

Research Journal of Pharmaceutical, Biological and Chemical Sciences

A Theoretical Study on the Vibrational and UV/VIS Spectra for the some 1, 3, 4-oxadiazole Derivatives by Using DFT Approach.

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ABSTRACT

1, 3, 4-oxadiazole and its derivatives are attractive molecules due to their biological and pharmaceutical properties. This work aim to obtain the theoretical structure, the vibrational spectra, UV-Vis spectra for the 1, 3, 4-oxadiazole, and its derivatives (1,3,4-oxadiazole-2-amine, 2,5-diamine-1,3,4-oxadiazole, and 5-chloro-1,3,4-oxadiazole-2-amine) Since there are no available experimental, and theoretical data in literature for these derivatives. The quantum chemical calculations of the density functional theory (DFT) using Becke's three-parameter hybrid level with the Lee-Yang-Parr correlation functional B3LYP method plus the basis set 6-311G++(2d,2p). Substitution of one or two electron - donating groups (-NH₂) in 2or 5 positions on the oxadiazole ring destabilizes the HOMO and LUMO levels with a decrease in the energy gap resulting in a red shifting in the absorption spectrum (λ_{max}). The first (a), and second (b) absorption peaks in the electronic spectra and IR vibration frequencies for both C=N and C-H bonds of the oxadiazole derivatives are red-shifted in the presence of the -NH₂ group. The molecular electrostatic potential maps for all these molecules show a negative potential over the electronegative atoms (nitrogen ring atoms), and a positive potential over the carbon and hydrogen atoms.

Keywords: DFT method; 1, 3, 4-oxadiazole-2-amine; 2,5-diamine-1, 3, 4-oxadiazole; 5-chloro-1, 3, 4-oxadiazole-2-amine; Vibrational analysis; UV/Vis Spectra.

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INTRODUCTION

1, 3, 4-oxadiazole is thermally stable molecule. Oxadiazole is a very weak base due to the inductive effect of the three heteroatom [1]. The 1, 3, 4-oxadiazole undergoes different reactions including electrophilic and nucleophilic substitution thermal, and photochemical [2, 3]. This compound and its derivatives attracted the attention of researchers because of its biological and pharmaceutical properties [4 - 6]. It was first prepared in 1965 by Ainsworth employing thermolysis of ethyl formate formyl hydrazone at atmospheric pressure [7]. In 1972 Nygaard et al [8] determined the structure of 1, 3, 4-oxadiazole by a microwave studies. Since the equilibrium structure of 1, 3, 4-oxadiazole cannot be accurately determined by the microwave technique only. Therefore a quantum chemical calculations (with appropriate uncertainties) fitted with the moments of inertia, employed by Demaison et al [9] using the mixed estimation of the internal coordinates approach gives more accurate result. Their calculations were confirmed by the extrapolation technique.

The experimental and theoretical vibrational spectra (Infrared spectra) were investigated for this molecule [10-13]. El-azhary [11] theoretically studied the molecular structure and the harmonic vibrational spectra of this molecule employing the DFT, MP2, and HF methods with the same basis set /6-31G^{**}. He concluded that the scaled calculated spectra by the DFT/6-31G^{**} method revealed good agreement results with experimental spectra than those calculated by the MP2/6-31G^{**} or HF/6-31G^{**} methods. Then Kwiatkowski et al [12] obtained a scaled ab initio calculations of vibrational frequencies based on both the DFT and MP2 methods with the standard 6-31G (d,p) basis set. Hegelund with coworker [13] studied the High-resolution of the IR spectra for the four fundamental bands of 1,3,4-oxadiazole in gaseous (ranging between 800 and 1600 cm⁻¹), plus the theoretical calculations of optimize geometry, and the complete set of anharmonic frequencies using DFT method. But Karimi [14] investigated factors affecting the stability as well as the structural properties for oxadiazole and thiadiazole isomers employing the DFT and Ab Initio B3LYP/6-311+G^{**} level, plus the Nuclear Magnetic Resonance (NMR). They found that the relative stabilities of these molecules as follow 1, 2, 3-oxadiazole, 1, 2, 4-oxadiazole, 1, 2, 5-oxadiazole and 1, 3, 4-oxadiazole. Many studies demonstrated that the density functional theory DFT-B3LYP method together with the 6-31G* basis set or higher levels is able to give accurate results for the energies, molecular structures, and infrared vibrational frequencies [11, 12, 15, 16]. So in view of the excellent previous results obtained by the DFT-B3LYP method, and since there are no available experimental and theoretical data in literature for the 1, 3, 4-oxadiazole derivatives. Therefore the aim of this study is to obtain the theoretical structure, the vibrational spectra, UV-Vis spectra for the 1, 3, 4-oxadiazole **OD**, and its derivatives (1,3,4-oxadiazole-2-amine **ODA**, 2,5-diamine-1,3,4-oxadiazole **ODDA**, and 5-chloro-1,3,4-oxadiazole-2-amine **CODA**).

