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Research Article

Structural and theoretical study based on DFT calculations of 3-Methyl-4-[3-ethoxy-(2-*p*-metilbenzenesulfonyloxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one

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ABSTRACT

The molecular structure optimization of 3-Methyl-4-[3-ethoxy-(2-*p*-metilbenzenesulfonyloxy)-benzylidenamino]-4,5-dihydro - 1*H*-1,2,4-triazol-5-one was obtained using the HF method and "B3LYP, B3PW91" functionals in the DFT method at the 6-31G (d, p) basis sets. The structure characterization performed using infrared (FT-IR), ^{13}C-NMR and ^{1}H-NMR spectral tools. Computational IR data was obtained at the Veda4f program. Theoretical ^{1}H/ ^{13}C-NMR(DMSO) isotropic shift values were assigned according to the GIAO method in the DMSO solvent. All the experimental data were available in the literature, these values are consistent with the calculated. Also, the theoretical results of different functionals were compared with each other. The HOMO-LUMO energies and energy difference (eV) were calculated and three-dimensional images are drawn. The no need to use the electronic parameters have been found using the energy difference (ΔE). The thermodynamics properties, mulliken atomic charges, geometric properties, dipole moments, total energy were calculated. The non linear optical (NLO) analysis was carried out. Additionally, with the MEP surface map, the nucleophilic and electrophilic regions of the molecule were determined.

Keywords: GIAO, Veda4f, MEP, HOMO, LUMO, NLO.

3-Metil-4-[3-etoksi-(2-*p*-metilbenzensülfoniloksi)-benzilidenamino]-4,5-dihidro-1*H*-1,2,4-triazol-5-on'nun DFT hesaplamalarına dayalı yapısal ve teorik çalışması

ÖZ

3-Metil-4-[3-etoksi-(2-*p*-metilbenzensülfoniloksi) - benziliden amino]-4,5-dihidro-1*H*-1,2,4-triazol-5-on moleküler yapı optimizasyonu 6-31G (d, p) temel setinde HF metodu ve DFT metodunda B3LYP, B3PW91 fonksiyonları kullanılarak elde edilmiştir. Yapı karakterizasyonu kızılötesi (FT-IR), ^{13}C-NMR ve ^{1}H-NMR spektral araçları kullanılarak gerçekleştirildi. Hesapsal IR verileri Veda4f programında elde edilmiştir. Teorik ^{1}H/^{13}C-NMR isotropik kimyasal kayma değerleri DMSO çözücüsünde GIAO metoduna göre belirlenmiştir. Literatürde tüm deneysel veriler mevcuttu, bu değerler hesaplananlar ile uyumludur. Ayrıca farklı fonksiyonellerin teorik sonuçları birbirleriyle karşılaştırıldı. HOMO-LUMO enerjileri ve enerji farkı (eV) hesaplanmış ve üç boyutlu şekilleri çizilmiştir. Birçok elektronik parametre bu enerji farkı kullanılarak bulunmuştur. Termodinamik özellikler, mulliken atomik yükleri, geometrik özellikleri, dipol moment, toplam enerji hesaplanmıştır. Doğrusal olmayan optik (NLO) analizi gerçekleştirildi. Ayrıca MEP yüzey haritası ile molekülün nükleofilik ve elektrofilik bölgeleri belirlenmiştir.

Anahtar Kelimeler: GIAO, Veda4f, MEP, HOMO, LUMO, NLO.

1. INTRODUCTION

Schiff's bases, which are synthesized from the reaction of aromatic/heteroaromatic carbonyl groups such as aldehydes or ketones with primary amines. These are significant compound for organic chemistry. 1,2,4-Triazol derivatives are well-known organic compounds. Therefore, many studies that include their molecular, biological and structural properties are available in the literatüre.[1-7] Functional groups in the structure of Schiff bases determine their active biological activity characteristics.[8-10] Theoretical studies for Schiff bases have been done on a computer. In this study, we surveied many calculations parameters of molecule with different functionals. The compound characterized theoretically and experimentally with different techniques such as ^{1}H/^{13}C-NMR, FT-IR. All computations were done with DFT(B3LYP/ B3PW91) and HF methods at the 6-31G(d,p) basis set in the Gaussian 09 W packet program.[11-13] Vibration frequencies at the same theoretical levels were calculated, and the optimized structure (Figure 1) and vibration band spectrum were made with Gauss-View program.[14] The theoretical calculations ^{1}H/^{13}C-NMR were performed by using HF/ B3PW91/ B3LYP 6-31G(d,p) and carbon/ proton chemical shifts were assigned using the method GIAO.[15] Calculated and experimental values were written in the necessary places at equation δ exp=a+b. δ calc. and graphics were drawn. Experimental data in the literature[16] were used. To determine the theoretical data, the Veda4f program was used.[17] The theoretical IR values in the gas phase were calculated at the HF and DFT 6-31G (d, p) basis sets, these data are scalled by scaled factors[18]. In addition, finally, the LUMO-HOMO energies, E_{LUMO}-E_{HOMO} energy gap (ΔEg), dipole moments, mulliken charges, total energy, geometric properties, electronic parameters (ionization potential (I), softness (σ), electronegativity (χ), electron affinity (A) and global hardness (η)), thermodynamics some data (entropy (S), thermal energies (E) and thermal capacity (CV)) were examined. Thus, many substantial theoretical properties of the compound were studied by variant calculation lines. Substances showing nonlinear optical properties can change the frequency, reflection, polarization, and phase of the incident light. For this reason, these materials have started to be used in the production of optical devices, photonics industry, telecommunications, information processing, and computer technology.[19] In recent years, theoretical properties, especially the non-linear properties for organic and organometallic compounds in the numerous studies have been investigated.[20-22] It is understood from the literature, that, organic compounds containing metal complexes with coordinated metal centres attract more attention.[23] The delocalization of conjugated π electrons and π bond conjugation are present in the structure of nonlinear optics. In addition, the optical properties of organic compounds can be increased by adding donor-acceptor groups to the structure. In this study, the HF method and different two function such as B3PW91, B3LYP of the DFT method have also been used to examine the nonlinear optical properties of a substance and theoretically the parameters such as the static dipole moment μ (Debye), the static polarizability α (esu) and the static first-order hyperpolarizability β (esu) are calculated. Theoretical NLO analysis results were crosscheck the data of the urea reference in the literatüre.[24]

