

## Research Article



## The Molecular Structural and Spectroscopic Study (IR, Raman, UV and NMR) for 2-Carbaldehyde oxime-5-nitrothiophene Molecule by the DFT Method

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### ABSTRACT

Thiophene and its derivatives are attractive molecules due to their biological and pharmaceutical properties. The optimized geometry, harmonic vibrational frequencies, infrared intensities and Raman activities (through the region 3900–50  $\text{cm}^{-1}$ ), of 2-carbaldehyde oxime-5-nitrothiophene (CONT) molecule, were calculated by density functional theory (DFT/B3LYP) method plus the basis set 6-311G++(2d,2p). The electronic properties such as the UV spectra, molecular electrostatic potential (MEP), the highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) energies were computed by Time-dependent TD-DFT approach. The chemical shifts of the nuclear magnetic resonance (NMR) were computed by the Gauge-Invariant Atomic Orbital (GIAO) method. From the optimized geometry parameters, the most stable conformer of CONT molecule was plane, because all its dihedral angles were approximately equal zero or 180°. The thiophene ring bond angle of  $S_1-C_2-C_3$  was lower than the bond angle of  $S_1-C_5-C_4$  due to the smaller nitro group attached at  $C_5$  position. The UV spectra of this compound in gas phase and in solvent (ethanol) showed two peaks presented at (343.73, 369.41), and (256.15, 260.73) nm respectively. A red shift was observed during the transferring from gas phase to polar solvent therefore the transition is  $\pi-\pi^*$ . The two protons of thiophene ring of CONT molecule, demonstrated lower chemical shift than the other protons belong to the imine, and OH groups.

**Keywords:** 2-carbaldehyde oxime- 5-Nitrothiophene, Vibrational spectra, NMR spectra, UV spectra, MEP, and DFT.

### INTRODUCTION

Thiophene belongs to the class of the heterocyclic compounds, which containing five member ring with one heteroatom (sulfur)<sup>1</sup>. This compound and its derivatives have wide biological and pharmacological properties such as antiallergic, analgesic, antitumor, antibacterial and ocular hypotensive activities<sup>2</sup>. The members of 5-nitrothiophene derivatives have been prepared based on the antibacterial affects isosteric furan compounds. Among the simplest nitrothiophene derivative is the 2-carbaldehyde oxime- 5-nitrothiophene (CONT)<sup>3</sup>. Since there are no experimental or theoretical treatments for this derivative, this encourages us to study it.

The DFT method produces accurate data with low cost for molecular optimized geometry, and vibrational wave numbers in the ground state. The electronic absorption spectra for optimized molecule and electronic properties such as HOMO, LUMO energies, and the molecular electrostatic potential (MEP), with the time dependent density functional theory (TD-DFT) are of a particular interest give a satisfactory theoretical result when compared with experiment<sup>4</sup>. The GIAO method gives a reliable calculation for the nuclear magnetic shielding tensors and reliable magnetic properties<sup>5</sup>.

The aim of the present work is to characterize the preferred conformation of CONT molecule, plus the calculations of its harmonic vibrational (IR, and Raman), UV, and NMR spectra which determined by a quantum

chemical calculations using the DFT (B3LYP) method with the 6-311++G (2d, 2p) basis set level.

### Computational Details

In order to find the most stable optimized geometry for CONT molecule, four various possible suggesting conformers were investigated and then the lowest total energy conformer was selected. A further investigations were done to evaluate the harmonic vibrational frequencies, IR intensities, Raman activity, performing the DFT method with a hybrid functional B3LYP (Becke's three parameter hybrid functional employing the LYP correlation functional) with the Gaussian 09 program<sup>6</sup>.

The electronic absorption spectra for six electronic transitions, with its vertical excitation energies and the oscillator strengths, plus the HOMO and LUMO energies<sup>7, 8</sup>. These calculations used the lowest energy optimized structure which obtained from B3LYP/6-311++G (2d,2p) in gas phase, and including the solvent ethanol effect.

The NMR isotropic shielding was calculated using Gaussian program, by the GIAO method<sup>9, 10</sup> at the B3LYP/6-311++G(2d,2p) level for the optimized structure in gas phase, and in the dimethyl sulfoxide (DMSO) as a solvent. In order to express the chemical shifts,  $\delta$  (ppm), the tetramethylsilane (TMS) compound was used as a reference.



