Investigation of Spectroscopic and Electronic Properties of 2-Hydroxyacetophenone Methanesulfonylhydrazone By Dft Method

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Abstract: - Sulfonamides are broad-spectrum antibacterial chemicals that work against gram-positive and gramnegative bacteria. Sulfonamides were widely employed soon after their discovery, and this resulted in a large reduction in bacterial illnesses. In this study, firstly we performed geometrical optimization. After this, investigated spectroscopic (such as ¹H-NMR, ¹³C-NMR and FT-IR) and electronic properties of 2hydroxyacetophenone methanesulfonylhydrazone by theoretically. As a result of the vibrational frequencies, ¹H-NMR and ¹³C-NMR calculations, it was seen that the theoretical values were compatible with the experimental values. In addition, HOMO-LUMO molecular orbital energies, nonlinear optical (NLO) properties and molecular electrostatic potential (MESP) of 2-hydroxyacetophenone methanesulfonylhydrazone compound were investigated. As a result of calculations, the energy band gap between the HOMO and LUMO orbitals of the studied compound was found 4.65 eV and first static hyperpolarizability was found as 4674.7×10^{-33} esu (approximately 12.34 times larger than urea). All calculations were performed using DFT/B3LYP/6-311++G (d, p) level of theory and Gaussian 09 and Gauss View 5.0 package programs.

Key-Words: -FT-IR, NMR, NLO, DFT, HOMO- LUMO, MESP

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1 Introduction

Sulfonamides are among the most used antibiotics in the world. It has been used clinically since 1968. They have been applied in the treatment of infections, especially urinary tract and upper respiratory tract infections. Their low prices, low toxic effects and superior efficacy against common bacterial diseases have made them stand out. Between 1935 and 1948, 4500 sulfonamide derivatives were synthesized and their antimicrobial activities were investigated. However, only 0.5 percent of these compounds were used as drugs. Sulfonamides are in the structure of para amino benzene sulfonilamide and provide the bacteriostatic effect of the amino benzene ring, which is the active part [1].

Sulfonamides are antibacterial compounds has a broad spectrum of antimicrobial activity against Gram-positive and Gram-negative bacteria. The majority of sulfonamide formulations are offered as a combination of a sulfonamide and one of the synthetic diaminopyrimidines, trimethoprim or ormethoprim.

In addition to antibacterial and antitumor properties, sulfonamides also have many pharmacological properties such as anti-carbonic anhydrase, diuretic, hypoglycemic antithyroid and protease inhibitory activity. Examples of these are the carbonic anhydrase inhibitor acetazolamide (in clinical use for more than 45 years), widely used diuretic furosemide, hypoglycemic agent torasemide, anticancer sulfonamide E7070 used in further clinical studies, HIV protease inhibitor used in the treatment of HIV infection and AIDS amprenavir and metalloprotease inhibitors can be given [2].

In this study, firstly, 2-hydroxyacetophenone methanesulfonylhydrazone compound was optimized and the minimum energy stable structure was obtained. After obtaining the stable structure of the molecule, vibration frequencies, ¹H-NMR and ¹³C-NMR calculations were first performed on this structure. Finally, we have studied HOMO and LUMO molecular orbital energies, nonlinear optical properties (NLO), electrostatic potential maps (MESP) in the DFT/B3LYP/6-311++ G (d, p) theoretical plane.

2 Materials and Methods

Molecular modeling and spectroscopic methods are among the scientific research methods that are widely used to examine the molecular behavior and structural properties of chemical and biological systems. In this study, spectroscopic and some

electronic properties of the 2-hydroxyacetophenone methanesulfonylhydrazone molecule were investigated theoretically by using DFT method. First, we will optimize the structure of 2hydroxyacetophenone methanesulfonylhydrazone compound synthesized by Saliha ALYAR [3]. The lowest energy structure will be obtained by the DFT/B3LYP/6-311++G (d, p) method. After calculating the vibrational frequencies of this compound, ¹H and ¹³C NMR calculations will be made in the DMSO phase and compared with the experimental results. Finally, HOMO and LUMO molecular orbital energies, nonlinear optical properties (NLO) and molecular potential energy surface (MESP) maps will be examined using the DFT/B3LYP/6-311++G (d, p) basis set. Theoretical results will be understood by comparing them to experimental values. All theoretical calculations are performed using two software packages Gaussian 09 and Gauss View 5.0 [4,5].

