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Calculation of Some Theoretical Properties of 3-(*p*-Methoxybenzyl)-4-(4-Hydroxybenzylidenamino)-4,5-Dihydro-1*H*-1,2,4-Triazol-5-One with DFT

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Abstract: In this study, the quantum chemical computations of 3-(*p*-methoxybenzyl)-4-(4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one that is a triazole derivaties were calculated using DFT method in the 6-311++G(d,p) basis set. Firstly, the molecule was optimized for the most stable positions of the atoms. The nuclear magnetic rezonans (^{13}C-NMR and ^{1}H-NMR) data were calculated with the GIAO method in the Gaussian O9W package program and the results were compared with the experimental values in the literature. Furthermore, theoretical infrared (IR) vibration frequencies values which were scaled with certain scala factor were obtained using the Veda 4 program. In this study, compound's thermodynamic parameters such as (entropy S^0, heat capacity CV^0 and enthalpy H^0), geometric properties (bond angle and length), electronic parameters (global hardness (η), electron affinity (A), electronegativity (χ), softness (σ) and ionization potential (I), E_{LUMO}-E_{HOMO} energy gap, HOMO-LUMO energy), dipole moment, mulliken atomic charges were also studied.

Keywords: DFT, The Gaussian O9W, HOMO-LUMO, NLO.

Introduction

Schiff Bases are compounds containing azomethine (-CH=N-) in their structure. These compounds are obtained result of reaction of primary amine with aldehyde or kethone (Berhanu et al., 2019, Antony et al., 2019). The seynthesis of Schiff Base can be done by different methods such as solvent free and catalyst, solvent and cataysy free or solvent free by microvwave irradiation (Uddin et al., 2020). The Schiff bases are compouns that have used for biological, medicinal, clinical, pharmacological, and analytical applications (Zafar et al., 2021). For years, researcers have interested in Schiff Bases and their derivatives synthesis due to taking short time and obtanied high yield (Kardaş et al., 2016; Bahçeci et al., 2017; Beytur et al., 2019; Irak and Beytur, 2019; Gürsoy Kol et al.,2020; Koç et al., 2020; Kotan et al., 2020; Beytur, 2020; Uğurlu & Beytur, 2020; Beytur & Avinca, 2021; Boy et al., 2021). In addition, since these compounds have active (-HC=N-) structure they have enabled the synthesis of new active compounds. Literatüre surveys have shown that Schiff Bases and their derivatives are very important compounds both in healty fields as bioactive molecule and technology fields as catalist, sensor (Antony et al., 2019; Ashraf et al., 2021). Especially, metal complexs of Shchiff Bases have tested anti-bacterial (Chohan et al., 2001), anti-fungal (Chohan et el., 2010) herbidical and anticancer (Duff et al., 2012; Kaczmarek et al.,2018; Gowdhami et al., 2021).

Many investigaters raported that 1,2,4- Triazol derivatived Schiff bases have also shown pharmacologcial properties as anti-microbial (Bayrak et al., 2009; Kotan, 2021) anti-oxidant (Manap et al., 2020), antileishmanial (Süleymanoğlu et al., 2017), anti-fungal, anti-bacterial (Jin et al., 2018) anti-cancer,anti-diabetic

(Zafar et al., 2021). In this study, teorical analysis of 3-(*p*-methoxybenzyl)-4-(4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one was performed with Gaussian O9W package program (Frichs et al., 2009). The nuclear magnetic rezonans values, theoretical infrared (IR) values, thermodynamic parameters of bioactive triazole derivative compound were found and interpered by the comparing experimental data.

Results and Discussion

Gaussian Computations

All quantum chemical computations were calculated by using Gaussian 09W packet program. The three-dimensional structure of molecule was drawn in the GaussView program (Dennington et al., 2009). The optimized geometric stable structure and formule is shown in Figure 1.

