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Experimental (Ft-Ir, ^{13}c/ ^{1}h-Nmr) and Dft Studies of 3-(*P*-Methylbenzyl)-4-(4-Methylthiobenzylidenamino-4,5-Dihydro-1*h*-1,2,4-Triazol-5-One

Gul KOTAN
Kafkas University

Murat BEYTUR
Kafkas University

Haydar YUKSEK
Kafkas University

Abstract: The 3-(*p*-Methylbenzyl)-4-(4-methylthiobenzylidenamino-4,5-dihydro-1*H*-1,2,4-triazol-5-one Schiff base was synthesized for investigated some theoretical properties. Firstly, the molecule was optimized with density functional theory (DFT) method and at the 6-311++G(d,p) basis set of Gaussian 09 program. From the optimized geometry of the molecule, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy and thermodynamics properties (heat capacity CV^0, entropy S^0 and enthalpy H^0), electronic calculations (global hardness (η), electron affinity (A), electronegativity (χ), ionization potential (I), softness (σ)), dipole moments, bond lengths, bond angles, the mulliken charges, the molecular surface maps (molecular electrostatic potential (MEP), the electron density, MEP contour and the total density), the energy gap ($\Delta Egap = E_{LUMO}-E_{HOMO}$), IR vibrational frequency, the electric dipole moment, the static polarizability (α) and the static first-order hyperpolarizability (β) values were calculated with B3LYP/ 6-311++G (d, p). Finally, the ^{1}H NMR and ^{13}C-NMR chemical shift values was calculated with gauge independent atomic orbital (GIAO) method. All theoretical spectral data were compared with experimental data obtained from the literature and regression analysis graphs were drawn.

Keywords: B3LYP, DFT, HOMO-LUMO, GIAO.

Introduction

Schiff bases are reactive organic compounds that carry the (-CH=N-) azomethine group and are synthesized by the condensation reaction of an aldehyde or ketone with a primary amine (Zoubi et al., 2017). Schiff base reactions allow the establishment of carbon-nitrogen bonds in organic synthesis, therefore are also used as starting molecules for the transition to different heterocyclic compounds (Kotan et al., 2021a; 2022b). Schiff base derivatives of 1,2,4-triazoles have also been found to acquire pharmacological activities (Zahid et al., 2010; Balram et al., 2010; Wang et al., 2010; Hu et al., 2012).

Compounds synthesized with aromatic amines have an oxygen carrier role in cancer treatment, and in addition to all these, these compounds play an important role in the structure of many drugs, especially antibiotics, in agriculture and pesticides, polymer and dye industry (Serin et al., 1988) esides these, recently, it has been popular to theoretically compute the structural, spectroscopic, thermodynamic and electrical characteristics of molecule systems using quantum chemical computing techniques. For this, all calculations of the molecule were carried out using the B3LYP function and the 6-311G++(d,p) basis set of the DFT method (Frisch et al., 2009; Wolinski et al., 1990), which is popular among quantum chemical computational approaches.

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

Results and Discussion

Theoretical Study

The Gaussian View (Denington et al.,2009) molecular visualization tool and the Gaussian 09W (Frisch et al., 2009) package program were used for all computations in this investigation. The target molecule was first optimized to reach the most stable conformer and shown Figure 1.