3. Results and Discussion

The conformation analysis of the 2hydroxyacetophenone methanesulfonylhydrazone was performed by Alyar et al. and it was found to have seven different conformations [6]. In the conformation analysis study performed with the B3LYP/ 6-31G** basis set, it was found that the most stable conformer was found in the vacuo. In this study, geometric optimization calculation was made with the DFT B3LYP/6-311++G(d,p) basis set using the lowest energy structure of these seven conformations and its stable structure was found as follows.



Figure 1.Optimizestructureof2-Hydroxyacetophenonemethanesulfonylhydrazone3.1Vibrational Assignment of 2-

Hydroxyacetophenone Methanesulfonylhydrazone

The marks of the fundamental vibration frequencies determined for the stable structure of the 2-

hydroxyacetophenone methanesulfonylhydrazone molecule at lowest energy were created and interpreted in this portion of our study. 2hydroxyacetophenone methanesulfonylhydrazone is a 27-atom compound having 75 fundamental vibration frequencies. The experimental FT-IR spectrum of the 2-hydroxyacetophenone methanesulfonylhydrazone molecule is given in Fig. 2. The experimental and theoretical vibration frequencies are listed in the Table 1.



Figure 2 Experimental FT-IR spectrum of 2hydroxyacetophenone methanesulfonylhydrazone molecule [3]

In aromatic molecules, C-H stretching vibrations are generally observed in the range of 3000-3100 cm⁻¹, in-plane and out-of-plane bending vibrations are observed in the range of 1275-1000 cm⁻¹ and 900-690 cm⁻¹, respectively [7]. S. Alyar symmetric and asymmetric stretching C-H vibrations observed at 3016 and 2971 cm⁻¹ [3]. While the symmetric C-H ring stretching vibrations were calculated at 3202, the asymmetric C-H stretching vibrations calculated at 3186 and 3172 cm⁻¹ for the 2-hydroxyacetophenone methanesulfonylhydrazone by using the B3LYP/6-311++G(d,p) method.

C-H ring vibration frequencies are higher than CH₂ and CH₃ vibration frequencies. In aromatic ring systems, the C-H stretching vibrations of the methyl group, which can generally be called the electron donating group, are expected to occur asymmetrically at 2980 cm⁻¹ and symmetrically at 2870 cm⁻¹[8-10]. The CH₃ asymmetric and symmetric stretching vibrations observed at 2908, 2850 and 2820 cm⁻¹ by S. Alyar [3]. In our study symmetric and asymmetric CH₃ stretching vibrations calculated at 3177, 3165, 3152 and 3084 cm⁻¹. The symmetric CH₃ stretching vibrations calculated at 3065 and 3024 cm⁻¹.

Table	1.	Vibrational	assignments	of	2-
Hydrox	yace	tophenone Me	thanesulonylhy	drazoi	ne by
DFT B	BLYF	P/6-311++ G (d p) level of the	eorv	