COMPUTATIONAL DETAILS

The quantum chemical calculations of the DFT [17] using Becke's three-parameter hybrid level [18] with the Lee-Yang-Parr correlation functional B3LYP method [19, 20] plus the basis set 6-311G++(2d,2p) for the mentioned compounds were carried out using Gaussian 09 software [21]. The optimized geometrical parameters, harmonic vibrational frequencies, IR intensities, Raman activity, and the HOMO and LUMO energies were calculated. Furthermore the electronic absorption spectra, with its vertical excitation energies plus the oscillator strengths were computed with the time dependent density functional theory (TD-DFT) at B3LYP/6-311++G(2d,2p) level.

RESULTS AND DISCUSSION

Molecular geometry

The fully optimized geometric parameters of the molecules under study are presented in table 1, and figure 1.

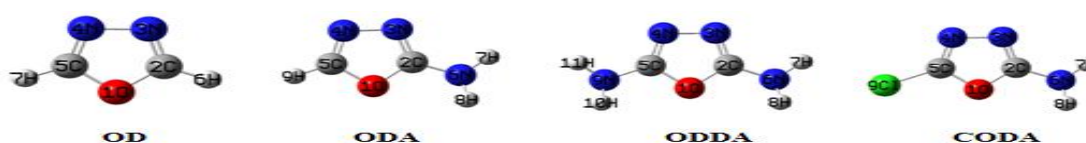


Figure 1. The calculated molecular structure for the studied compound along with the atom numbering scheme.

Table 1. The optimized geometry data of OD, ODA, ODDA, and CODA molecules, plus the available theoretical and experimental data.

Structural parameter	Exp.(9)	Exp. (13)	other work(9)	other work (11)	DFT 6-311G++ (2d,2p) This work			
	oxadiazole (OD)					ODA	CODA	ODDA
Bond length in (Å ^o)								
O ₁ -C ₂	1.354	1.357	1.356	1.360	1.359	1.357	1.362	1.371
O ₁ -C ₅						1.374	1.371	1.371
C ₂ =N ₃	1.285	1.284		1.283	1.284	1.294	1.293	1.284
N ₄ =C ₅						1.278	1.276	1.284
C ₂ -N ₆						1.365	1.363	1.372
C ₂ -H ₆	1.074	1.075	1.075	1.079	1.075			
N ₃ -N ₄	1.406		1.401	1.405	1.405	1.406	1.409	1.419
C ₅ -Cl							1.702	
C ₅ -H ₉						1.075		
N ₆ -H ₇						1.007	1.008	1.008
N ₆ -H ₈						1.007	1.008	1.009
Bond angle in degree								
C ₂ -O ₁ -C ₅	101.4	101.6	101.8	101.5	101.7	101.5	101.0	101.3
O ₁ -C ₂ =N ₃	113.8	113.3	113.2	113.4	113.3	113.5	113.4	113.5
O ₁ -C ₂ -N ₆						117.7	117.5	116.9
N ₃ =C ₂ -N ₆						128.7	128.9	129.5
O ₁ -C ₂ -H ₆	118.1		118.2	118.0	118.2			
N ₃ =C ₂ -H ₆	128.2		128.6	128.6	128.6			
C ₂ =N ₃ -N ₄	105.6	105.8	105.9	105.8	105.9	105.4	105.7	105.8
N ₃ -N ₄ =C ₅						106.6	105.9	105.8
O ₁ -C ₅ =N ₄						113.0	113.9	113.5
O ₁ -C ₅ -Cl							117.3	
N ₄ =C ₅ -Cl							128.8	
O ₁ -C ₅ -H ₉						117.8		
N ₄ =C ₅ -H ₉						129.2		
C ₂ -N ₆ -H ₇						113.5	113.5	112.4
C ₂ -N ₆ -H ₈						115.7	115.9	114.8
H ₇ -N ₆ -H ₈						114.1	114.2	112.9
Dihedral angle in degree								
C ₅ -O ₁ -C ₂ =N ₃					0.0	0.2	0.2	0.0
C ₅ -O ₁ -C ₂ -N ₆						-176.6	-176.5	-176.6
C ₅ -O ₁ -C ₂ -H ₆					180.0			
C ₂ -O ₁ -C ₅ =N ₄					0.0	0.1	0.2	0.0
C ₂ -O ₁ -C ₅ -H ₇					180.0			
C ₂ -O ₁ -C ₅ -Cl							-179.4	
C ₂ -O ₁ -C ₅ -N ₉								176.6
C ₂ -O ₁ -C ₅ -H ₉						-179.6		
O ₁ -C ₂ =N ₃ -N ₄					0.0	-0.4	-0.5	0.0
H ₆ -C ₂ =N ₃ -N ₄					180.0			
N ₆ -C ₂ =N ₃ -N ₄						175.9	175.7	176.0
O ₁ -C ₂ -N ₆ -H ₇						-167.0	-168.1	-168.7
O ₁ -C ₂ -N ₆ -H ₈						-32.3	-33.0	-37.8
N ₃ =C ₂ -N ₆ -H ₇						16.7	15.8	15.4
N ₃ =C ₂ -N ₆ -H ₈						151.4	150.9	146.2
C ₂ =N ₃ -N ₄ -C ₅					0.0	0.5	0.6	0.0
N ₃ -N ₄ -C ₅ -H ₉						179.3		
N ₃ -N ₄ =C ₅ -Cl							179.1	
N ₃ -N ₄ =C ₅ -N ₉								-176.0
O ₁ -C ₅ -N ₉ -H ₁₀								37.8
O ₁ -C ₅ -N ₉ -H ₁₁								168.7