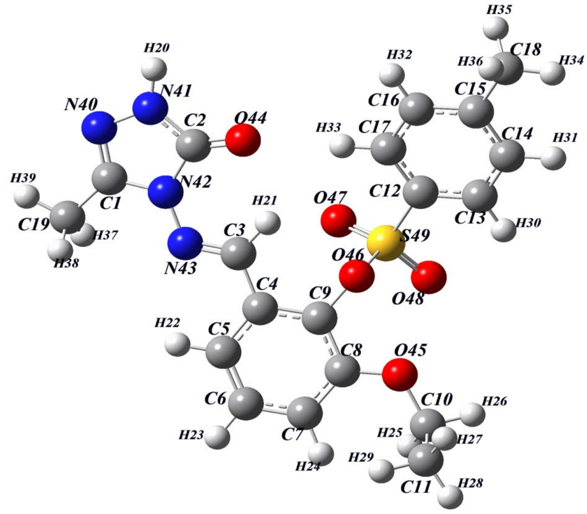

Figure 1. The Gausview structure of the molecule.

2. RESULTS AND DISCUSSION

2.1. NMR analysis

^{13}C and ^{1}H-NMR spectral values calculated no need with using the gauge invariant atomic orbitals method are listed in Table 1 together with the experimental values. While the experimental NH proton signal in the ^{1}H-NMR is at 11.83 ppm (DMSO), the calculated values with B3PW91, B3LYP, HF are 8.72, 8.63, 7.80 (DMSO) ppm, respectively. This is because of the characteristic NH proton. In the ^{1}H-NMR, peak of N=CH proton was found for 9.62 ppm (experimental), 11.57 ppm (B3PW91), 11.35 ppm (B3LYP), 10.62 ppm (HF). The aromatic protons were assigned 7.39-7.71 ppm in the experimental and 8.24-9.82 ppm (B3PW91), 8.07-8.95 ppm (B3LYP), 8.16-9.32 ppm (HF). ^{13}C NMR spectra of compound showed at 145.63 (C1), 147.6 (C2), 151.73 (C3), 116.48-150.73 and 128.14-144.05 (aromatic C) in the experimental, and 147.15 for B3PW91, 150.84 for B3LYP, 145.60 for HF (C1), 149.86 for B3PW91, 153.31 for B3LYP, 146.99 for HF (C2), 150.00 for B3PW91, 152.56 for B3LYP, 146.94 for HF (C3), 116.45-134.13 and 129.37-148.71 for B3PW91, 118.98-156.99 and 131.51- 151.60 for B3LYP, 118.01- 146.43 and 122.54-147.80 (HF) in the calculation. In the theoretical R^2 values are B3PW91 (DMSO): ^{1}H:0.8985, ^{13}C: 0.9983; B3LYP (DMSO): ^{1}H: 0.9011, ^{13}C: 0.9976; HF (DMSO): ^{1}H: 0.8824,^{13}C: 0.9940.A linear graph was obtained for the experimental and theoretical chemical shift values by looking at the R values (Table 2), the graphs (Figure 2.1 and Figure 2.2).

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Table 1. ^{1}H/ ^{13}C-NMR(DMSO) isotropic chemical shifts (δ/ppm) B3PW91, B3LYP, HF