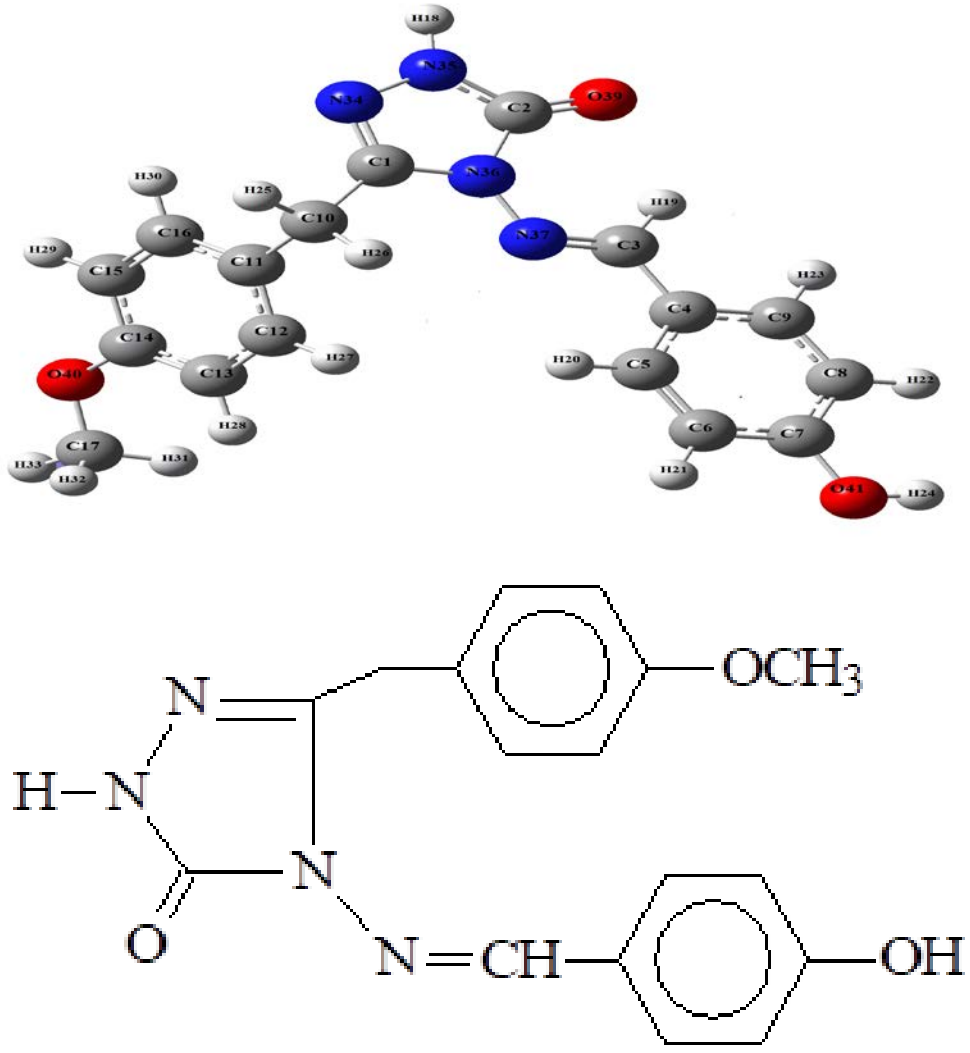


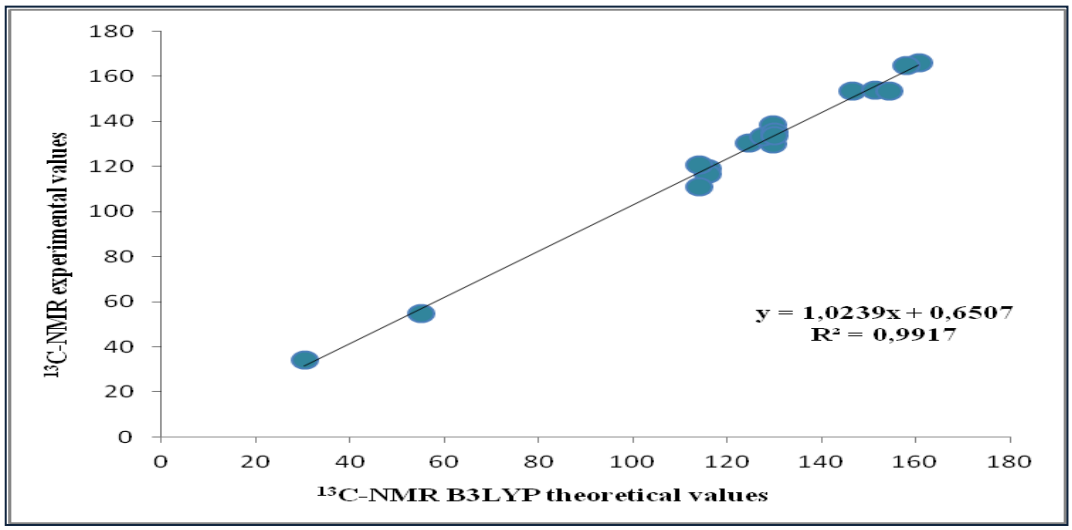
Figure 1. The optimized structure and formule of the molecule

The R^2 Values of the Compound

The GIAO method (Wolinski et al., 1990) was used for nuclear magnetic rezonans analysis of molecule. The experimental data in literatüre and calculational results were evuluated and were listed in Table 1. The proton and carbon chemical shifts ratios of compound were abtained according to results and R^2 valuse of compound were composed and shown in Figure 2.