$N_4=C_5-N_9-H_{10}$								-146.2
$N_4=C_5-N_9-H_{11}$								-15.4

The calculated molecular structure of the **OD** to C_{2v} point group symmetry is in good agreement with the previous experimental and theoretical results [9, 11, 13], table 1.

Both **ODA**, **CODA** molecules belongs to C_1 , and the **ODDA** molecule to C_s point group.

The C–Cl bond length reveal a considerable decrease when substituted in the place of C–H, this was in **CODA** molecule. Also the results show that the electronegative substituent of the Cl on ring seen also in oxadiazole derivatives [22]. The results demonstrate that the C–Cl bond length is 1.702 Å trend to shorting the $C_5=N_4$ (1.276 Å) bonds which adjacent to the substituent, but the bond length of $C_2=N_3$ is longer (1.293 Å). The O_1-C_5 bond (1.371 Å) is longer than O_1-C_2 bond (1.362 Å).

In the **OD** molecule the bond angles around the C_2 atom ($O_1-C_2-H_6$, $O_1-C_2-N_3$ and $N_3-C_2-H_6$) are 118.2, 113.3, and 128.6 degree respectively where the total sum equal to 359.9 degree, and the total sum for the three angles around the center of the C_5 atom equal 359.9 degree. This indicating that the C_2 , and C_5 atoms related to sp^2 hybridization type. The same results are obtained for all the oxadiazole derivatives, table 1.

Vibrational analysis

The compute harmonic vibrational frequencies with the complete assignment for all molecules under study (**OD**, **ODA**, **ODDA**, and **CODA**) are reported in tables 2, 3, 4, 5 respectively.

The **OD** molecule is planar, which has 7 atoms with 15 normal modes of vibrations. The fundamental modes are distributed as: $\Gamma_{vib} = 6A_1 + 2A_2 + 2B_1 + 5B_2$. All these vibrations are active in both Infrared and Raman except the A_2 species which is active in Raman only. This work results show reasonable agreement when compared with experimental, and the theoretical scaling frequencies data of El-azhary [11], plus the anharmonic frequencies of Hegelund et al [13].

The **ODDA** molecule has 27 normal modes are distributed as $\Gamma_{vib} = 14A' + 13A''$. All these fundamental vibrations are active in both Infrared and Raman.

ODA, **CODA** molecules have a non-planar structure. Both molecules have 9 atoms with 21 normal modes of vibrations, belongs to one class of the C_1 symmetry A . Also all these fundamental vibrations are active in both Infrared and Raman.

C-H vibrations:

The data demonstrate that the CH symmetric and asymmetric stretching band values for **OD** were 3291, 3285 cm^{-1} respectively which are coincidence with experimental results [11]. The CH stretching for **ODA** appears at 3290 cm^{-1} . The vibrations of C–H (symmetric and asymmetric) out-of-plane bending for **OD** molecule are evaluated at 872, and 841 cm^{-1} consequently. But the frequency at 1239 cm^{-1} can be assigned as C–H in-plane bending, which is agreed with experimental data. While in the **ODA** molecule the same vibration is 1253 cm^{-1} .

Ring vibrations:

The N–N stretching vibrations for all molecules are not pure (mixed with several other motions), and the higher value is belonged to **CODA** molecule.

The C=N symmetric and asymmetric stretching frequencies for **OD** molecule, are at 1558, and 1534 cm^{-1} consequently, and increase in oxadiazole derivatives according to the following order **CODA**, **ODA**, and **ODDA**.