No	Experimental	B3PW91	Differ. B3PW91	B3LYP	Differ. B3LYP	HF	Differ. HF
C1	145.63	147.15	-1.52	150.84	-5.21	145.60	0.03
C2	147.6	149.86	-2.26	153.31	-5.71	146.99	0.61
C3	151.73	150.00	1.73	152.56	-0.83	146.94	4.79
C4	128.75	134.13	-5.38	137.03	-8.28	126.58	2.17
C5	117.27	117.19	0.08	119.67	-2.40	118.01	-0.74
C6	128.22	129.38	-1.16	131.76	-3.54	126.14	2.08
C7	116.48	116.45	0.03	118.98	-2.50	123.19	-6.71
C8	150.73	153.62	-2.89	156.99	-6.26	146.43	4.30
C9	137.39	138.74	-1.35	142.71	-5.32	134.65	2.74
C10	64.23	67.84	-3.61	71.84	-7.61	60.04	4.19
C11	13.99	18.91	-4.92	22.54	-8.55	11.89	2.10
C12	132.21	137.01	-4.80	141.52	-9.31	124.46	7.75
C13	128.14	129.37	-1.23	131.51	-3.37	128.91	-0.77
C14	129.81	130.63	-0.82	132.67	-2.86	122.54	7.27
C15	144.05	148.71	-4.66	151.60	-7.55	147.80	-3.75
C16	129.81	131.60	-1.79	133.81	-4.00	123.77	6.04
C17	128.14	129.71	-1.57	132.40	-4.26	129.04	-0.90
C18	20.94	27.83	-6.89	30.54	-9.60	17.82	3.12
C19	10.95	18.32	-7.37	21.03	-10.08	10.50	0.45
H20	11.83	8.72	3.11	8.63	3.20	7.80	4.03
H21	9.62	11.57	-1.95	11.35	-1.73	10.62	-1.00
H22	7.41	8.93	-1.52	8.74	-1.33	8.75	-1.34
H23	7.4	8.55	-1.15	8.37	-0.97	8.28	-0.88
H24	7.39	8.24	-0.85	8.07	-0.68	8.16	-0.77
H25	3.92	5.38	-1.46	5.30	-1.38	3.95	-0.03
H26	3.92	5.48	-1.56	5.41	-1.49	4.58	-0.66
H27	1.15	2.17	-1.02	2.50	-1.35	0.86	0.29
H28	1.15	1.97	-0.82	1.94	-0.79	1.35	-0.20
H29	1.15	2.55	-1.40	2.15	-1.00	1.19	-0.04
H30	7.71	9.11	-1.40	8.95	-1.24	8.91	-1.20
H31	7.49	8.62	-1.13	8.49	-1.00	8.11	-0.62
H32	7.49	8.82	-1.33	8.60	-1.11	8.27	-0.78
H33	7.71	9.82	-2.11	9.71	-2.00	9.32	-1.61
H34	2.35	3.06	-0.71	3.14	-0.79	2.58	-0.23
H35	2.35	3.62	-1.27	3.52	-1.17	2.98	-0.63
H36	2.35	3.55	-1.20	3.25	-0.90	2.88	-0.53
H37	2.25	3.41	-1.16	3.33	-1.08	2.81	-0.56
H38	2.25	3.40	-1.15	3.32	-1.07	2.86	-0.61
H39	2.25	3.08	-0.83	2.97	-0.72	2.54	-0.29

Table 2. The correlation data for chemical shifts

	^{13}C				^{1}H			
	R^2	**S. hata**	**a**	**b**	**R^2**	**S. hata**	**a**	**b**
B3PW91	0.9983	1.9748	1.0339	-6.5366	0.8985	1.0691	0.9970	-1.0278
B3LYP	0.9976	2.3632	1.0340	-9.6467	0.9011	1.0553	1.0137	-1.0110
HF	0.9940	3.7231	0.9940	2.4840	0.8824	1.1509	0.9406	-0.0659

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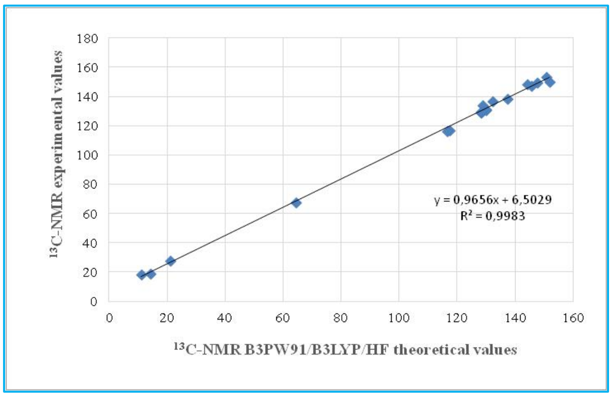

Figure 2.1. The ^{13}C-NMR correlation graphs for B3LYP/B3PW91/HF 6-31G(d,p) /DMSO chemical shifts

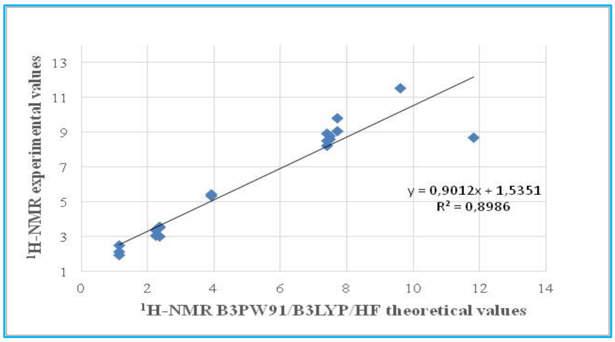

Figure 2.2. The ^{1}H-NMR correlation graphs for B3LYP/B3PW91/HF 6-31G(d,p) /DMSO chemical shifts

2.2. FT-IR analysis

Infrared vibration frequency values were obtained using the Veda 4 program and these values were multiplied with appropriate scala factors such as 0.9576 for B3PW91/ 6-31G(d,p) level, 0.9617 for B3LYP/ 6-31G(d,p) level, 0.8992 for HF/ 6-31G(d,p) level. The frequency data found in the calculations are positive. The vibration bands of the N-H in the experimental IR spectrum are observed at 3171 cm^{-1} and the theoretical N-H peaks are calculated in the 3562 cm^{-1} for B3PW91, 3114 cm^{-1} for B3LYP, 3104 cm^{-1} for HF. Single weak band at 1696 cm^{-1} in the experimental spectrum was assigned to C=O vibration, the calculated peaks for B3PW91/B3LYP/HF are observed 1754/1739/1763 cm^{-1}, respectively. While the experimental C-N peak is at 1596 cm^{-1}, the calculated C-N peak is at 1613 cm^{-1} (B3PW91), 1621 cm^{-1} (B3LYP) and 1718 cm^{-1} (HF). Two weak bands at 1341 and 1152 cm^{-1} in the experimental spectrum were assigned to S=O and S-O vibrations, and respective calculated values are 1341, 1152 cm^{-1} (B3PW91), 1312, 1099 cm^{-1} (B3LYP) and 1310, 1100 cm^{-1} (HF). IR spectra were drawn with obtained values according to DFT(B3PW91/ B3LYP), HF methods (Figure 3). Theoretically IR values were compared with experimentally IR values. The experimental and calculated harmonic vibrational frequencies of molecule were found a linear correlation and are shown in the Figure 3. The results of this comparison were found corresponding with each other of values and were listed in the Table 3.