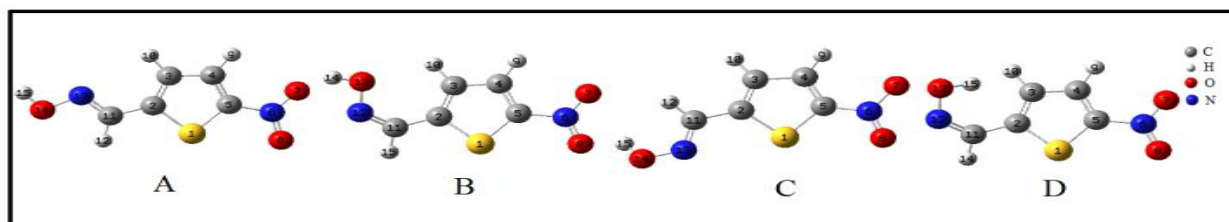
## RESULTS AND DISCUSSION

### Molecular geometry

The structures obtained for all the suggested conformers were shown in Figure 1. Where the calculated total energies result of A = -926.33100555, B = -926.33023871, C = -926.32370981, D = -926.31696020 eV. These results demonstrated that conformer (A) has the global minimum energy. Therefore the (A) form is the most stable one.

The calculations revealed that the conformer (A) is plane molecule because all its dihedral angle approximately equal zero or 180°. The optimized structural parameters of (A) form were indicated in Table 1. The calculated bond length values were compared with general experimental X-ray data in analogy aromatic compounds, where bond length of C<sub>5</sub>-NO<sub>2</sub> was 1.468, N<sub>6</sub>=O<sub>8</sub> 1.217, N<sub>13</sub>-O<sub>14</sub> 1.281 and S-C (in thiophene molecule) 1.712 Å<sup>11</sup>.

Generally the calculated data revealed that most of the optimized bond lengths are a little bit higher than the experimental values.



**Figure 1:** The numbering scheme for the four possible conformers of 2-carbaldehyde oxime-5-nitrothiophene.

**Table 1:** The optimized geometry data for the CONT molecule.

DFT 6-311G++ (2d,2p)					
Bond length (Å <sup>o</sup> )		Bond angle (degree)			
S <sub>1</sub> -C <sub>2</sub>	1.745	C <sub>2</sub> -S <sub>1</sub> -C <sub>5</sub>	90.233	C <sub>5</sub> -N <sub>6</sub> -O <sub>8</sub>	117.082
S <sub>1</sub> -C <sub>5</sub>	1.723	S <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	111.4	O <sub>7</sub> -N <sub>6</sub> -O <sub>8</sub>	125.330
C <sub>2</sub> =C <sub>3</sub>	1.384	S <sub>1</sub> -C <sub>2</sub> -C <sub>11</sub>	116.977	C <sub>2</sub> -C <sub>11</sub> -N <sub>13</sub>	130.411
C <sub>2</sub> -C <sub>11</sub>	1.449	C <sub>3</sub> -C <sub>2</sub> -C <sub>11</sub>	131.622	N <sub>13</sub> -C <sub>11</sub> -H <sub>12</sub>	112.285
C <sub>3</sub> -C <sub>4</sub>	1.406	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	113.076	C <sub>11</sub> -N <sub>13</sub> -O <sub>14</sub>	113.550
C <sub>4</sub> =C <sub>5</sub>	1.369	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	111.806	N <sub>13</sub> -O <sub>14</sub> -H <sub>15</sub>	102.705
C <sub>3</sub> -H <sub>10</sub>	1.074	S <sub>1</sub> -C <sub>5</sub> -C <sub>4</sub>	113.483		
C <sub>4</sub> -H <sub>9</sub>	1.077	C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	122.725		
C <sub>11</sub> -H <sub>12</sub>	1.083	C <sub>3</sub> -C <sub>4</sub> -H <sub>9</sub>	125.477		
C <sub>5</sub> -N <sub>6</sub>	1.434	C <sub>4</sub> -C <sub>3</sub> -H <sub>10</sub>	124.197		
C <sub>11</sub> =N <sub>13</sub>	1.281	C <sub>5</sub> -C <sub>4</sub> -H <sub>9</sub>	122.716		
N <sub>6</sub> -O <sub>7</sub>	1.226	C <sub>2</sub> -C <sub>11</sub> -H <sub>12</sub>	117.303		
N <sub>6</sub> -O <sub>8</sub>	1.250	S <sub>1</sub> -C <sub>5</sub> -N <sub>6</sub>	120.125		
N <sub>13</sub> -O <sub>14</sub>	1.394	C <sub>4</sub> -C <sub>5</sub> -N <sub>6</sub>	126.391		
O <sub>14</sub> -H <sub>15</sub>	0.962	C <sub>5</sub> -N <sub>6</sub> -O <sub>7</sub>	117.586		

Theoretical calculations results are obtained for isolated molecules in gaseous phase, while the experimental are gained from molecule in liquid or in solid state. From Table 1 it was observed that the thiophen ring single C-C bond distance was 1.4065 Å<sup>o</sup>, and the C=C bond length 1.3847, and 1.3696 Å<sup>o</sup>.