Table 2. Theoretical vibrational frequencies and the assignment of the OD molecule compare with other experimental and theoretical data.

No.	Sym.	Freq. (cm ⁻¹)	IR intensity (Km mol ⁻¹)	Raman activity (A ⁴ amu ⁻¹)	ab initio [13]	DFT 6-31G** other work [11]	Exp.[11]	Assignment
ν_1	A ₁	3291	0.61	135.18	3150	3180	3169	ν_{as} CH
ν_2		1558	46.76	34.84	1527	1529	1534	ν_{as} C=N + β_s CH
ν_3		1300	0.30	20.22	1275	1275	1272	β_s CH + β ring (ring def.)
ν_4		1104	37.14	6.59	1085	1093	1092	β_s CH + ν_{as} COC
ν_5		974	4.17	4.96	948	952	951	ν_{as} NN + ν_{as} COC) (ring β)
ν_6		946	35.73	0.07	926	923	920	β_s CH + β ring (ν_{as} NN + ν_{as} COC)
ν_7	A ₂	841	0.00	0.17	825	823	825	α_s CH γ
ν_8		675	0.00	0.33	666	655	653	γ_{as} CH + γ ring (ring pucker.)
ν_9	B ₁	872	21.62	0.45	854	849	852	α_s CH γ
ν_{10}		644	35.75	0.39	633	633	625	HCOCH γ
ν_{11}	B ₂	3285	3.35	28.53	3144	3147	3167	ν_{as} CH
ν_{12}		1534	4.56	0.17	1494	1500	1541	ν_{as} C=N + β_{as} CH
ν_{13}		1239	1.47	5.11	1215	1217	1215	β_{as} CH
ν_{14}		1083	45.00	1.10	1044	1081	1078	ν_{as} COC + β CH
ν_{15}		951	0.00	0.38	935	935	925	CH + β ring (ring def.) β

Table 3. Theoretical vibrational frequencies (cm⁻¹), IR intensity, Raman activities and the assignment of the ODA.

No.	Sym.	Freq. (cm ⁻¹)	IR intensity (Km mol ⁻¹)	Raman activity (A ⁴ amu ⁻¹)	Assignment
ν_1	A	3681	54.26	45.26	ν_{as} NH ₂
ν_2		3580	50.34	145.75	ν_s NH ₂
ν_3		3290	1.72	89.38	ν CH
ν_4		1673	347.05	34.04	δ NH ₂ + ν_{as} N=CN
ν_5		1612	52.17	11.81	δ NH ₂ + ν_s C=N
ν_6		1561	19.09	17.11	ν_{as} C=N + δ NH ₂
ν_7		1428	47.49	1.51	ρ NH ₂ + ν_s COC + β CH
ν_8		1253	2.94	10.97	β CH
ν_9		1134	1.29	8.91	ρ NH ₂
ν_{10}		1080	55.82	8.02	ν CO + β CH
ν_{11}		1000	23.34	5.66	ρ NH ₂ + β CH ν NN +
ν_{12}		968	16.41	4.62	β CH + β ring (ring def.) + ρ NH ₂
ν_{13}		957	6.91	1.06	β CH + β ring (ring def.) + ρ NH ₂
ν_{14}		812	7.14	1.02	γ CH + γ COC
ν_{15}		753	46.80	1.84	ω NH ₂ + ring pucker. + γ CH
ν_{16}		730	2.04	6.29	ω NH ₂ + γ OCN + γ CH
ν_{17}		650	22.62	0.27	γ CH + γ ring (ring pucker.)
ν_{18}		583	219.63	0.57	ω NH ₂
ν_{19}		412	1.43	1.59	τ NH ₂ + ring clock wise (β ring)
ν_{20}		312	35.85	0.23	τ NH ₂
ν_{21}		276	14.88	0.45	τ NH ₂ + γ ring

Table 4. The theoretical vibrational frequencies (cm⁻¹), with its assignment for the ODDA molecule.