Table 1. ^{13}C and ^{1}H-NMR(DMSO) isotropic chemical shifts (δ/ppm)

No	Experimental	DFT	No	Experimental	DFT
C1	146,46	153,52	H18	11,85	8,07
C2	151,37	153,68	H19	9,50	10,67
C3	154,23	153,44	H20	7,65	9,17
C4	124,42	130,47	H21	6,87	7,85
C5	129,65	129,84	H22	6,87	7,54
C6	115,87	118,79	H23	7,65	8,08
C7	160,62	166,05	H24	10,14	5,40
C8	115,87	116,65	H25	3,94	4,44
C9	129,65	138,56	H26	3,94	4,74
C10	30,23	33,93	H27	7,22	8,38
C11	127,66	132,96	H28	6,86	7,42
C12	129,82	135,12	H29	6,86	7,68
C13	113,85	110,97	H30	7,22	8,21
C14	158,06	164,66	H31	3,70	4,22
C15	113,85	120,60	H32	3,70	4,30
C16	129,82	133,62	H33	3,70	4,65
C17	55,01	54,47			



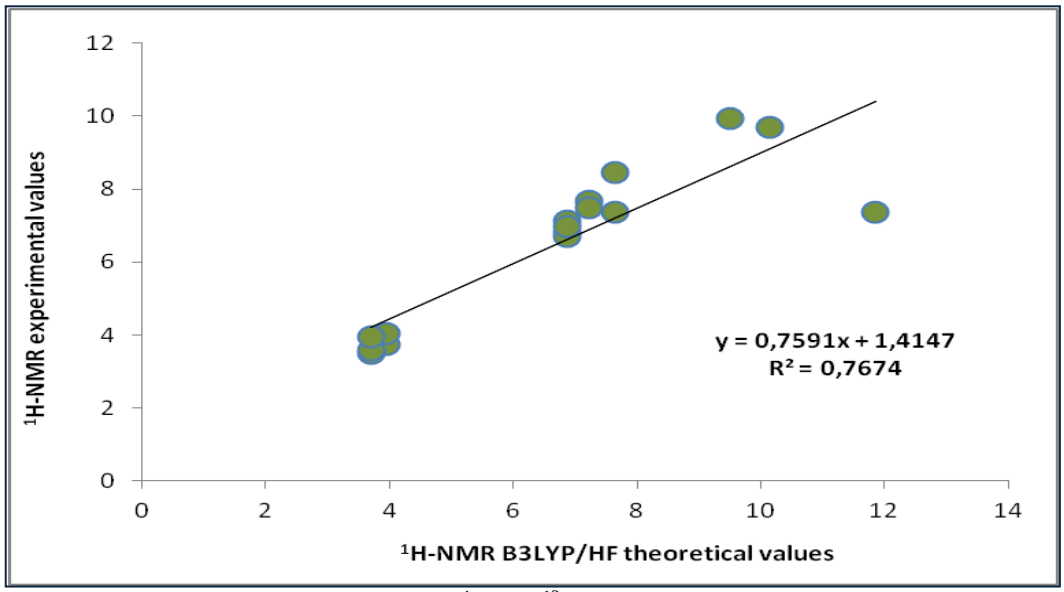


Figure 2. The correlation graphs ^{1}H and ^{13}C NMR chemical shifts for B3LYP

FT-IR Study of Molecule

The veda 4f program was used for calculate theoretically IR values of compound. The obtained scala vibration values of compound were compared with data in literatüre (Jamróz, 2004). Theoretically IR details and experimentally IR values were listed in Table 2.

Table 2. Significant vibrational frequencies (cm^{-1})

Vibrational frequencies	Experimental IR	Scaled B3LYP
ν (OH)	3161	3707
ν (NH)	3118	3565
ν (C=O)	1714	1747
ν (C=N)	1608,1598	1613
1,4-Disübstitüe-benzen	839	860

Molecular Geometric Parameter

The bond lenght data of Schiff base were calculated by using B3LYP/ 6-311++G(d,p) basis set and then interpreted by using experimental data (Çoruh et al., 2003; Köysal et al., 2006; Ustabaş, et al., 2007). The theoretically values were given in Tablo 3.

