser beam. It is well known that the higher values of dipole moment, polarizability, and hyperpolarizability are important for more active NLO properties. In this study dipole moment, polarizability and first hyperpolarizability of the titled molecule were investigated by using B3LYP method at 6-311G+(d,p) basis set. The following formulas are used for calculating the magnitude of total static dipole moment (μ), polarizability (α) and first hyperpolarizability (β):

$$\mu=\left(\mu_x^2+\mu_y^2+\mu_z^2\right)^{\frac{1}{2}}$$

$$\alpha=\frac{1}{3}\left(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}\right)$$

$$\beta=\sqrt{\left(\beta_{xxx}+\beta_{yyy}+\beta_{zzz}\right)^2+\left(\beta_{yyy}+\beta_{xxy}+\beta_{yzz}\right)^2+\left(\beta_{zzz}+\beta_{xxz}+\beta_{yyz}\right)^2}$$

Where, the total static dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) using the *x*, y, *z* components are defined as (Abraham et al., 2008; Karamanis et al., 2008). The energy gap ΔE_g, dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) values of conformer ct of the titled molecule are investigated as a function of the two torsional angle using B3LYP/6-311G+(d,p) level of theory (Govindarajan et al., 2012) (Table 5).

Tablo 5. Calculated polarization and hyperpolarizability values of the molecule (B3LYP/6-311G+(d,p) and HF/6-311G+(d,p)

	B3LYP	**HF**		**B3LYP**	**HF**
μ_x	-2.2250 debye	-3.8219 debye	**β_{xxx}**	7774.61 a.u.	3821.35 a.u.
μ_y	6.7852 debye	-0.8012 debye	**β_{xxy}**	1053.82 a.u.	538.44 a.u.
μ_z	2.3422 debye	2.0819 debye	**β_{xyy}**	823.08 a.u.	495.47 a.u.
μ_{Toplam}	7.2818 debye	4.4253 debye	**β_{yyy}**	-340.62 a.u.	161.42 a.u.
α_{xx}	74.364 a.u.	60.185 a.u.	**β_{xxz}**	-1001.26 a.u.	-903.63 a.u.
α_{yy}	41.696 a.u.	37.522 a.u.	**B_{xyz}**	-154.56 a.u.	-181.90 a.u.
α_{zz}	33.325 a.u.	30.965 a.u.	**B_{yyz}**	-309.57 a.u.	-202.32 a.u.
α	$49.795x10^{-24}$ esu	$42.891x10^{-24}$ esu	**β_{xzz}**	-295.06 a.u.	87.33 a.u.
$\Delta\alpha$	$37.560x10^{-24}$ esu	$26.556x10^{-24}$ esu	**β_{yzz}**	669.31 a.u.	523.13 a.u.
β_x	-9651.51 a.u.	4855.26 a.u.	**B_{zzz}**	1193.83 a.u.	866.30 a.u.
β_y	-1496.43 a.u.	-944.53 a.u.	**B**	8.567^{-30} esu	$5.006x10^{-30}$ esu
β_z	1568.10 a.u.	1476.75 a.u.			

Conclusion

In this paper, the structure of the titled compound is characterized by using ^{1}H, ^{13}C NMR and FT-IR spectroscopic methods. The molecular structures, vibrational frequencies, ^{1}H and ^{13}C NMR chemicals shifts, UV–vis spectroscopies, HOMO and LUMO analyses and atomic charges of 2-[3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acide obtained have been calculated by using DFT/B3LYP and HF methods. By considering the results of experimental works it can be easily stated that the ^{1}H and ^{13}C NMR chemical shifts, and vibrational frequencies spectroscopic parameters obtained theoretically are in a very good agreement with the experimental data. Also, the electronic structure of titled compound are determined electronic structure identifiers such as the Energy of the Highest Occupied Molecular Orbital, Energy of the Lowest Unoccupied Molecular Orbital, molecular hardness, chemical softness, electronegativity, chemical potential, electrophilicity index, nucleophilicity index and dipole moment. Finally, in this study, The nonlinear optical properties of the compound were calculated theoretically. It was found that the molecule concerned had a higher hyperpolarizability value than urine ($0.77x10^{-30}$esu).

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