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Table 3. Significant vibrational frequencies (cm^{-1})

Vibrational frequencies	**Experimental (cm)$^{-1}$**		**Computationals**	
	IR	**Scaled B3PW91**	**Scaled B3LYP**	**Scaled HF**
ν NH	3171	3562	3114	3104
ν C=O	1696	1754	1739	1763
ν C=N	1596	1613	1621	1718
ν S=O	1341 and 1152	1312 and 1099	1288 and 1121	1310 and 1100

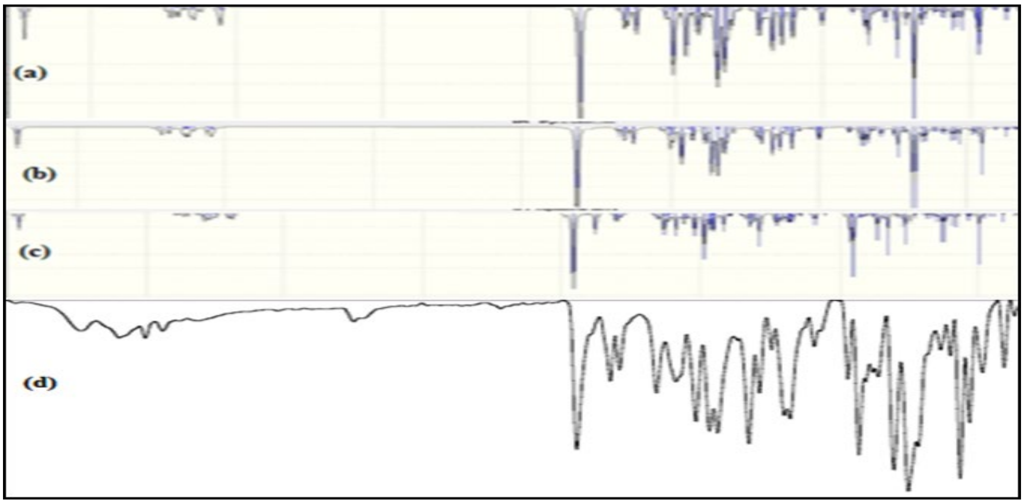

Figure 3. Theoretical IR spectrums and simulated with B3PW91(a)/ B3LYP(b)/ HF(c)/ Experimental(d)

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2.3. Molecular geometry

The bond lengths, mulliken atomic charges and bond angles calculated by the HF and DFT method with 6-31G(d,p) basis set (Table 4-6). According to this data, the highest bond length is between C(49)-C(12) atoms that these values are 1.779/1.770/1.754 Å for B3LYP/B3PW91/HF methods. Additionally, respective the bond lengths in the triazole ring N40-N41, N40-C1, C2-O44, C2-N42, N42-C1 are calculated 1,381/1.372/1,371;1,226/1.224/1.205;1.415/1,411/1.38; 1.415/1.411/1.385 Å at the HF/ B3LYP/ B3PW91 (Table 4). In the literature, N-N, C=O, N=C bond lengths are assigned as 1.404, 1.212, 1.280 Å.[25,26] The calculated bond length values are consistent with literature values. The highest bond angle is between N(41)-C(2)-N(44), which is 129.412/129.466/129.028^0 for B3LYP/ B3PW91/HF (Table 5). The mulliken charge distribution of the atoms was done[27].

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Table 4. The calculated bond lengths with B3LYP/ B3PW91/ HF 6-31G(d,p)