	311/0	511 0 (a,p) ie vei	or theory
Mode	Exp. [3]	Calculation	intensity	Assignment
75	3203	3495	56.6033	ν (NH)
74		3420	681.3920	v (OH)
73	3016	3202	16.7665	v _s (CH) _{ring}
72	2971	3194	22.4374	v_{as} (CH) _{ring}
71		3186	10.2276	vas (CH)ring
70		3177	0.2492	v_{as} (CH ₃)
69		3172	4.0027	v_{as} (CH) _{ring}
68	2908	3165	0.2680	ν_{as} (CH ₃)
67	2850	3152	9.0952	v_{as} (CH ₃)
66	2820	3084	8.5982	V_{as} (CH ₃)
64	2820	3026	0.1450	V_{s} (CH ₃)
63		1652	64 0405	$v_{s}(CC)_{ring} +$
05		1052	01.0105	β (COH)
62	1622	1638	146.4921	v (N=C) + v(CC)
61	1573	1602	46.9113	$v(\text{CC})_{\text{rmg}}$
				$v(CC)_{ring} +$
				β (COH)
60	1500	1526	74.8089	$\nu(CC)_{ring} +$
				β (CCH) _{ring}
59		1500	14 0140	+ p(COI) B(CH ₂) + B
57		1500	14.0140	$(CCH)_{ring}$
58	1451	1486	107.1856	$v(CC)_{ring} + v$
				$(CO) + \beta$
				B (COH)
57		1483	16.6019	β (C14H ₃)
56	1425	1448	0.3717	β (C14H ₃)
55	1410	1443	10.3779	β (C14H ₃)
54		1427	71.1543	β (CCH) _{ring}
				$+\beta$ (COH)
53		1409	80 4363	+ p(RI9II) B(CCH) \approx
55		1409	00.4505	$+\beta$ (COH)
				$+\beta$ (N19H)
				+ γ (C14H ₃)
52	1389	1398	52.7811	β (COH) +
				β (N19H) +
51	1270	1254	11.6000	γ (C14H ₃)
50	1370	1350	6 9798	$\gamma(CC) +$
50	1557	1550	0.9790	v(C4C13) +
				$v(CN) + \gamma$
				(C14H ₃)
49		1332	149.3994	$\nu(CC)_{ring} +$
				v(C3O) +
				V(C4C13)+
48	1322	1303	430 7531	$p(CCII)_{ring}$
-10	1322	1505	450.7551	β (N19H)
47	1299	1275	99.0513	v(CC) _{ring} +
				$v(C3O) + \beta$
16	1050	10.45	1 40 1 500	(CCH) _{ring}
46	1250	1245	140.1580	$V(CC)_{ring} + B(C3OU) \perp$
				B (CCH)
45	1241	1183	19.8577	β (CCH) _{ring}
44	1172	1152	9.8055	$\nu(CC)_{ring} +$
				$v(NN) + \beta$
				(CCH) _{ring}
43	1153	1122	211.8099	$s(SO_2) + (CC)$
				$v(CC)_{ring} +$
				$v(mn) + \beta$
1	1	1	1	(CCII)ring

42		1097	185.5429	$v(CC)_{ring} +$
				$v(NN) + \beta$
				(CCH) _{ring} +
				β (CCC) _{ring}
41		1092	152.5505	$v(CC)_{ring} +$
				β (CCH) _{ring}
				$+ \gamma (C14H_{2})$
40	1045	1054	40 7272	$\gamma(CC) = + \gamma$
10	1010	1001	10.7272	$(C14H_2)$
30	1034	1047	22 8648	v (C14H ₂)
29	1054	000	22.0040	γ (C14H3)
30		999	27.2300	γ (C14II ₃)
37		995	0.0990	τ (CCCC) _{ring}
				$+\tau$
				(CCCH) _{ring}
36		984	169.4419	γ (C24H ₃)
35		978	4.3147	v(C13C14)
				+γ(C14H ₃)
				$+ \gamma (C24H_3)$
34		963	3.1680	τ (CCCC) _{ring}
				+τ
				(CCCH) _{ring}
33	840	882	151.7558	v(SN) +
				v(C13C14)
				$+ \gamma (C14H_2)$
32		870	1 75	τ (CCCC)
52		070	1.75	$+\tau$
				(CCCH)
21	779	845	11 2204	$v(CO) \pm$
51	//8	045	11.5504	$v(CO) + \rho$
				V(SN) + p
20		7((70 2957	(CCC) _{ring}
30		/66	/9.285/	τ (CCCC) _{ring}
				$+\tau$
				(CCCH) _{ring}
				+τ
				(CCCO) _{ring}
29	746	/53	7.0328	v(SN) +
				v(C13C14)
				+ β
				(CCC) _{ring}
28		732	193.8310	τ
				(CCOH) _{ring}
				$+\tau$
				(CCCC) _{ring}
				+τ
				(CCCH) _{ring}
27	727	708	86.9478	v(CS) +
				v(C13C14)
				+τ
				(CCOH)ring
L		L	1	(

O - H stretching vibration generally gives a strong band in the region of 3550 –3700 cm⁻¹. However, when there is an interaction between other existing groups, the O - H stretching vibration shifts to around 3200 cm⁻¹. In this study, the O - H stretching vibration were calculated at 3420 cm⁻¹.