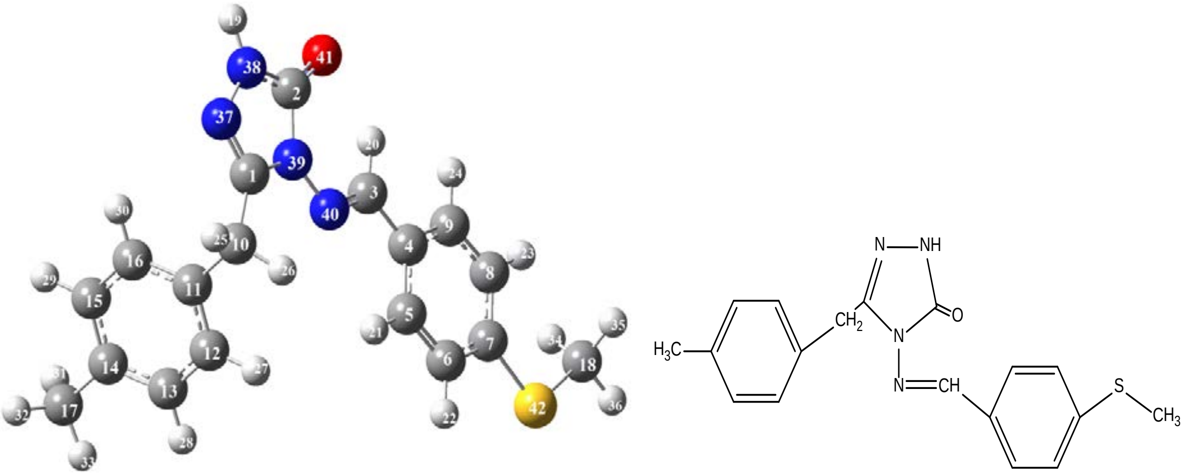


Figure 1. The optimized molecule structure

Table 1. The experimental and theoretical ^{13}C and ^{1}H-NMR chemical shift data

No	Experimental	DFT/6-311++G/DMSO	Differ/DMSO
C1	148.11	147.34	0.77
C2	154.91	148.57	6.34
C3	153.07	149.43	3.64
C4	131.59	128.79	2.80
C5	130.43	122.92	7.51
C6	127.34	125.25	2.09
C7	144.71	148.23	-3.52
C8	127.34	120.93	6.41
C9	130.43	132.88	-2.45
C10	32.50	30.42	2.08
C11	137.47	133.67	3.80
C12	128.61	129.36	-0.75
C13	130.77	129.13	1.64
C14	134.48	130.02	4.46
C15	130.77	128.97	1.80
C16	128.61	127.54	1.07
C17	22.38	17.90	4.48
C18	15.92	12.80	3.12
H19	11.94	7.52	4.42
H20	9.62	10.10	-0.48
H21	7.72	8.35	-0.63
H22	7.35	7.59	-0.24
H23	7.35	7.17	0.18
H24	7.72	7.54	0.18
H25	3.99	3.94	0.05
H26	3.99	4.16	-0.17
H27	7.35	7.72	-0.37
H28	7.35	7.49	-0.14
H29	7.35	7.54	-0.19
H30	7.35	7.67	-0.32
H31	2.24	2.51	-0.27
H32	2.24	2.53	-0.29
H33	2.24	2.04	0.20
H34	2.53	2.41	0.12
H35	2.53	2.42	0.11
H36	2.53	2.41	0.12

NMR analysis

^{1}H and ^{13}C NMR chemical shifts of the title compound in ground state using the optimized molecular structure have been calculated by B3LYP. These spectral calculations such as the proton and carbon shift values were performed using the GIAO technique (Wolinski et al., 1990). The specified compound's ^{13}C /^{1}H NMR chemical shift values (Table 1) are in line with the results of the experiment and created graps with regrasion analysis.