Table 3. Bond legths theoretical and experimental

Bond Lenght (Å)	B3LYP (Å)	Literatüre (Å)
N(37)-C(3)	1.28	1.28
N-C	1.36	1.47
C2=O39	1.21	1.21
N-N	1.37	1.35
Fenil halkasındaki C-C	1.40	1,40
Fenil halkasındaki C-H	1.08	1.08

Table 4. The calculated bond legths (A^0) theoretical data

bond lengths	DFT	bond lengths	DFT
C(1)-N(34)	1.29	C(15)-C(16)	1.38
C(1)-N(36)	1.38	C(16)-H(30)	1.08
C(1)-C(10)	1.49	N(37)-C(3)	1.28
N(34)-N(35)	1.37	C(3)-H(19)	1.08
N(35)-H(18)	1.00	C(3)-C(4)	1.46
N(35)-C(2)	1.36	C(4)-C(5)	1.40
C(2)-N(36)	1.41	C(5)-H(20)	1.08
C(2)-O(39)	1.21	C(5)-C(6)	1.38
N(36)-N(37)	1.37	C(6)-H(21)	1.08
C(10)-H(25)	1.09	C(6)-C(7)	1.40
C(10)-H(26)	1.09	C(7)-O(41)	1.36
C(10)-C(11)	1.52	O(32)-H(26)	0.96
C(11)-C(12)	1.39	C(7)-C(8)	1.39
C(12)-H(27)	1.08	C(8)-H(22)	1.08
C(12)-C(13)	1.39	C(8)-C(9)	1.39
C(13)-H(28)	1.08	C(9)-H(23)	1.08
C(13)-C(14)	1.39	C(4)-C(9)	1.40
C(14)-C(15)	1.40		
C(15)-H(29)	1.08		

MEP Analysis

The molecular electrostatic potential (MEP) data of compound (Süleymanoğlu et al., 2022) were obtained with the B3LYP/6-311++G(d,p) basis set. Negative and positive regions of the molecule were detected. The positive potential regions are nearby the hydrogen and in blue but the negative potential region are on electronegative

oxygen, nitrogen atoms and in red. In our compound, the electronegative atom, oxygen, is surrounded by red, while the acidic N-H proton is blue (Mathammal et al., 2016). The MEP map of the title compound are displayed in Figure 5.

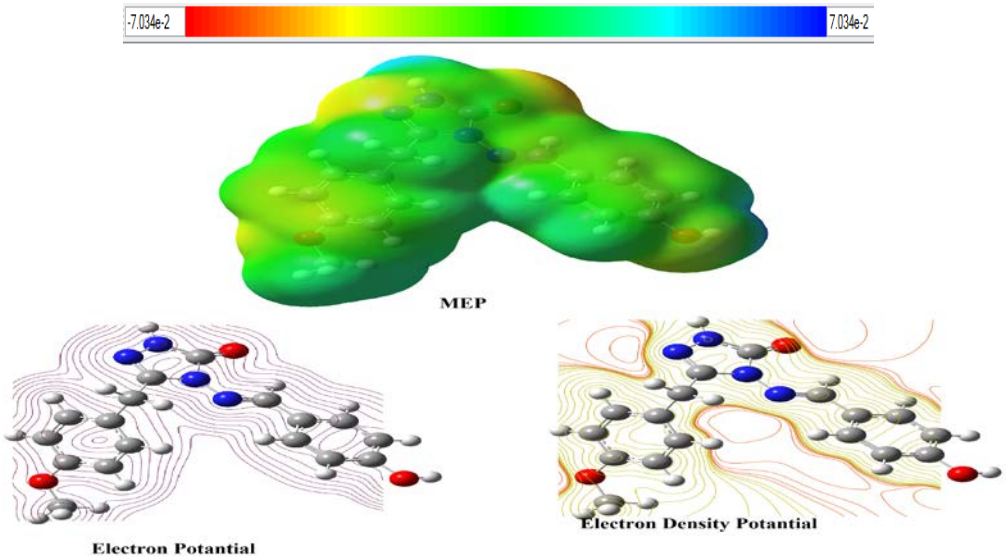


Figure 5. MEP and surface contour maps

Table 5. The calculated dipole moments and total energy data of the molecule

	Dft
μ_x	0.9190
μ_y	-1.4469
μ_z	1.1203
μ_{Toplam}	2.0477
Total energy	-1102.36299926

Mulliken Charge

Mulliken atomic charges of atoms in molecule were detected by same method. It is important for quantum chemical calculations because atomic charges have an effect on the reactivity and electrostatics of molecules (Mulliken et al., 1955).