C - N stretching vibrations are experimentally observed in the range of 1357 cm-1 –1313 cm⁻¹ for the 2Cl-5NBAK molecule. Theoretically, this vibration was calculated in the ranges of 1403 cm⁻¹ - 1378 cm⁻¹ and 1364 cm⁻¹ - 1354 cm⁻¹ in HF and B3LYP/6-311++G (d, p), respectively [11]. The C=N stretching vibrations observed at 1622 and 1573 cm⁻¹ by Alyar [3]. In this study, the C=N stretching vibration was calculated at 1638 and 1602 cm⁻¹.

In the FT-IR spectrum, the peak at 1322 cm⁻¹ indicates the asymmetric sulfoxide $(-SO_2)$ group stretching, and the peak at 1153 cm⁻¹ indicates the

symmetrical sulfoxide $(-SO_2)$ group stretching. While asymmetric sulfoxide $(-SO_2)$ group stretching vibration calculated at 1303 cm⁻¹, the symmetrical sulfoxide $(-SO_2)$ group stretching was calculated at 1122 cm⁻¹.

3.2 NMR Results of 2-Hydroxyacetophenone Methanesulfonylhydrazone

NMR analysis in molecular structures allows us to have an idea about the number of carbon and hydrogen atoms in the structure of the molecule. NMR analysis of molecule 2-hydroxyacetophenone methanesulfonylhydrazone was theoretically carried out.

Experimental ¹H-NMR and ¹³C-NMR values of 2methanesulfonylhydrazone hydroxyacetophenone molecule have not been found in the literature. calculations Theoretical NMR of the 2methanesulfonylhydrazone hydroxyacetophenone molecule were made in the DFT/ B3LYP and GIAO method on the base set 6-311++G(d,p). In Table 2, the theoretically calculated ¹H and ¹³C NMR chemical shift values of 2-hydroxyacetophenone methanesulfonylhydrazone molecule using DMSO solution are listed.

In the structure of the 2-hydroxyacetophenone methanesulfonylhydrazone molecule, hydrogen atoms are located in the aromatic ring and the methyl group. The (¹H) NMR signals for the protons in the aromatic ring were calculated at 7.34 (H7), 6.94(H8), 7.58(H9) and 6.93 (H10) ppm values.

Theoretical mean values of $({}^{1}H)$ NMR chemical shift was calculated as 2.24 and 3.96 ppm for C14H₃ and C24H₃, respectively.

Chemical shifts of carbon atoms in molecules with aromatic rings in their structure are usually obtained at a value of 100-150 ppm [12,13]. Six of the carbon atoms in the 2-hydroxyacetophenone methanesulfonylhydrazone molecule are located in the phenyl ring. Two other carbon atoms are located in the CH₃ functional groups. The ¹³C NMR chemical shift values for (C1-C6) were found to be between 131.77-118.36 ppm theoretically.

Table	2.	The	experiment	al ¹ H	and	¹³ C-	NMR
chemic	al s	hifts	(ppm) togetl	ner wit	hin th	e calc	culated
data		fe	or	2-hydi	oxya	cetopł	nenone
methanesulfonvlhydrazone							

Assignment	\Box (calc)
C ₃	159.90
C13	157.44
C ₁	131.77
C5	129.09
C ₄	119.53
C6	118.36
C ₂	116.88
C ₂₄	43.30
C14	12.086
H12	10.68
H9	7.58
H ₇	7.34
H_8	6.94
H_{10}	6.93
H ₂₀	6.55
H ₂₇	6.35
H25	2.98
H ₂₆	2.56
H16	2.55
H ₁₅	2.10
H17	2.06