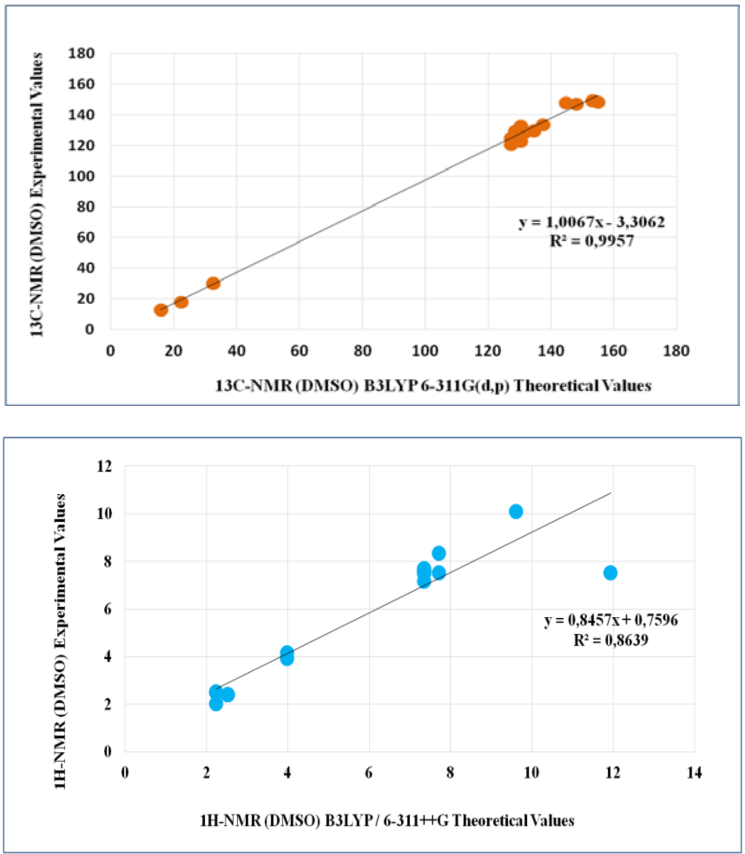


Figure 2. The experimental/calculation ^{13}C and ^{1}H-NMR data and graps

Mulliken Charges Analysis

The mulliken charges (Mulliken et al., 1955) of molecule were calculated with B3LYP 6-311++ G(d,p). While the mulliken charge values of C1, C2, C3 and all protons in the molecule are positive, C4-C18, all the N37-N40, O41 and S42 atoms are negative. The C2 atom, which is attached to the electronegative oxygen atom, has the highest electropositivity.

Table 2. The calculated Mulliken charges

	DFT		DFT		
C1	0.394	C16	-0.033	H30	0,111
C2	0.576	C17	-0.287	H31	0,140
C3	0.156	C18	-0.530	H32	0,136
C4	-0.211	H19	0.258	H33	0,120
C5	-0.005	H20	0,158	H34	0,170
C6	-0.088	H21	0,124	H35	0,170
C7	-0.202	H22	0,112	H36	0,172
C8	-0.081	H23	0,113	N37	-0,240
C9	-0.048	H24	0,106	N38	-0,332
C10	-0,195	H25	0,169	N39	-0,418
C11	-0.138	H26	0,155	N40	-0,230
C12	-0.069	H27	0,093	O41	-0,407
C13	-0.078	H28	0,092	S42	0,176
C14	-0.121	H29	0,094		
C15	-0.084				

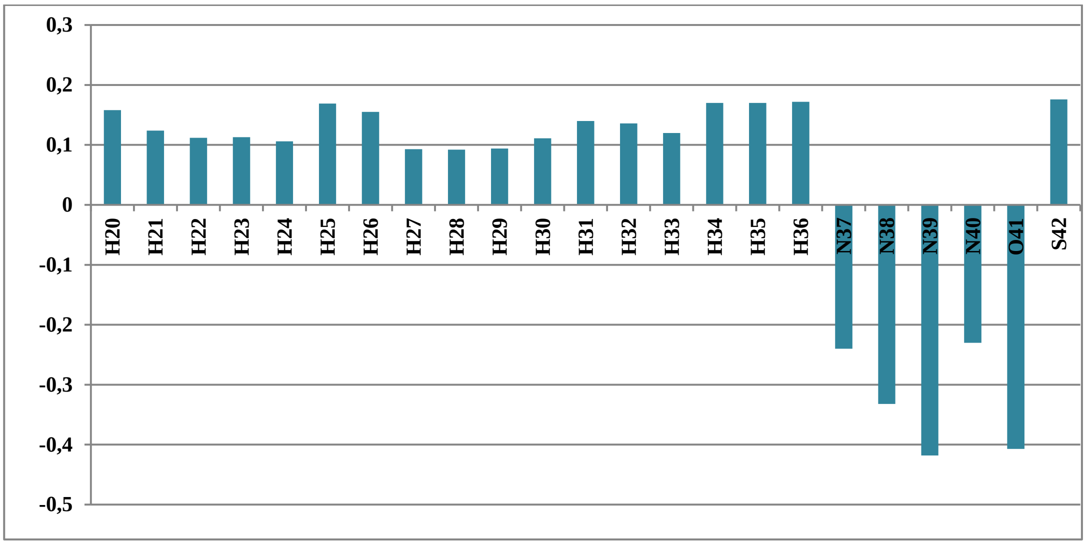


Figure 3**.** The calculated Mulliken charges with B3LYP

Molecular Geometry (Bond length)

The optimized structure was used to calculate the molecule's bond length values, which were then compared to values reported in the literature. The theoretically C1-N37, C1-N39; C2-N38, C2-N39 bond lengths (B3LYP) are 1.29, 1.38, 1.36, 1.41 Å, respectively and experimentally value is 1.47 Å. According to published research and the computed value of the C3=N40 bond length is 1.28 Å. The literature value for the benzene ring's C-C bond length was determined to be 1.39 Å using B3LYP (Sudha et al., 2018; Moreno-Fuquen et al., 2021). The theoretical C-H bond length is 1.08 Å (B3LYP), and published measurements of indicate that this value. Length measurements found in all literature and experimental measurements overlap. The N(38)-H(19) has the shortest bond length, and it is equal to 1.00 Å. This is because the proton is an N-H proton. Additionally, the predicted C=O is 1.21 Å and the observed C=O peak is 1.21 Å (Ocak et al., 2003).