Bond Lengths	B3LYP	B3PW91	HF	Bond Lengths	B3LYP	B3PW91	HF
C(1)-N(40)	1.300	1.299	1.269	C(11)-H(27)	1.093	1.093	1.086
C(1)-N(42)	1.388	1.384	1.378	C(11)-H(28)	1.095	1.094	1.083
C(1)-C(19)	1.486	1.481	1.488	C(11)-H(29)	1.093	1.093	1.084
N(41)-N(40)	1.381	1.372	1.371	C(8)-C(9)	1.411	1.409	1.390
N(41)-H(20)	1.006	1.005	0.990	C(9)-C(4)	1.403	1.400	1.390
N(41)-C(2)	1.368	1.365	1.344	C(9)-O(46)	1.394	1.388	1.384
C(2)-O(44)	1.226	1.224	1.205	O(46)-S(49)	1.694	1.681	1.612
C(2)-N(42)	1.415	1.411	1.385	S(49)-O(47)	1.461	1.457	1.425
N(42)-N(43)	1.375	1.365	1.367	S(49)-O(48)	1.459	1.454	1.420
N(43)-C(3)	1.288	1.286	1.258	S(49)-C(12)	1.779	1.770	1.754
C(3)-H(21)	1.082	1.084	1.069	C(12)-C(13)	1.394	1.391	1.383
C(4)-C(3)	1.465	1.462	1.477	C(12)-C(17)	1.396	1.395	1.388
C(5)-C(4)	1.406	1.404	1.391	C(13)-C(14)	1.392	1.391	1.384
C(9)-C(4)	1.403	1.400	1.390	C(13)-H(30)	1.083	1.084	1.073
C(5)-H(22)	1.083	1.083	1.072	C(14)-H(31)	1.086	1.086	1.075
C(5)-C(6)	1.385	1.383	1.379	C(14)-C(15)	1.401	1.398	1.389
C(6)-H(23)	1.085	1.086	1.075	C(15)-C(16)	1.402	1.402	1.393
C(6)-C(7)	1.399	1.397	1.385	C(16)-H(32)	1.086	1.086	1.075
C(7)-H(24)	1.082	1.083	1.074	C(16)-C(17)	1.392	1.389	1.379
C(8)-C(7)	1.398	1.396	1.384	C(17)-H(33)	1.085	1.086	1.074
C(8)-O(45)	1.353	1.348	1.349	C(15)-C(18)	1.509	1.504	1.509
O(45)-C(10)	1.431	1.425	1.417	C(18)-H(34)	1.093	1.092	1.083
C(10)-H(25)	1.096	1.097	1.086	C(18)-H(35)	1.097	1.096	1.086
C(10)-H(26)	1.093	1.093	1.081	C(18)-H(36)	1.093	1.094	1.084
C(10)-C(11)	1.524	1.519	1.518				

Table 5. The calculated bond angles with B3LYP/ B3PW91/HF 6-31G(d,p)

Bond Angle	B3LYP	B3PW91	HF	Bond Angle	B3LYP	B3PW91	HF
N(40)-C(1)-N(42)	111,513	111.396	111,345	C(8)-O(45)-C(10)	120,154	119,832	117,816
N(40)-N(41)-C(2)	114,522	114.668	113,736	O(45)-C(10)-H(25)	110,123	110.168	109,841
N(40)-N(41)-H(20)	120,440	120.393	120.993	O(45)-C(10)-H(26)	104,239	104.265	104,837
H(20)-N(41)-C(2)	125,037	124.938	125,265	O(45)-C(10)-C(11)	112,321	112.391	110,708
N(41)-C(2)-O(44)	129,412	129.466	129,028	C(10)-C(11)-H(27)	110,190	110.189	109,686
O(44)-C(2)-N(42)	129,285	129.315	128,958	C(10)-C(11)-H(28)	109,929	109.990	110,562
N(40)-C(1)-C(19)	125,131	125.260	125,417	C(10)-C(11)-H(29)	112,010	112.052	111,496
N(42)-C(1)-C(19)	123,356	123.344	123,238	C(9)-O(46)-S(49)	114,563	116.841	119,909
C(1)-C(19)-H(37)	110,904	110.896	110,474	O(46)-S(49)-O(47)	107,146	107.217	106,916
C(1)-C(19)-H(38)	110,978	110.959	110,537	O(46)-S(49)-O(48)	110,244	109.417	109,150
H(39)-C(19)-C(1)	108,650	108.621	108,548	S(49)-C(12)-C(13)	118,735	118.746	119,105
H(37)-C(19)-H(38)	107,340	107.388	107,886	S(49)-C(12)-C(17)	119,463	119.446	119,528
H(37)-C(19)-H(39)	109,498	109.501	109,736	C(12)-C(13)-C(14)	118,724	118.717	119,022
H(38)-C(19)-H(39)	109,450	109.457	109,653	C(12)-C(13)-H(30)	119,906	119.848	120.005
N(42)-N(43)-C(3)	118,260	118.335	119,143	H(30)-C(13)-C(14)	121,369	121.434	120.971
N(43)-C(3)-H(21)	122,415	122,445	122,518	C(13)-C(14)-H(31)	119,352	119,354	119,290
H(21)-C(3)-C(4)	118,122	118.289	117,909	H(31)-C(14)-C(15)	119,552	119.545	119,931
C(3)-C(4)-C(5)	122,025	121.978	121,745	C(13)-C(14)-C(15)	121,095	121.101	120,878
C(4)-C(5)-H(22)	118,657	118.600	118,873	C(14)-C(15)-C(18)	120,768	121.029	120,931
H(22)-C(5)-C(6)	121,361	121.469	120,831	C(14)-C(15)-C(16)	118,603	118.603	118,860
C(4)-C(5)-C(6)	119,981	119.930	120,295	C(15)-C(16)-H(32)	119,625	119.614	119,771
C(5)-C(6)-H(23)	119,879	119.896	119,920	H(32)-C(16)-C(17)	118,946	118.978	119,081
H(23)-C(6)-C(7)	118,986	118.970	119,641	C(16)-C(17)-H(33)	120,392	120.521	120,338
C(5)-C(6)-C(7)	121,129	121.127	120,394	H(33)-C(17)-C(12)	121,258	121.110	120,937
C(6)-C(7)-H(24)	119,517	119.485	120,858	C(15)-C(18)-H(34)	111,529	111.621	111,406
H(24)-C(7)-C(8)	120,349	120.333	118,745	C(15)-C(18)-H(35)	110,844	110.894	110,541
C(7)-C(8)-C(9)	120,132	118,405	118,693	C(15)-C(18)-H(36)	111,399	111.212	111,042
C(7)-C(8)-O(45)	125,717	125.785	121,215				

The electronegative nitrogen (N), oxygen (O) atoms have negative charge values. C2 atom is surrounded by three electronegative atoms (N41, N42, O44) have negative charges values. The H20-H39 have positive atomic charge values. Also, there is an exceptional case where the sulfur atom is electronegative atom but possitive charged and has the highest mulliken charge. This value is 1.273/1.299/1.723^{0} for B3LYP/B3PW91/HF methods (Table 6). This is because, the sulfur atom is surrounded by three oxygen atoms which are more electronegative atom than the sulfur.