3.3 HOMO-LUMO Analyze

By looking at the electron density distribution of a structure, information about the ionization potential. electron affinity, chemical hardness and softness parameters, electrostatic potential and molecular orbital shapes can be obtained. Molecular orbitals are called HOMO-LUMO. Here HOMO is the tendency of the molecule to donate electrons, and the occupied orbital is the highest energy. LUMO, on the other hand, is the tendency of the molecule to gain electrons and is the lowest vacant orbital [14]. When the energy difference (ΔE) of the molecule is large, the electron distribution undergoes less change and the polarization is low. The distribution of frontier orbitals can reveal information about a molecule's reactivity and the active site. Figure 3 depicts the HOMO-LUMO frontier orbital compositions for 2methanesulfonvlhvdrazone hvdroxvacetophenone computed using the DFT/6-311++G(d,p) levelof theory. The energy difference between HOMO and LUMO given in Figure 3 is 4.65 eV. Its large size indicates that the molecule is stable and durable in terms of thermodynamics. In addition, the molecule does not react with itself, dimerization. polymerization does not take place.



Figure 3. The frontier molecular orbitals of the 2-hydroxyacetophenone methanesulfonylhydrazone

3.4 Nonlinear Optical (NLO) Properties

Nonlinear optical materials have been of great interest in recent years due to their potential applications in the field of optoelectronics, namely telecommunications, optical computing, optical data storage, optical switching, and various photonic technologies [15,16]. In organic materials, optical properties are determined by polarizability. The polarizability of an atom or molecule is a measure of how easily the nucleus and electrons can be displaced from their stable states. The easily displaced electrons in an atom or molecule are the valence electrons that are furthest from the nucleus. Therefore, it has a great contribution to the polarizability of valence electrons [17].

Although the method for estimating initial static hyperpolarizability from Gaussian 09 data was previously reported, it's everything summed up here. The output of Gaussian 09 yields ten components of the equation 3 x 3 x 3 matrix as β xxx; β xxy; β xyy; β yyy; β xxz; β xyz; β yyz; β xzz; β yzz; β zzz; from which the x, y, and z components of are computed. One popular technique for presenting the value of β in a single form is to consider use the Equation (1) to solve for the average of the three independent values for as a quasi-pythagorean problem.

The following Equation (2) is the entire equation for obtaining total first static hyperpolarizability from Gaussian09 output:

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2]$$

 $)^{2} + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^{2}]^{1/2}$(2)

Because Gaussian 09's β values are expressed in atomic units (a.u.), the estimated β_{total} values were translated to electrostatic units (esu) (1 a.u. = 8.6393x 10⁻³³ esu). In addition, the total dipole moment and average polarizability of the compound were calculated using the Equation (3) and Equation (4). $\mu = \left[(\mu_x^2 + \mu_y^2 + \mu_z^2) \right]^{1/2}$ (3)

$$<\alpha> = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$
 (4)

Because of its characteristics in the research of nonlinear optical properties, urea is regarded a generic reference. The NLO characteristics of the molecules under consideration are assessed by comparing them to urea. Urea values acquired from DFT/B3LYP/6-31G calculations (d), $\mu = 1.3732$ Debye, $\alpha = 3.8312$ Å³ and $\beta = 0.37289*10^{-30}$ cm⁵/ esu. [18].

The computed electric dipole moment, polarizability, and first-order hyperpolarizability properties of the investigated substance are provided in Table 3.

Table 3. The electric dipole moment μ (D), the mean polarizability $\langle \alpha \rangle$ and the first hyperpolarizability (β_{tot}) of 2-hydroxyacetophenone methanesulfonylhydrazone

Parameter		Parameter	
μx	-1.1594	β _{xxx}	-320.8
μ_y	1.2844	β _{xxy}	164.1
μz	1.5800	β _{xyy}	2.1
μ _{tot}	2.3431	β _{yyy}	86.6
α _{xx}	232.66	β _{xxz}	71.2
α _{xy}	3.09	β _{xyz}	-37.5
α_{yy}	154.32	βyyz	45.9
α_{xz}	-4.30	β _{xzz}	-80.8
α_{yz}	3.11	βyzz	28.0
α_{zz}	102.56	β _{zzz}	118.6
<α>(a.u)	163.18 a.u	$\beta_{tot}(a.u)$	541.1
<α>(esu)	24.18*10 ⁻²⁴ (esu)	β _{tot} (esu)	4674.7*10-
			³³ esu