Table 3. The calculated Bond length

Bond length	B3LYP	Bond length	B3LYP
C(1)-C(10)	1.48	C(14)-C(17)	1.50
C(1)-N(37)	1.29	C(17)-H(31)	1.09
C(1)-N(39)	1.38	C(17)-H(32)	1.09
N(37)-N(38)	1.36	C(17)-H(33)	1.09
N(38)-H(19)	1.00	N(40)-C(3)	1.28
C(2)-N(39)	1.41	C(3)-H(20)	1.08
C(2)-N(38)	1.36	C(3)-C(4)	1.45
C(2)-O(41)	1.21	C(4)-C(5)	1.40
N(39)-N(40)	1.36	C(5)-H(21)	1.08
N(38)-H(19)	1.00	C(5)-C(6)	1.37
C(10)-H(25)	1.09	C(6)-H(22)	1.08
C(10)-H(26)	1.09	C(6)-C(7)	1.40
C(10)-C(11)	1.51	C(7)-C(8)	1.39
C(11)-C(12)	1.39	C(7)-S(42)	1.76
C(12)-H(27)	1.08	S(42)-C(18)	1.80
C(12)-C(13)	1.39	C(18)-H(34)	1.09
C(13)-H(28)	1.08	C(18)-H(35)	1.09
C(13)-C(14)	1.39	C(18)-H(36)	1.09

FMO's Analysis

The Frontier Molecular orbitals are HOMO and LUMO (Fukui, 1986). They are filled high-energy and empty low-energy, respectively. The energy difference between "ΔEg" the two orbitals gives us information about the stability of the molecule and using these values, the numerical value of many electronic parameters is calculated and Figure 4.

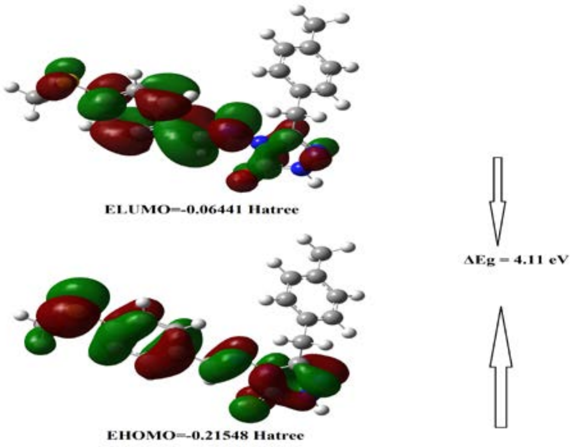


Figure 4. HOMO-LUMO and ΔEg

Table 4. The electronic parameters data of the molecule

		B3LYP			
		Hatree	eV	kcal/mol	KJ/mol
	LUMO	-0,06441	-1,75264	-40,4175	-169,108
	HOMO	-0,21548	-5,86336	-135,214	-565,743
A	Electron Affinity	0,06441	1,75264	40,4175	169,108
I	Ionization Potential	0,21548	5,86336	135,214	565,743
ΔE	Energy gap	0,15107	4,11072	94,7969	396,634
χ	Electronegativity	0,139945	3,808	87,8159	367,426
Pi	Chemical potential	-0,139945	-3,808	-87,8159	-367,426
ω	Electrophilic index	0,000739661	0,02013	0,46414	1,94198
IP	Nucleophilic index	-0,01057075	-0,28764	-6,63317	-27,7535
S	Molecular softness	13,2389	360,24	8307,45	34758,7
η	Molecular hardness	0,075535	2,05536	47,3984	198,317

Thermodynamic Analysis

The calculations of the thermodynamic parameters were done at B3LYP 298.150 K and 1 atm of pressure. Entropy: S (cal/ molK), Heat Capacity: CV(Cal/ Mol-Kelvin), Enthalpy: E (Kcal/ mol)" values are important thermodynamic parameters that should be known in a chemical reaction.