Furthermore the C<sub>2</sub>-C<sub>11</sub> bond length was 1.4492; this is larger than the C<sub>3</sub>-C<sub>4</sub> bond distances (1.4065 Å<sup>o</sup>) of the thiophene ring.

The calculated thiophene ring bond angle S<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> was 111.4, and of S<sub>1</sub>-C<sub>5</sub>-C<sub>4</sub> was 113.4 degree where the oxime group attached at C<sub>2</sub>. The angle S<sub>1</sub>-C<sub>5</sub>-C<sub>4</sub> is larger because

the smaller nitro group attached at C<sub>5</sub> position. This variation in bond angle can be related to the steric effect.

### Vibrational analysis

CONT molecule consist 15 atoms, therefore it contain 39 modes of fundamental vibrations. These modes are spread into the irreducible representation under C<sub>1</sub> symmetry as Γ<sub>vib</sub> = 39A. All these modes are found to be active in both the Raman scattering and infrared absorption. The detailed vibrational assignment for the fundamental modes of CONT, plus the calculated vibrational frequencies, IR intensities and Raman activities were presented in Table 2.

### Oxygen–hydrogen vibrations

The O-H group showed three types of vibration: stretching, in and out-of-plane bending. The strong band observed at  $3825\text{ cm}^{-1}$  in IR spectrum which assigned as O-H stretching. The in-plane bending mode of O-H group identified at  $1440$ ,  $1382$ , and  $1355\text{ cm}^{-1}$ . The O-H out-of-plane bending mode for the free molecule observed at  $440\text{ cm}^{-1}$ .

### Carbon–hydrogen vibrations

The heteroaromatic organic compounds and its derivatives were very close to benzene structure, illustrating multiple weak bands lie in the region of  $3100\text{--}3000\text{ cm}^{-1}$  due to C-H stretching vibrations<sup>12</sup>. The computed data demonstrated that the stretching band values for C-H<sub>ring</sub> were  $3244$ ,  $3230\text{ cm}^{-1}$ . The pure out-of-plane bending vibrations for C-H<sub>ring</sub> were  $940$ , and  $841\text{ cm}^{-1}$  and the mixed  $\gamma$  C-H<sub>ring</sub> appeared at  $759$  and  $499\text{ cm}^{-1}$ . The pure out of plane =C-H vibration occurred at  $973\text{ cm}^{-1}$ . Frequencies at  $1480$ ,  $1382$ , and  $1143\text{ cm}^{-1}$  can be assigned as C-H<sub>ring</sub> in-plane bending. This is indicating that the impact of substitution NO<sub>2</sub> group in the molecule ring do not much influence the vibration

of aromatic C-H. The experimental values for the C-H in-plane and out-of-plane bending vibrations were existed in the range between  $1300\text{--}1000\text{ cm}^{-1}$  and  $1000\text{--}750\text{ cm}^{-1}$  respectively<sup>13</sup>. The C-H stretching vibration belong to oxime group was appeared at  $3116\text{ cm}^{-1}$ .

### Nitro group vibrations

Since aromatic nitro compounds have strong absorptions assigned to the asymmetric and symmetric stretching vibrations for the NO<sub>2</sub> group which appeared at  $1570\text{--}1485\text{ cm}^{-1}$  and  $1370\text{--}1320\text{ cm}^{-1}$  regions, so hydrogen bonding has a little effect on the NO<sub>2</sub> asymmetric stretching vibrations<sup>14,15</sup>. In **CONT** compound, the bands occurred at  $1566$ ,  $1542$ , and  $1354\text{ cm}^{-1}$  corresponding to asymmetric and symmetric stretching modes of nitro group respectively. The band at  $824\text{ cm}^{-1}$  was assigned as NO<sub>2</sub> scissoring mode. The deformation vibrations of NO<sub>2</sub> group (wagging, rocking and twisting) contributed to different normal modes in the low frequency zone. In this study, the NO<sub>2</sub> wagging and rocking vibrations observed at  $(759, 61)$ , and  $(505, 209, 107)\text{ cm}^{-1}$ .

**Table 2:** The theoretical vibrational frequencies ( $\text{cm}^{-1}$ ), of the 2-carbaldehyde oxime–5-nitrothiophene molecule and their assignments of the normal modes.