Table 3 shows the components of β as well as the final β_{total} values determined by Gaussian 09 for the 2-hydroxyacetophenone methanesulfonylhydrazone. The studied compound has the greatest hyperpolarizability value of 4674.7 x10⁻³³ esu, which is nearly 12.34 times larger than that of urea. We can say that the studied compound present large nonlinear optical activity and it can be used for nonlinear optical applications.

3.5 Molecular Electrostatic Potential (MESP)

The interactions of molecules and atoms in the molecule with each other are possible by determining the electron density distribution (i.e. very dense and less dense regions) in the molecule. MESP, or "Molecular Electrostatic Potential" maps, give the three-dimensional electrostatic potential shape of the molecule surface. Electrostatic potential maps are verv useful for visualizing varying charge distributions. The molecular electrostatic potential (MESP) describes the interaction energy between the unit positive charge and the molecular charge distribution of the system. Negative regions of the molecular potential energy surface are associated with electrophilic reactivity (relative abundance of electrons), positive ones with nucleophilic reactivity [19].

The surface seen on the MESP map gives molecular size and shape values as well as electrostatic potential. In MESP maps, the regions indicated in red represent the region with negative electron density, while the regions indicated in blue and white are represented by color codes to show regions with positive charges in terms of electron density. The interpretation of these maps is very important in determining the location of the active regions of the reactions that will take place in the molecule. The color indicator chart shows a transition from blue to red, and this color transition can be correlated with electron density on the map [20]. Regions with low electron density have high potential, while regions with dense electrons have low potential. With the calculation made in the gas environment, it is seen in Figure 4 that the electron-rich regions are located on the O22, O23 and O11 oxygen atoms attached to the benzene ring at the SO₂ end. The electron-poor regions are on the hydrogen atoms attached to the benzene ring and on the hydrogen atoms in the methyl components.



Figure 4. MESP map of 2-hydroxyacetophenone methanesulfonylhydrazone molecule

Considering the MESP map results support the N-H...O bond for all methods. Thus, nucleophilic and electrophilic regions were determined for the molecule. In this case, it will allow us to foresee where the reaction should be carried out in the new molecules to be synthesized.

The DFT/B3LYP/6-311++G (d, p) level of theory was used to construct molecular electrostatic potential energy surfaces of 2-hydroxyacetophenone methanesulfonylhydrazone compounds.

4 Conclusion

In this study, quantum chemical calculations of the sulfonamide compound 2-hydroxyacetophenone methanesulfonylhydrazone which was synthesized by S. Alyar before, were made.

First, the minimum energy structure of this compound, which has seven different conformations, was selected and the structure was optimized using the DFT B3LP/6-311++G (d, p) method. Then, using the stable structure of the studied molecule, FT-IR, ¹H-NMR and ¹³C-NMR calculations were performed, vibration frequencies and chemical shift values were analyzed. In the FT-IR study, it was seen that the experimental and theoretical results were compatible with each other.

Finally, the HOMO-LUMO molecular orbital energies, nonlinear optical properties and molecular potential energy surfaces of the studied compound were investigated. As a result of the calculations, the energy band gap of the studied compound was 4.65 eV and its hyperpolarizability was calculated as 4674.7×10^{-33} esu (approximately 12.34 times larger than urea).

As a result of the calculations, it was determined that the studied compound showed moderate nonlinear optical properties.

References

[1] Muthu Prabhu, A. A., Venkatesh, G. and Rajendiran, N. 2010. Spectral characteristics of sulfa drugs: effect of solvents, pH and β -cyclodextrin. *Journal of solution chemistry*, Vol., No.7, 2010, pp. 1061-1086.

[2] Casini, A., Scozzafava, A., Mastrolorenzo, A., Supuran, T. C., Sulfonamides and Sulfonylated Derivatives as Anticancer Agents, *Current Cancer Drug Targets*, Vol.2, 2002, pp. 55-75.