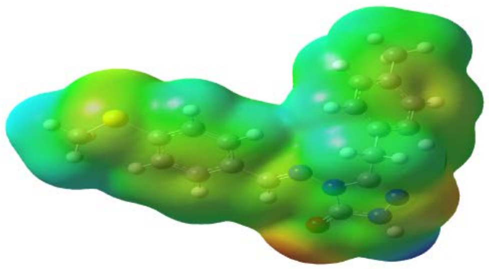
Table 5. The theoretical thermodynamic properties

Rotational temperatures (Kelvin)	DFT
A	0.01333
B	0.00531
C	0.00406
Rotational constants (GHZ)	
A	0.27780
B	0.11061
C	0.08470
Thermal Energies E(kcal/mol)	
Translational	0.889
Rotational	0.889
Vibrational	220.517
Total	222.295
Thermal Capacity CV(cal/mol-K)	
Translational	2.981
Rotational	2.981
Vibrational	77.929
Total	83.891
Entropy S(cal/mol-K)	
Translational	43.349
Rotational	36.067
Vibrational	88.766
Total	168.183

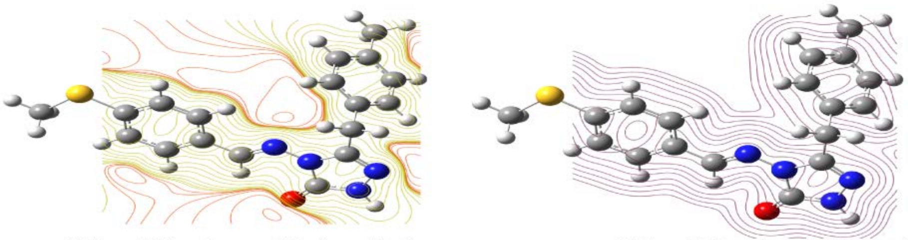
Zero-point correction (Hartree/Particle)	0.331824
Thermal correction to Energy	0.354250
Thermal correction to Enthalpy	0.355194
Thermal correction to Gibbs Free Energy	0.275285
Sum of electronic and zero-point Energies	-1388.657724
Sum of electronic and thermal Energies	-1388.635298
Sum of electronic and thermal Enthalpies	-1388.634354
Sum of electronic and thermal Free Energies	-1388.714263
Zero-point vibrational energy (Kcal/mol)	208.22247

MEP and Surface Maps

By dividing the molecule's atoms into electrophilic and nucleophilic areas in vacuum, the molecular electrostatic potential (MEP) is created. The biological identification of the molecule and the location of intramolecular hydrogen bonding sites, as well as the identification of electron-dense and low-electron areas, all depend on MEP analysis. Understanding the relative polarity of the molecule via MEP is visual. MEP is useful for locating hydrogen bond interaction sites as well as electrophilic and nucleophilic reaction sites since it is connected to electronic densities. The regions of N-H acidic protons are blue, regions of electronegative atoms such as oxygen are red, other places are green (Scrocco et al., 1978).



MEP



The Electron Potential **The Electron Density**

Figure 5. The MEP and Surface maps

FT-IR Vibrational Frequency Calculations

The most often used theoretical techniques for predicting the structure through comparison of anticipated and observed IR spectra are DFT-based calculations because of their affordable computing costs and generally trustworthy findings. All FT-IR calculations were obtained using the Veda 4 program (Jamróz, 2004). The vibrational frequencies were calculated at B3LYP/ 6-311G++(d,p) level of theory for the optimized structure and the obtained frequencies were scaled by 0.9970 (Merrick et al., 2007). The scaled infrared values were compared with the experimental values and are presented in the Table 6.