Table 6. The calculated mulliken charges datas B3LYP/ B3PW91/HF 6-31G(d,p)

	B3LYP	B3PW91	HF		DFT	B3PW91	HF
C1	0.524	0.535	0.594	**H26**	0.125	0.131	0.134
C2	0.824	0.858	1.062	**H27**	0.128	0.154	0.111
C3	0.153	0.149	0.230	**H28**	0.110	0.142	0.137
C4	0.088	0.053	-0.071	**H29**	0.118	0.135	0.125
C5	-0.119	-0.140	-0.131	**H30**	0.134	0.168	0.209
C6	-0.091	-0.129	-0.145	**H31**	0.091	0.127	0.158
C7	-0.133	-0.166	-0.167	**H32**	0.098	0.141	0.165
C8	0.369	0.202	0.402	**H33**	0.164	0.154	0.248
C9	0.210	0.373	0.305	**H34**	0.119	0.159	0.129
C10	0.045	-0.014	0.099	**H35**	0.135	0.134	0.145
C11	-0.335	-0.409	-0.352	**H36**	0.123	0.196	0.137
C12	-0.203	-0.242	-0.376	**H37**	0.146	0.172	0.161
C13	-0.072	-0.098	-0.090	**H38**	0.141	0.166	0.152
C14	-0.128	-0.150	-0.172	**H39**	0.140	0.167	0.160
C15	0.132	0.104	0.017	**N40**	-0.335	-0.338	-0.351
C16	-0.127	-0.153	-0.170	**N41**	-0.433	-0.466	-0.565
C17	-0.067	-0.091	-0.091	**N42**	-0.408	-0.443	-0.617
C18	-0.382	-0.048	0.347	**N43**	-0.330	-0.332	-0.328
C19	-0.368	-0.434	-0.359	**O44**	-0.547	-0.557	-0.670
H20	0.288	0.311	0.339	**O45**	-0.512	-0.510	-0.670
H21	0.167	0.194	0.236	**O46**	-0.631	-0.626	-0.795
H22	0.105	0.141	0.184	**O47**	-0.529	-0.527	-0.681
H23	0.092	0.128	0.163	**O48**	-0.502	-0.504	-0.641
H24	0.094	0.129	0.172	**S49**	1.273	1.299	1.723
H25	0.106	0.153	0.102				

2.4. FMO's analysis

Frontier molecular orbitals were defined the electronic transitions, kinetic stability, optical and electric properties.[28] The molecular orbital surfaces for LUMO: lowest unoccupied molecular orbital, HOMO: highest occupied molecular orbital are shown in Figure 4. The energy levels are 4.4307/4.4186/10.976 eV for different HF- DFT methods. The energy difference (ΔEg) between LUMO - HOMO orbitals is a basic feature that provides important information about the stability and some electronic properties of the structure.[29] We can say that, the structure calculated with the DFT (B3LYP) set is more stable than the others. The positions of the LUMO-HOMO orbitals of the molecule were calculated with all three basic sets, and it was seen that these orbitals are usually concentrated in the triazole and benzene ring. The electronic properties of molecule such as electron affinity (*A*), softness (*S*), chemical potential (*Pi*), electronegativity (χ), Nucleophilic index (*IP*), global hardness (η), electrophilic index(ω), chemical potential (μ) and ionization potential (*I*) was calculated using the equations given below for B3PW91/B3LYP/HF basis sets are showed in Table 7.

Table 7. The calculated electronic structure parameters of the molecule

	eV	B3PW91	B3LYP	HF
	LUMO	-1,57632	-1,50067	2,30556
	HOMO	-6,0005	-5,91914	-8,67015
A	Electron affinity	1,57632	1,50067	-2,30556
I	Ionization potential	6,0005	5,91914	8,67015
ΔE	Energy gap	4,42419	4,41847	10,9757
χ	Electronegativity	3,78841	3,70991	3,18229
Pi	Chemical potential	-3,78841	-3,70991	-3,18229
ω	Electrophilic index	0,02144	0,02053	0,03753
IP	Nucleophilic index	-0,30798	-0,30121	-0,6418
S	Molecular softness	334,716	335,148	134,92
η	Molecular hardness	2,21209	2,20924	5,48785

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$\eta = (I - A)/2$ (Kimyasal Sertlik)
$\mu = -(I + A)/2$ (Kimyasal potansiyel)
$\chi = (I + A)/2$ (Elektronegativite)
$S = 1/2\eta$ (Kimyasal yumuşaklık)
$\omega = \mu^2 / 2\eta$ (Elektrofilik indexs)
$I = -E_{HOMO}$ (İyonizasyon potansiyeli)
$A = -E_{LUMO}$ (Elektron yoğunluğu)