[3]Alyar, S., 2-Hidroksiasetofenon metansülfonilhidrazon bileşiğinin yapı ve spektrumlarının denelve teorik olarak incelenmesi. MSc. Thesis, Gazi University, 2003. [4] Frisch, M., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R. and Fox, D. J. 2009. Gaussian 09 Revision D. 01, 2009. Gaussian Inc., 6: 100-106.

[5] Dennington, R., Keith, T. and Millam, J. GaussView Version 5.0, Semichem Inc., 322 page, UK.2009.

[6] Alyar, S., Özmen, Ü. Ö., Karacan, N., Şentürk, O. Ş. and Udachin, K. A. 2008. Tautomeric properties, conformations and structure of 2hydroxyacetophenone methanesulfonylhydrazone.

[7] Stuart, B.H., *Infrared Spectroscopy: Fundamentals and Applications*. John Wiley and Sons, 2004.

[8] Govindarajan, M., Ganasan, K., Periandy, S., Karabacak, M., Mohan, S., Vibrational spectroscopic analysis of 2-chlorotoluene and 2-bromotoluene: A combined experimental and theoretical study. *Spectrochimica Acta Part A.*, Vol. 77, 2010, pp. 1005–1013.

[9] Colthup, N.B., Lawrence, H. D., Wiberley, S. E. 1990. *Introduction to Infrared and Raman Spectroscopy*, Academic Press, 1990.

[10] Socrates, G., *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley and Sons Ltd, 2001.

[11] Çetin, M., Theoretical investigation of geometric structure, IR and NMR spectroscopic structures of molecules containing some nitrobenzoic acid. MSc. Thesis, Sakarya University, 2013.

[12] Pihlaja, K. and Kleinpeter, E., *Carbon-13 NMR* chemical shifts in structural and stereochemical analysis. VCH Publishers, 1994.

[13] Kalinowski, H. O., Berger, S., Braun, S. and Griffiths, L., *Carbon-13 NMR spectroscopy*. Wiley, 1989.

[14] Gümüş, H. P. and Atalay, Y., 3-hidroksi-4hidroksimiinometil-5-hidroksimetil-1, 2dimetilpiridinyum iyodid molekülünün geometrik yapısının incelenmesi. *Sakarya Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, Vol. 21, No.3, 2017, pp.564-571.

[15] Prasad, P.N. and Williams, D.J., *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, 1991.

[16] Kanis, D.R., Ratner, M.A., Marks, T.J., Design and Construction of Molecular Assemblies with Large Second-Order Optical Nonlinearities. Quantum Chemical Aspects. *Chemical Reviews*. Vol.94, No.1, 1994, 195-242.

[17] Bosshard, C., Sutter, K., Pretre, P., Flörsheimer, M., Kaatz, P. and Günter, P., *Organic Nonlinear Optical Materials*. Gordon and Breach Publishers, 1990. [18] Meganathan, C., Sebastian, S., Sivanesan, I., Lee, K. W., Jeong, B. R., Oturak, H. and Sundaraganesan, N., Structural, vibrational (FT-IR and FT-Raman) and UV–Vis spectral analysis of 1phenyl-3-(1, 2, 3-thiadiazol-5-yl) urea by DFT method. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol.95, 2012, pp. 331-340.

[19] Kecel-Gunduz, S., Bicak, B., Celik, S., Akyuz, S., and Ozel, A. E., Structural and spectroscopic investigation on antioxidant dipeptide, l-Methionyll-Serine: A combined experimental and DFT study. *Journal of Molecular Structure*, Vol.1137, 2017, pp. 756-770.

[20] Günay, N., Pir, H. and Atalay, Y., Lasparaginyum pikrat molekülünün spektroskopik özelliklerinin teorik olarak incelenmesi. *SAÜ Fen Edebiyat Dergisi*, Vol.1, 2011, pp. 15-32.

Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

Hamit ALYAR was responsible writing-review and editing.

Imad Ali TALAB carried out the simulation and the optimization.

Saliha ALYAR is responsible for the preparation of the tables and the pictures.

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