Table 6. The theoretical and calculated infrared data

vibrational frequencies	Experimental IR	Scaled B3LYP
ν (NH)	3160	3680
ν (C=O)	1708	1703
ν (C=N)	1592	1636
1,4-Disübstitüe-benzen	814	885

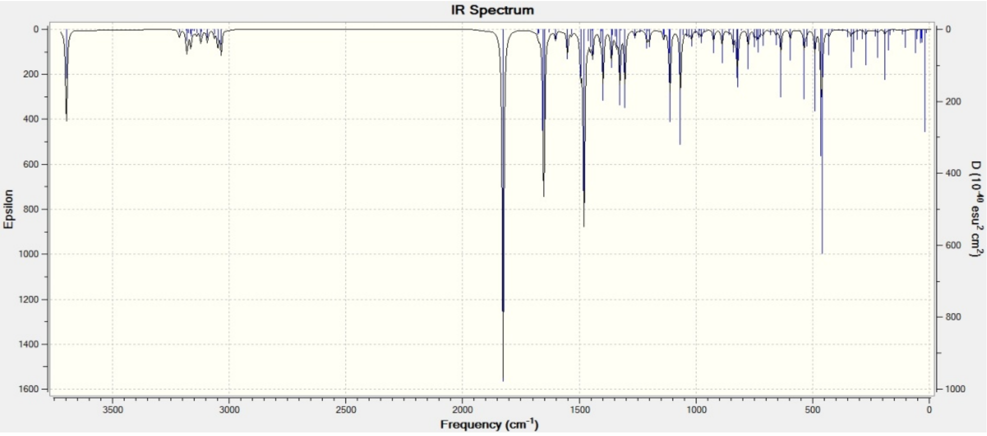


Figure 6. The IR spectrum with DFT(B3LYP)

NLO Analysis

This study is extended to the determination of the electric dipole moment, total energy, the isotropic polarizability and the first hyperpolarizability of the title compound. These fundamental nonlinear parameters with the B3LYP functional and 6-311++G(d,p) basis set were calculated **μ_{toplam}:** the dipole moment at **α_{total}:** the mean polarizability, **$\Delta\alpha$:** the anisotropy of polarizability and **β^{0}:** first hyperpolarizability parameters, 2.0549 Debye; $15.431x10^{-24}$ esu; $34.438x10^{-24}$ esu and $17.480x10^{-30}$ esu respectively. Table 6 displayed the title compound's NLO properties and their constituent parts. The primary reference material for NLO qualities is the urea molecule. According to published data, the NLO parameters are: **α_{total}:** $5.07643717x10^{-24}$ esu, **$\Delta\alpha$:** $=2.13568262x10^{-24}$ esu, and **β^{0}** $= 7.2228469891x10^{-31}$ esu. The NLO values were 3, 17, and 2.5 times more than urea as compared to the reference material (Cassidy et al., 1979).

Table 7. The total energy **E_{total}** (Hatree), the electric dipole moment **μ** (D), the average polarizability **α_{total}** (10^{-24} esu) and first hyperpolarizability **β_{total}** (10^{-30} esu) of molecule

	B3LYP
E_{total}	-1388.98954760
μx	1.7426
μy	0.4075
μz	1.0099
μToplam	2.0549
αxx	371.2751113
αxy	-50.1919306
αyy	258.6258227
αxz	-0.9272771
αyz	15.6887311
αzz	167.185716
α_{total}	$15.431x10^{-24}$ esu
Δα (esu)	$34.438x10^{-24}$ esu
βxxx	1826.19193
βxxy	-671.5883607
βxyy	195.1065759
βyyy	-15.0618249
βxxz	-66.004
βxyz	3169,11.4577
βyyz	71.6571607
βxzz	-35.3789271
βyzz	39.7490469
βzzz	-2.0826927
β_{total}	$17.480x10^{-30}$ esu

Conclusions

The ^{13}C and ^{1}H-NMR, IR, and structural parameters are all obtained using the DFT technique and the 6-311G++(d,p) basis set. The experimental findings were compared to these calculations. These results are quite similar to the experimental data, as shown by the chemical shift values from the $^{13}C/^{1}H$-NMR and IR calculations. The R liner indicated that the theoretical and observed ^{13}C chemical shift ratios were related. The graph of the proton NMR regression analysis, however, showed a divergence brought on by acidic proton. The vibration frequency measurements for IR were all positive. Nucleophilic and electrophilic regions were found on the molecular surfaces. On the basis of the computed energy differences and electronic properties, molecule orbitals were produced.

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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Author Information

Gül Kotan
Kafkas University
Kafkas University, Kars Vocational School, Kars, Turkey
Contact E-mail: *gulkemer@hotmail.com*

Murat Beytur
Kafkas University
Faculty of Science and Letters, Department of Chemistry, Kars, Turkey

Haydar Yuksek
Kafkas University
Faculty of Science and Letters, Department of Chemistry,
Kars, Turkey

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