Table 6. The calculated mulliken charges datas of the molecule

NO	DFT	NO	DFT
C1	0,371	H20	0,108
C2	0,532	H21	0,107
C3	0,131	H22	0,093
C4	-0,17	H23	0,1
C5	-0,013	H24	0,25
C6	-0,095	H25	0,148
C7	0,165	H26	0,137
C8	-0,127	H27	0,088
C9	-0,058	H28	0,102
C10	-0,178	H29	0,102
C11	-0,131	H30	0,097
C12	-0,054	H31	0,111
C13	-0,14	H32	0,11
C14	0,175	H33	0,129
C15	-0,088	N34	-0,222
C16	-0,035	N35	-0,312
C17	-0,132	N36	-0,383
H18	0,249	N37	-0,212
H19	0,138	O39	-0,392

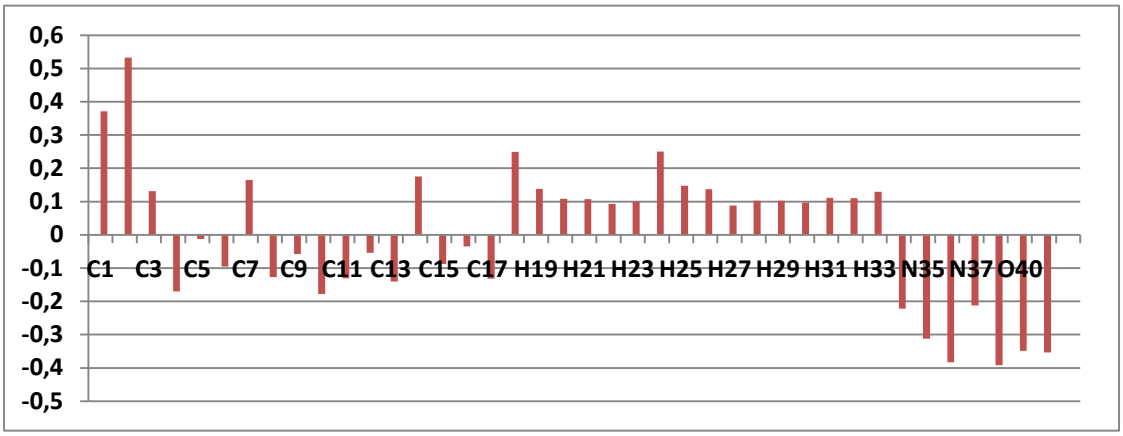


Figure 6**.** The mulliken charge data

The results of calculating the Mulliken atomic charge distributions of the compound in the gas phase were given in Table 5 and also shown the mulliken charge data graphic in Figure 6. According to data of the B3LYP program, "C4, C5, C6, N35, N36, N37, O39" atoms are negatively charged, "H18-H33" and "C1, C2-C13" are positively charged.

Frontier Molecular Orbitals

The energy values and combinations of HOMO and LUMO of compound were measured with DFT (B3LYP) 6-311++G (d,p) basis set. (Fukui, 1982). All electronic parameters have been determined using "ΔEg" value obtained of the Schiff base (Table 7).