No.	Sym.	Freq. (cm ⁻¹)	IR intensity (Km mol ⁻¹)	Raman activity (A ⁹⁴ amu ⁻¹)	Assignment
ν_1	A'	3664	66.35	40.78	ν_{as} NH ₂
ν_2		3567	10.83	325.90	ν_s NH ₂
ν_3		1717	183.42	76.00	ν_s C=N + δ NH ₂
ν_4		1628	23.35	1.75	δ NH ₂
ν_5		1455	5.51	1.10	CNH β
ν_6		1156	0.22	23.47	ρ NH ₂ + ring def.
ν_7		1008	27.46	6.79	ρ NH ₂ + ν NN
ν_8		968	15.17	5.92	ρ NH ₂ + β N=CO (ring def.)
ν_9		760	94.73	0.77	ω NH ₂ + ring puck. (γ ring)
ν_{10}		676	27.37	12.18	ω NH ₂ + ν_s COC
ν_{11}		637	193.87	0.23	ω NH ₂
ν_{12}		334	5.44	1.74	τ NH ₂
ν_{13}		264	66.74	0.92	τ NH ₂
ν_{14}		208	10.80	0.27	τ NH ₂ + γ COC
ν_{15}	A''	3664	24.78	62.99	ν_{as} NH ₂
ν_{16}		3566	61.26	26.91	ν_s NH ₂
ν_{17}		1658	390.41	8.59	δ NH ₂ + β ring
ν_{18}		1602	81.27	0.54	δ NH ₂ + ν_{as} C=N
ν_{19}		1339	140.63	0.76	ρ NH ₂ + ν_{as} COC (ring def.)
ν_{20}		1145	4.50	3.70	ρ NH ₂
ν_{21}		981	41.28	0.06	ν_{as} COC (β ring)
ν_{22}		786	13.16	3.12	ω NH ₂ + β ring (ring def.)
ν_{23}		704	26.91	1.06	ω NH ₂ + γ ring (ring puck.)
ν_{24}		629	179.66	0.43	ρ NH ₂ + γ ring
ν_{25}		483	8.91	0.45	ρ NH ₂ + ring clock wise (β ring)
ν_{26}		357	12.38	0.22	γ NH + γ ring
ν_{27}		222	0.05	0.29	τ NH ₂

The frequencies of the following values 1104 and 1083 cm⁻¹ for the **OD** can be characterized as COC symmetric and asymmetric stretching mixing with the CH in-plane-bending vibration. Also the frequencies of 974 and 946 cm⁻¹ are belonged to the ring deformation (NN associated with COC stretching motions). In **ODA** molecule the ν_{10} mode (1080 cm⁻¹) is analyzed as CO stretching plus CH in-plane-bending vibration. The two modes at 968, and 957 cm⁻¹ consists many motions, one of them is ring deformation, table 3. In **ODDA** molecule the normal following modes ν_{10} , ν_{19} , ν_{21} , and ν_{22} (at frequencies 676, 1339, 981, 786 cm⁻¹ respectively) are assigned as COC stretching vibration combined with many other different motions, table 4. The COC stretching vibration ν_6 , ν_9 , ν_{11} , ν_{12} modes in **CODA** molecule are mixed with other various motions, table 5.

Table 5. The theoretical vibrational frequencies, IR intensities and Raman activity with its assignment for the 21 normal modes of the CODA molecule.

No.	Sym.	Freq. (cm ⁻¹)	IR intensity (Km mol ⁻¹)	Raman activity (A ⁹⁴ amu ⁻¹)	Assignment
ν_1	A	3680	58.11	49.18	ν_{as} NH ₂
ν_2		3578	61.91	164.96	ν_s NH ₂
ν_3		1677	352.72	45.68	δ NH ₂ + ν_{as} N=CN
ν_4		1614	37.28	13.15	δ NH ₂ + ν_s C=N

ν_5		1551	145.90	19.41	$\nu_{as} C=N + \delta NH_2$
ν_6		1426	21.81	0.62	$\rho NH_2 + \nu_s COC$
ν_7		1167	182.49	3.37	$\nu OC=N + \rho NH_2$
ν_8		1138	0.03	16.51	ρNH_2
ν_9		1032	30.48	9.99	$\rho NH_2 + \nu NN + \beta COC$
ν_{10}		973	12.51	3.86	$\beta ring (\beta N=CO)$
ν_{11}		969	14.53	5.17	$\rho NH_2 + \nu CO + \beta C=NN$
ν_{12}		758	25.87	2.95	$\omega NH_2 + \beta ring (ring def.)$
ν_{13}		738	7.43	3.00	$(ring\ puck \equiv \gamma ring) + \omega NH_2$
ν_{14}		668	0.30	0.35	$(ring\ puck \equiv \gamma ring) + \tau NH_2$
ν_{15}		582	247.26	0.71	ωNH_2
ν_{16}		490	2.07	6.30	$\nu CCl + \beta ring$
ν_{17}		459	2.23	2.39	$\tau NH_2 + ring\ clock\ wise (\beta ring)$
ν_{18}		347	19.29	0.41	$\tau NH_2 + \gamma ring$
ν_{19}		287	13.46	0.57	τNH_2
ν_{20}		244	13.95	2.30	$\rho NH_2 + \beta CICO$
ν_{21}		182	1.58	0.20	$\omega NH_2 + \gamma CICO$

NH₂ vibrations:

The frequency of 3681 cm⁻¹ is assigned as NH₂ asymmetric vibration, but the symmetric vibration is 3580 cm⁻¹ in **ODA** molecule. This results are approximately equal to the frequencies of the **CODA** molecule (3680, 3578 cm⁻¹), and higher than the values of the similar vibrations in **ODDA** molecule (3664, and 3567 cm⁻¹).