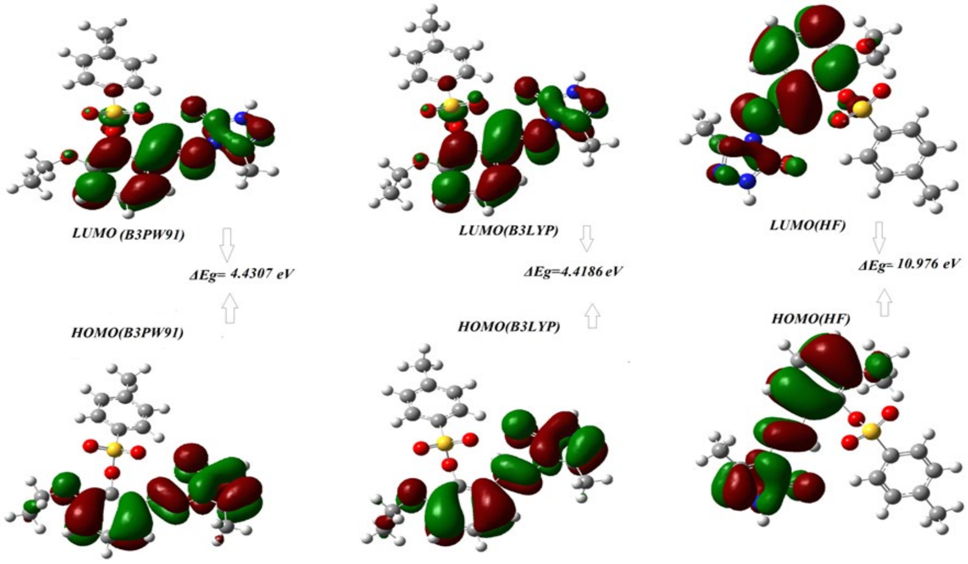

Figure 4. HOMO-LUMO and ΔE*g* energy of the molecule

2.5. Thermodynamics properties

Thermodynamics calculations were calculated with diverse three method such as HF and B3PW91, B3LYP at the 6-31G(d,p) basis set under 1 atm pressure and at 298.150 K. The electronic, rotational, translational and vibrational data, Entropy, Enthalpy were computed and were seen in table 8. The zero-point vibrational energies were calculated as 238.0056, 237.1275, 254.8937 kcal/mol by different methods. The computed thermal energy (E), heat capacity (Cv), entropy (S) values are 255.394/254.559/271.244kcal/mol;190.252/189.833/184.120 cal; 103.033/103.369/95.763 cal for B3PW91/ B3LYP/ HF, respectively.

2.7. The surface maps

The immersive shapes of MEP known as molecular electrostatic potential maps. The surface of MEP map was shown molecular shape, size, charge distribution and electrostatic potential value. Molecular electrostatic potential, molecular electrophilic and nucleophilic determination of regions where reactions may occur and the formation of intramolecular hydrogen bonds provides important information. The regions with the highest electron density are around the O44, O45, O46, O47, O48 atoms. The section of the electronegativity oxygen atom is red colour in the MEP. The around of hydrogen atoms are positive potential region. The -NH region is the region with the lowest electron density and is blue in the MEP map. Furthermore, the total density, contour maps (the electrostatic potential, the electron spin potential (ESP) map, the electron density are shown in Figure 5.

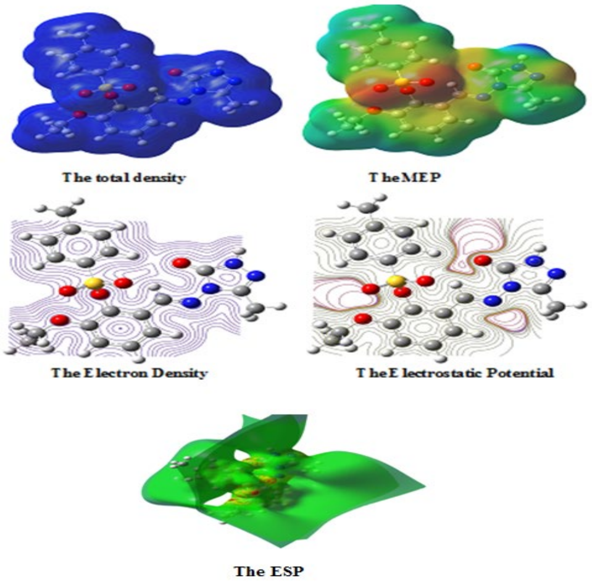

Figure 5. The calculated molecular surface maps of the molecule

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Table 8. The thermodynamics parameters of the molecule

Parameters	**B3PW91**	**B3LYP**	**HF**
Rotational temperatures (Kelvin)			
A	0.00773	0.00767	0.00853
B	0.00621	0.00621	0.00615
C	0.00371	0.00369	0.00396
Rotational constants (GHZ)			
A	0.16111	0.15973	0.17765
B	0.12940	0.12941	0.12819
C	0.07727	0.07681	0.08252
Thermal Energies E(kcal/mol)			
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	253.616	252.781	269.467
Total	255.394	254.559	271.244
Thermal Capacity CV(cal/mol-K)			
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	97.071	97.407	89.801
Total	103.033	103.369	95.763
Entropy S(cal/mol-K)			
Translational	43.968	43.968	43.968
Rotational	36.543	36.558	36.390
Vibrational	109.741	109.308	103.762
Total	190.252	189.833	184.120
Zero-point correction (Hartree/Particle)	0.379286	0.377887	0.406199
Thermal correction to Energy	0.406996	0.405665	0.432255
Thermal correction to Enthalpy	0.407940	0.406609	0.433199
Thermal correction to Gibbs Free Energy	0.317545	0.316413	0.345718
Sum of electronic and zero-point Energies	-1728.381703	-1728.935236	-1720.276579
Sum of electronic and thermal Energies	-1728.353993	-1728.907458	-1720.250523
Sum of electronic and thermal Enthalpies	-1728.353048	-1728.906514	-1720.249578
Sum of electronic and thermal Free Energies	-1728.443443	-1728.996710	-1720.337060
Zero-point vibrational energy (Kcal/mol)	238.00565	237.12754	254.89372