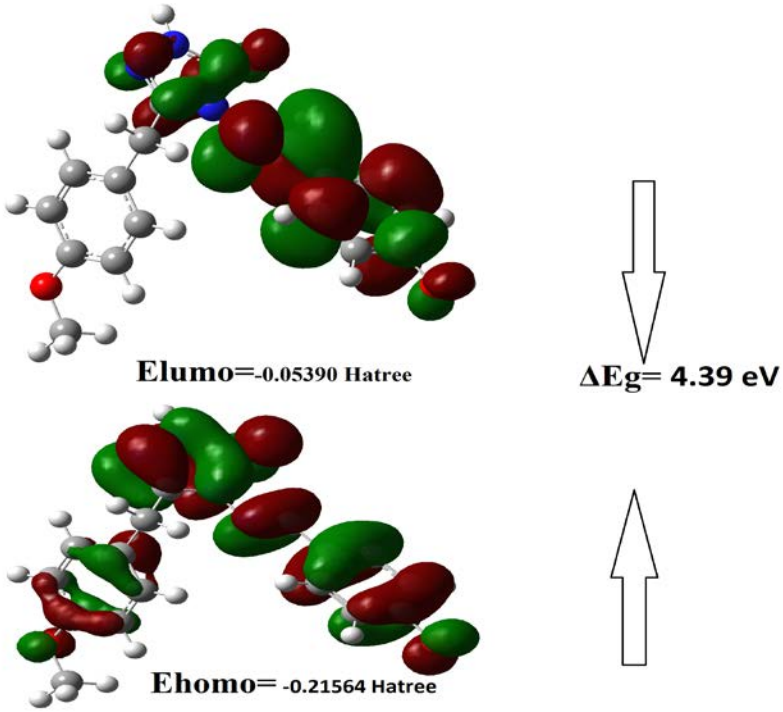


Figure 7. Homo-Lumo energy

Investigation of Thermodynamics Properties of Compound

Thermodynamic parameters such as Enthalpy "$H^{0"}$, Heat capacity "$CV^{0"}$ and Entropy "$S^{0"}$ of molecule were calculated 298.044 K and 1 atm of pressure. The obtained thermodynamic parameters at the B3LYP were given in the table 7 (Kotan et al., 2022).

Table 7. The calculated thermodynamic parameters of the molecule

Rotational temperatures (Kelvin)	DFT
A	0.01168
B	0.00711
C	0.00481
Rotational constants (GHZ)	
A	0.24347
B	0.14820
C	0.10029
Thermal Energies E(kcal/mol)	
Translational	0.889
Rotational	0.889
Vibrational	206.892
Total	208.670
Thermal Capacity CV(cal/mol-K)	
Translational	2.981
Rotational	2.981
Vibrational	74.597
Total	80.559
Entropy S(cal/mol-K)	
Translational	43.223
Rotational	35.739
Vibrational	79.543
Total	158.506
Zero-point correction (Hartree/Particle)	0.311533
Thermal correction to Energy	0.332536
Thermal correction to Enthalpy	0.333480
Thermal correction to Gibbs Free Energy	0.258169
Sum of electronic and zero-point Energies	-1102.051466
Sum of electronic and thermal Energies	-1102.030463
Sum of electronic and thermal Enthalpies	-1102.029519
Sum of electronic and thermal Free Energies	-1102.104830
Zero-point vibrational energy (Kcal/mol)	195.49012

Conclusions

The ^{13}C and ^{1}H-NMR, IR spectroscopic properties and structual parameters of compound were calculated by DFT method with the 6311G++(d,p) basis set. The results of teorical study were compared with the experimental data. The $^{13}C/^{1}H$-NMR and IR chemical shifts values of molecule were determined. According to these data , it can be said that obtained results are approixmate same as the experimental data. Experimental and theoretical ^{13}C chemical shifts ratios between acording to R^2 lineer a correlation were calculated and it' s graphics were obtained .When we evaluated data we can said that, R^2 chemical shifts values for ^{1}H-NMR was deviated due to acidic proton. In addition, nucleophilic and electrophilic regions were determined from the molecular surfaces for title compound.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

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References

Antony, R., Arun, T., & Manickam, S. T. D. (2019). A review on applications of chitosan-based Schiff bases. *International Journal of Biological Macromolecules*, *129*, 615-633.

Ashraf, M. A., Mahmood, K., Wajid, A., Maah, M. J., & Yusoff, I. (2011). Synthesis, characterization and biological activity of Schiff bases. *IPCBEE*, *10*(1), 185.

Bayrak, H., Demirbas, A., Karaoglu, S. A., & Demirbas, N. (2009). Synthesis of some new 1, 2, 4-triazoles, their Mannich and Schiff bases and evaluation of their antimicrobial activities. *European Journal of Medicinal Chemistry*, *44*(3), 1057-1066.

Beytur, M. (2020). Fabrication of platinum nanoparticle/boron nitride quantum dots/6-methyl-2-(3-hydroxy-4-methoxybenzylidenamino)-benzothiazole (ıls) nanocomposite for electrocatalytic oxidation of methanol. *Journal of the Chilean Chemical Society*, *65*(3), 4929-4933.

Beytur, M., & Avinca, I. (2021). Molecular, electronic, nonlinear optical and spectroscopic analysis of heterocyclic 3-substituted-4-(3-methyl-2-thienylmethyleneamino)-4, 5-dihydro-1H-1, 2, 4-triazol-5-ones: Experiment and DFT calculations. *Heterocyclic* Communications, *27*(1), 1-16.