There are three pure NH₂ twisting vibrations ν_{12} , ν_{13} , ν_{27} appeared at 334, 264, and 222 cm⁻¹ respectively in **ODDA** molecule, table 4. In **ODA**, and **CODA** molecules there is only one pure NH₂ twisting vibrations occurred at 312, and 287 cm⁻¹ consequently, tables 3, and 5.

C-Cl vibrations:

The frequency 490 cm⁻¹ belong to the ring-halogen modes is related to C-Cl stretching and associated with in-plane ring bending motion, table 5. The C-Cl in-plane bending is combined with rocking NH₂ vibration evaluated at 244 cm⁻¹. But the C-Cl out-of-plane vibration mixing with NH₂ wagging motion occurs at 182 cm⁻¹.

Electronic absorption spectra

The calculations include the electronic absorption spectra (UV-Visible) for the studied compounds, such as highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, the energy gaps ($\Delta E_g = \text{HOMO} - \text{LUMO}$), absorption wavelengths (λ_{max}), and oscillator strengths (f) based on the optimized geometry in water, and gas phase with major contributions, table 6. The calculations involving the vertical excitation energies perform according to the Frank-Condon principle determine the maximum absorption peak (λ_{max}) in an UV-Vis spectrum. There are no available data for all studied compounds except the **OD** molecule which was obtained by Kakitani using the improved self-consistent HMO theory [23]. Their values for λ_{max} was 203 nm, and $f = 0.173$. It is well known that their method is less accurate than the DFT, but still the λ_{max} value approximate to this work result, table 6.

In view of the absorption spectra calculations, when one H atom in **OD** molecule replaced by -NH₂ group reveal a red shift in both λ_{max} , (a) and (b), table 6. A longer red shift is noticed when two H atoms substituted by -NH₂ groups in **ODDA** molecule, while a blue shift occurred in **CODA**.

The first vertical excitation of **OD** molecule (in gas phase) predict that the electronic transition (a) appear at 211 nm with an oscillator strength f equal 0.0000. So it is forbidden to be measured experimentally.

At the second excitation (b), $\lambda_{\text{max}} = 181 \text{ nm}$ with $f = 0.0141$, which can be obtained experimentally. The same behavior is seen in water.

Table 6. The absorption wavelength, energies, and oscillator strengths of the OD, ODA, ODDA, and CODA compounds using the TD-DFT/ B3LYP/6-311++G(2d,2p) method.

compound	Gas				Water			Major contribution
		$\lambda(\text{nm})$	E(eV)	$f(\text{a.u.})$	$\lambda(\text{nm})$	E(eV)	$f(\text{a.u.})$	
OD	a	210.09	5.9013	0.0000	199.06	6.2285	0.0000	H→L (70%)
	b	181.47	6.8321	0.0141	178.25	6.9555	0.1449	H-2→L (46%) H→L+2 (54%)
ODA	a	228.31	5.4305	0.0108	211.67	5.8573	0.0103	H→L (70%)
	b	206.80	5.9954	0.1437	210.22	5.8977	0.1617	H→L+1(69%)
ODDA	a	263.20	4.7107	0.0046	240.34	5.1586	0.0004	H→L (70%)
	b	247.86	5.0023	0.0091	224.10	5.5325	0.0077	H→L+1 (70%)
CODA	a	229.77	5.3961	0.0092	218.09	5.6850	0.2390	H→L (81%) H→L+1 (19%)
	b	214.39	5.7830	0.0429	215.12	5.7634	0.0055	H→L+1 (37%) H→L+2 (63%)

The calculations of the **ODA** molecule (in gas phase, and water) predict intense electronic transitions at 228, and 212 nm with an oscillator strength of 0.0108, 0.0103 consequently. The more intense one appear at excitation (b) (207, 210 nm) with an oscillator strength (0.01437, 0.1617 respectively).

The two λ_{max} of **ODDA** molecule in gas phase and water presented at (263, 240 nm) with f (0.0046, 0.0004 respectively), but the value of f decrease in water.

The high intensity of λ_{max} for **CODA** molecule in water is 218 nm with large value of $f = 0.2390$.

Figure 2 demonstrate the distributions and the energy levels of the frontier orbitals (HOMO, LUMO). From this figure it can be seen that the HOMO in **OD** molecule is located over the ring atoms, but the LUMO orbital almost localized on the whole molecule.