2.7. NLO analysis

The compound within gaseous phase, the dipole moment (μ), the static polarizability (α) and the static hyperpolarizability (β) values were computed by the B3PW91/B3LYP/HF 6-31G(d,p) levels. Then, the μ_{total}, α_{total}, $\Delta\alpha$ and β values were calculated by using the following equantion 1-4. In the Gaussian 09W program, the 10 values obtained from the frequence output file provide the components "βxxx, βxxy, βxyy, βyyy, βxxz, βxyz, βyyz, βxzz, βyzz, βzzz" and 6 values provide " αxx, αxy, αyy, αxz, αyz, αzz" components, respectively. The polarizability α and hyperpolarity β values are found in the Gaussian 09 W output in atomic units (au), but the calculated values (α: 1 a.u. = $0.1482\text{x}10^{-24}$ esu; β: 1 a.u. = $8.6393\text{x}10^{-33}$esu) have been converted into electrostatic units (esu).[30] As a result of the calculation, the polarizability α (esu) 40.5608, 40.7313, 35.3210; the hyperpolarity β (esu) 44.726, 38.434, 25.514; Δα (esu) 30.7458, 43.872, 24.4372; total energy values E_{total} (Hatree) -1728.7609, -1729.3131, -1720.6827; dipole moments μ_{total} (Debye) 2.9995, 2.8513, 4.3705 for B3PW91/B3LYP/HF, respectively are obtained and are listed in the Table 9. These values were compared with urea used as reference material for NLO analysis.[24] The lowest values for static α_{total}, $\Delta\alpha$ and β_0 parameters are calculated for HF 6-31G(d,p) basis set. The calculated highest values are DFT 6-31G(d,p). When NLO values were compared with the urea reference, it was seen that the calculated values were high. This result showed that the target molecule studied could be a good non-linear optics. The calculated highest dipole moment and energy values are equal to 4.3705 D, -1720.6827 Hartee for HF 6-31G(d,p).

$$\mu_{total} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (1)$$

$$\alpha_{total} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6a_{xz}^2 + 6a_{xy}^2 + 6a_{yz}^2\right]^{1/2} \quad (3)$$

$$\beta_0 = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2\right]^{1/2} \quad (4)$$

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Table 9. The total energy E_{total} (Hatree), the electric dipole moment μ (Debye), the polarizability α_{total} (10^{-24} esu) and first hyperpolarizability β_{total} (10^{-30} esu) of molecule

	B3PW91	B3LYP	HF
E_{total}	-1728.7609	-1729.3131	-1720.6827
μx	-1.4211	-1.3036	0.9292
μy	-0.2443	-0.1692	0.3656
μz	-2.6302	-2.5303	-4.2549
μ_{total}	2.9995	2.8513	4.3705
αxx	52.0842	52.4450	43.9587
αxy	-2.1511	-2.0712	-0.6171
αyy	49.2834	49.6355	42.3741
αxz	0.9258	-0.096	-1.7200
αyz	3.5654	-0.05480	-3.3081
αzz	20.3148	20.1135	19.6304
α_{total}	40.5608	40.7313	35.3210
$\Delta\alpha$ (esu)	30.7458	43.8721	24.4372
βxxx	-174.5371	-222.6027	-87.7462
βxxy	2147.0301	2144.3528	1267.0015
βxyy	-524.7104	-392.4142	345.8169
βyyy	1762,4370	1534.7716	1091.8588
βxxz	-301.1789	-58.9649	41.2330
βxyz	-144.6296	-163.6300	-342.266
βyyz	-907,5031	-922.0171	-184.9104
βxzz	-82.9623	-126.6322	-275.2913
βyzz	185.603	17.9446	176.7186
βzzz	2225,8537	49.3528	370.4360
β_{total}	44.726	38.434	25.514

3. CONCLUSIONS

In this theoretical work, different calculations of determining target molecule were carried out by HF and DFT methods with the 6-31G(d, p) basis sets at the program package Gaussian G09W. The $^{1}H/^{13}C$-NMR chemical shifts and FT-IR data in the calculations are seen to be compatible with the empirical data. A linear correlation was observed in the R^2 values, but there is a slight deviation in the H-NMR correlation graph. The reason for this deviation is the N-H acidic proton (H20) in the molecule. Also, the infrared data was not found negative frequency and the only reason for this is the stability of the molecule. In addition, the LUMO-HOMO energy, geometric properties, ΔE energy gap, total energy, electronic some properties, dipole moments, thermodynamics data were calculated. The reliability of different methods in theoretical computation was discussed. The surface maps of molecule were visualized, and the most electrophilic and nucleophilic regions were detected. In addition, NLO analysis results were examined. The hyperpolarizability β, the polarizability α were compared with urea, and NLO "the non-linear optical" properties of the target compound were defined to be good.

Conflict of interests

I declare that there is no a conflict of interest with any person, institute, company, etc.

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