Berhanu, A. L., Mohiuddin, I., Malik, A. K., Aulakh, J. S., Kumar, V., & Kim, K. H., (2019). A review of the applications of Schiff bases as optical chemical sensors. *TrAC Trends in Analytical Chemistry*, *116*(3), 74-91.

Boy, S., Aras, A., Türkan, F., Akyıldırım, O., Beytur, M., Sedef Karaman, H., Manap, S., & Yüksek, H. (2021). Synthesis, spectroscopic analysis, and in vitro/in silico biological studies of novel piperidine derivatives heterocyclic Schiff-Mannich base compounds. *Chemistry & Biodiversity*, *18*(12).

Çiftçi, E., Beytur, M., Calapoğlu, M., Gürsoy Kol, Ö., Alkan, M., Toğay, V. A., Manap, S., & Yüksek. (2017). Synthesis, characterization, antioxidant and antimicrobial activities and DNA damage of some novel 2-[3-alkyl (aryl)-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl]-phenoxyacetic acids in human lymphocytes. *Research Journal of Pharmaceutical, Biological and Chemical Sciences, 9*(5), 1760-1771.

Chohan, Z. H., Munawar, A., & Supuran, C. T. (2001). Transition metal ion complexes of Schiff-bases synthesis, characterization and antibacterial properties. *Metal-Based Drugs*, *8*(3), 137-143.

Chohan, Z. H., Sumrra, S. H., Youssoufi, M. H., & Hadda, T. B. (2010). Metal based biologically active compounds: Design, synthesis, and antibacterial/antifungal/cytotoxic properties of triazole-derived Schiff bases and their oxovanadium (IV) complexes. *European Journal of Medicinal Chemistry*, *45*(7), 2739-2747.

Çoruh, U., Ustabaş, R., Sancak, K., Şaşmaz, S., & Kim, Y. (2003). Octane-1, 8-diylbis [3-ethyl-1H-1, 2, 4-triazol-5 (4H)-one]. *Acta Crystallographica Section E: Structure Reports Online*, *59*(9), 1277-1279.

Dennington. R.. Keith. T. & Millam, J. (2009). *GaussView. Version 5*. Semichem Inc. Shawnee Mission KS.

Duff, B., Thangella, V. R., Creaven, B. S., Walsh, M., & Egan, D. A. (2012). Anti-cancer activity and mutagenic potential of novel copper (II) quinolinone Schiff base complexes in hepatocarcinoma cells. *European Journal of Pharmacology*, *689*(1-3), 45-55.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R.,…Fox, D.J. (2009). *Gaussian 09. Revision C.01*. Pittsburg, PA: Gaussian Inc.

Fukui, K. (1982). Role of frontier orbitals in chemical reactions. *Science , 218*(4574), 747-754.

Gowdhami, B., Ambika, S., Karthiyayini, B., Ramya, V., Kadalmani, B., Vimala, R. T. V., & Akbarsha, M. A. (2021). Potential application of two cobalt (III) Schiff base complexes in cancer chemotherapy: leads from a study using breast and lung cancer cells. *Toxicology in Vitro*, *75*, 105201.

Gürsoy Kol, Ö., Manap, S., Ozdemir, G., Beytur, M., Agdaş, E., Azap, F., Yuca, S., Alkan, M. & Yüksek, H. (2020). Synthesis, antioxidant and antimicrobial activities of novel 4-(2-cinnamoyloxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one derivatives. *Heterocyclic Letters, 10*(4), 575-587.

Jamróz, M.H. (2004). Vibrational energy distribution analysis (VEDA): Scopes and limitations. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *114*, 220-230.

Jin, R. Y., Zeng, C. Y., Liang, X. H., Sun, X. H., Liu, Y. F., Wang, Y. Y., & Zhou, S. (2018). Design, synthesis, biological activities and DFT calculation of novel 1, 2, 4-triazole Schiff base derivatives. *Bioorganic chemistry*, *80*, 253-260.

Kaczmarek, M. T., Zabiszak, M., Nowak, M., & Jastrzab, R. (2018). Lanthanides: Schiff base complexes, applications in cancer diagnosis, therapy, and antibacterial activity. *Coordination Chemistry Reviews*, *370*, 42-54.

Kardaş, F., Manap, S., Gürsoy-Kol, Ö., Beytur, M., Yüksek, H. (2016). Synthesis and antioxidant properties of some3-alkyl(Aryl)-4-[3-ethoxy-2-(4-toluenesulfonyloxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-ones. *Der Pharma Chemica*, *8*(18), 274-281.