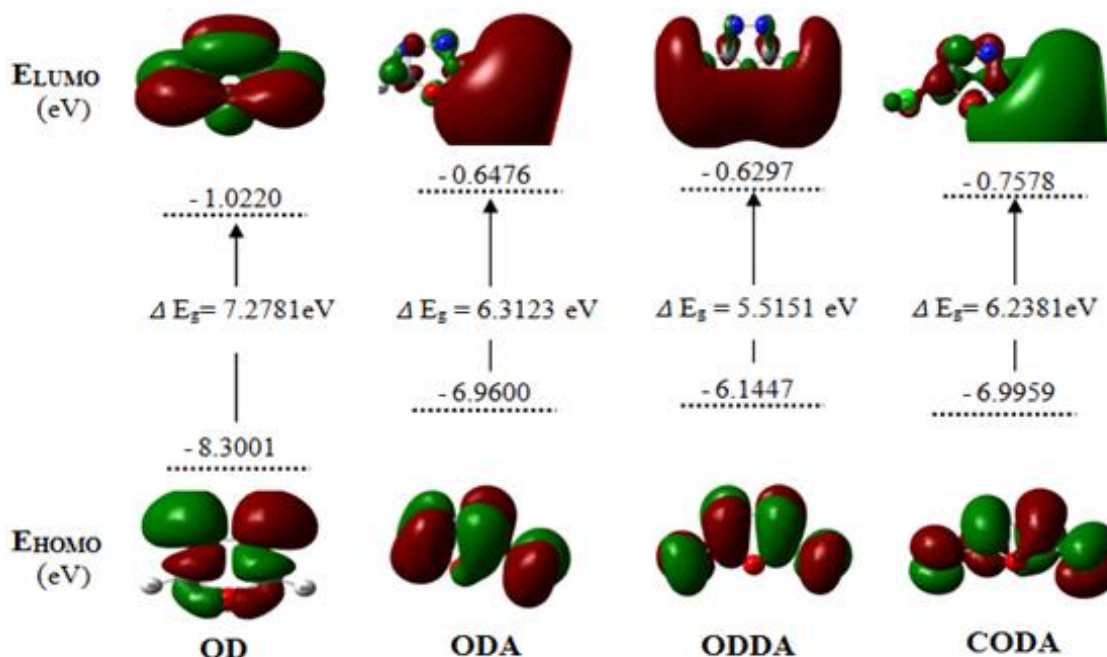


Figure 2. The atomic orbital compositions of the frontier molecular orbitals for the OD, ODA, ODDA, and CODA compounds, in gas phase.

In **ODA**, and **ODDA** the HOMO is located over all molecule atoms, but the LUMO appeared only on the nitrogen atom which belongs to the amine group. So the HOMO-LUMO transition implies an electron density transfer from molecule atoms to the amine group (nitrogen atom).

In **CODA** molecule the HOMO is diffused almost on the whole molecule, while LUMO presented on the amine group only.

It is well known that the smaller the ΔE_g express the charge transfer interactions taking place within the molecule [22]. The HOMO and LUMO are the most important orbitals effecting molecular chemical stability [24], The energy gap between them specifies the molecule kinetic stability, chemical reactivity, optical polarizability, and chemical hardness–softness [25,26]. The calculated ΔE_g for all molecules under study increasing in the following order **ODDA** < **CODA** < **ODA** < **OD** (5.5151, 6.2381, 6.3123, 7.2781 eV respectively). The low values main these molecules are more reactive and less stable.

Molecular electrostatic potential (MEP)

Molecular electrostatic potential is useful calculations in screening the molecular structure along with its physiochemical property [27]. The MEP give an approach to the electrophile attract to a negative regions, where the partial electronic negative charge is dominant. The red color represents the maximum negative region which offers a superior site for electrophilic attack. But the blue color point out to the maximum positive region, which prefer in nucleophilic attack. The importance of MEP map displays the molecular size, shape, negative, positive and neutral electrostatic potential regions which characterize by color scaling.