Koç, E., Yüksek, H., Beytur, M., Akyıldırım, O., Akçay, M., & Beytur, C. (2020). In vivo determination of antioxidant property of heterocyclic 4,5 dihydro-1H-1, 2, 4- triazol 5-one derivate in male rats (wistar albino). *Bitlis Eren University Journal of Science, 9,* 542-548.

Kotan, G., Gökce, H., Akyıldırım, O., Yüksek, H., Beytur, M., Manap, S., & Medetalibeyoğlu, H. (2020). Synthesis, spectroscopic and computational analysis of 2-[(2-sulfanyl-1H-benzo[d]imidazol-5-yl)iminomethyl]phenyl naphthalene-2-sulfonate. *Russian Journal of Organic Chemistry*, *56*(11), 1982-1994.

Kotan, G. (2021). Novel Mannich base derivatives: Synthesis, characterization, antimicrobial and antioxidant activities. *Letters in Organic Chemistry*, *18*(10), 830-841.

Kotan, G., Manap, S., & Yüksek, H.(2022). Synthesis, characterization, antioxidant and DFT studies of some novel Schiff base compounds. *Journal of Computational Biophysics and Chemistry*, *21*(1), 47-63.

Koysal, Y., Işık, Ş., Sancak, K., & Ünver, Y. (2006). 3, 3′-Diisopropyl-4, 4′-(hexane-1, 6-diyl) bis [1H-1, 2, 4-triazol-5 (4H)-one] dihydrate. *Acta Crystallographica Section E: Structure Reports Online*, *62*(9), 3907-3909.

Manap, S., Gürsoy Kol, Ö., Alkan, M., & Yüksek, H. (2020). Synthesis, in vitro antioxidant and antimicrobial activities of some novel 3-substitued-4-(3-methoxy-4-isobutyryloxybenzylideneamino)-4, 5-dihydro-1H-1, 2, 4-triazol-5-one derivatives. *Indian Journal of Chemistry,59B,* 271-282.

Mathammal, R., Sangeetha, K., Sangeetha, M., Mekala, R., & Gadheeja, S.(2016). Molecular structure, vibrational, UV, NMR, HOMO-LUMO, MEP, NLO, NBO analysis of 3, 5 di tert butyl 4 hydroxy benzoic acid. *Journal of Molecular Structure*, *1120*, 1-14.

Mulliken, R. S. (1955). Electronic population analysis on LCAO-MO molecular wave functions. *International Journal of Chemical Physics, 23*, 1833-1840. 1955.

Süleymanoğlu, N., Ustabaş, R., Direkel, Ş., Alpaslan, Y. B., & Ünver, Y. (2017). 1, 2, 4-triazole derivative with Schiff base; thiol-thione tautomerism, DFT study and antileishmanial activity. *Journal of Molecular Structure*, *1150*, 82-87.

Süleymanoğlu, N., Ustabaş, R., Güler, H. İ., Direkel, Ş., Çelik, F., & Ünver, Y.(2022). Bis-1, 2, 4-triazol derivatives: Synthesis, characterization, DFT, antileishmanial activity and molecular docking studyo. *Journal of Biomolecular Structure and Dynamics*, 1-11.

Uddin, M. N., Ahmed, S. S., & Alam, S. R. (2020). Biomedical applications of Schiff base metal complexes. *Journal of Coordination Chemistry*, *73*(23), 3109-3149.

Uğurlu G., & Beytur, M. (2020). Theoretical studies on the structural, vibrational, conformational analysis and nonlinear optic (NLO) property of 4-(methoxycarbonyl) phenylboronic acid. *Indian Journal of Chemistry-Section A, 59(*10), 1504-1512.

Ustabaş, R., Çoruh, U., Sancak, K., Uenver, Y., & Vazquez-Lopez, E. M. (2007). 1-(benzoylmethyl)-4-[(2, 4-dichlorobenzylidene) amino]-3-(2-thienylmethyl)-4, 5-dihydro-1H-1, 2, 4-triazol-5-one. *Acta Crystallographica Section E: Structure Reports Online*, *63*(6), 2982-2983.

Wolinski. K.. .Hilton. J. F.. & Pulay. P. J. (1990). Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations. *Journal of the American Chemical Society. 112,* 8251-8260.

Zafar, W., Sumrra, S. H., & Chohan, Z. H. (2021). A review: pharmacological aspects of metal based 1, 2, 4-triazole derived Schiff bases. *European Journal of Medicinal Chemistry*, *222*, 113602.

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