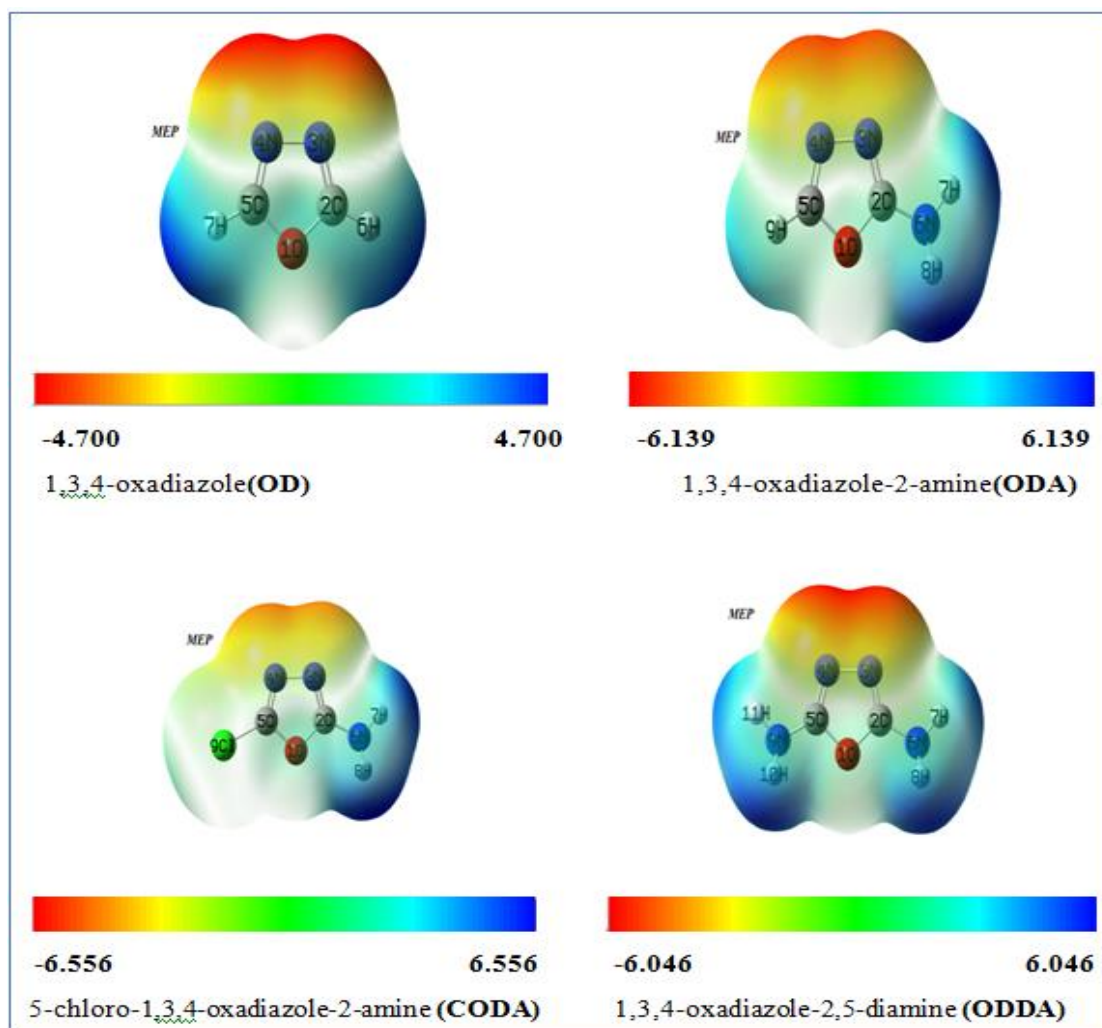


Figure 3. The molecular Electrostatic Potentials (MEP) for OD, ODA, ODDA, and CODA molecules (in gas phase).

Figure 3, presenting different colors map which relate to the different values of the electrostatic potential at the surface. The potential decreases in the order; red > orange > yellow > green > blue electron density surface. The color code of **OD** map are in the range between -4.700 (deepest red) and +4.700 (deepest blue), but the rest molecules ranging between the mean value of -6.247 to +6.247. The blue color indicates the strongest attraction and red the strongest repulsion. Regions of negative $V(r)$ are usually related to the lone pair of electronegative atoms, as seen from the MEP map [28]. The MEP maps for all these molecules show a negative potential over the electronegative atoms (nitrogen ring atoms), and positive potential over the carbon and hydrogen atoms. From these results, it can be concluded that the carbon atoms indicate the strongest attraction and the nitrogen ring atoms associated with the strongest repulsion.

CONCLUSIONS

Theoretical study for the oxadiazole derivatives is performed in order to display the effect of substituted groups, on the ring structure and the electronic properties. The concluding remarks are:

The substitution of one or two electron- donating groups ($-NH_2$) in 2or 5 positions on the oxadiazole ring destabilizes the HOMO and LUMO levels with a decrease in the energy gap resulting a red shift in the absorption spectrum.

The first (a), and second (b) absorption peaks of the electronic spectra and IR vibration frequencies for both C=N and C-H bonds are red-shifted in the presence of the $-NH_2$ group.

ACKNOWLEDGMENTS

The authors wish to thank the Department of Chemistry, College of Science, Al-Mustansiriya University, Baghdad, for allowing us to use their Gaussian program to accomplish the computer work.

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