No.	Sym.	Freq. ( $\text{cm}^{-1}$ )	IR intensity ( $\text{km mol}^{-1}$ )	Raman activity ( $\text{A}^{\text{e}4}\text{ amu}^{-1}$ )	Assignment
$\nu_1$	A	3825	208.97	318.55	$\nu_s$ O-H
$\nu_2$		3244	2.77	117.36	$\nu_s$ C-H ring
$\nu_3$		3229	0.15	49.86	$\nu_s$ C-H ring
$\nu_4$		3116	7.86	70.67	$\nu$ C-H
$\nu_5$		1666	7.17	749.19	$\nu$ C=N+ $\beta$ N-O-H
$\nu_6$		1566	57.46	88.71	$\nu_{as}$ NO <sub>2</sub> + $\nu_{as}$ C=C+ $\beta$ C-H
$\nu_7$		1541	198.95	33.92	$\nu_{as}$ NO <sub>2</sub> + $\nu_{as}$ C=C+ $\beta$ C-H
$\nu_8$		1480	80.30	983.67	$\nu_s$ C-C+ $\beta$ C-H ring+ $\beta$ C-H
$\nu_9$		1440	7.01	202.93	$\beta$ O-H+ $\beta$ C-H
$\nu_{10}$		1382	40.52	546.56	ring (def.)+ $\beta$ C-H ring+ $\beta$ O-H
$\nu_{11}$		1354	607.14	647.79	$\nu_s$ NO <sub>2</sub> + $\beta$ C-H ring+ $\beta$ O-H
$\nu_{12}$		1303	155.84	222.41	$\beta$ O-H + $\beta$ C-H
$\nu_{13}$		1256	34.63	18.004	$\beta$ C-H ring
$\nu_{14}$		1163	88.82	61.95	$\nu$ C-C ring+ $\beta$ C-H ring
$\nu_{15}$		1143	76.95	5.28	$\nu$ C-C+ ring (def.)+ $\beta$ C-H ring
$\nu_{16}$		1054	10.71	41.09	$\beta$ C-H ring
$\nu_{17}$		996	244.52	16.16	$\nu$ N-O
$\nu_{18}$		972	9.62	3.55	$\gamma$ C-H
$\nu_{19}$		940	0.62	0.52	$\gamma$ C-H ring
$\nu_{20}$		848	85.40	8.38	$\beta$ C-C=N
$\nu_{21}$		841	26.42	0.08	$\gamma$ C-H ring
$\nu_{22}$		823	20.04	42.46	$\delta$ NO <sub>2</sub> + $\nu$ C-S
$\nu_{23}$		759	23.60	0.32	$\gamma$ C-H ring+ $\omega$ NO <sub>2</sub>
$\nu_{24}$		757	0.07	7.33	ring (def.)+ $\nu$ (C-S-C)
$\nu_{25}$		656	2.85	11.73	ring (def.)



$\nu_{26}$	604	2.72	0.99	$\gamma$ C=N-OH +ring puck
$\nu_{27}$	505	0.10	3.63	$\beta$ C=N-OH+ $\nu$ C-S+ $\rho$ NO <sub>2</sub>
$\nu_{28}$	498	2.97	0.25	$\gamma$ C=N-OH+ $\gamma$ C-H ring
$\nu_{29}$	457	12.85	0.77	$\beta$ C=N-OH+ $\beta$ C-S-C
$\nu_{30}$	440	133.09	0.59	$\gamma$ O-H
$\nu_{31}$	401	7.91	10.57	$\gamma$ C=N-OH
$\nu_{32}$	340	0.46	0.92	$\gamma$ C-H+ Ring puck.
$\nu_{33}$	306	2.17	0.92	$\beta$ C=N-O+ $\beta$ (C-S-C)
$\nu_{34}$	208	1.01	0.42	ring clock wise+ $\rho$ NO <sub>2</sub>
$\nu_{35}$	200	1.41	0.17	$\gamma$ ring
$\nu_{36}$	128	0.05	0.60	$\gamma$ C=N-OH
$\nu_{37}$	107	2.33	1.06	$\beta$ C=N-OH+ $\rho$ NO <sub>2</sub>
$\nu_{38}$	85	0.07	0.28	$\tau$ NO <sub>2</sub>
$\nu_{39}$	60	1.10	0.22	$\gamma$ C=N-O-H+ $\omega$ NO <sub>2</sub>

### Carbon–nitrogen vibrations

The identification of C=N vibrations was a very difficult task, since it consisting several mixing bands in this region. In methanimine compound, the experimental data was assigned that C=N stretching absorption vibration in the region of 1638cm<sup>-1</sup>. But this study result (for CONT molecule) demonstrated that these bands observed at 1667 cm<sup>-1</sup>. The slight shift in wave number is due to the fact that force constants of the C=N bond increases due to the resonance with the thiophen ring. . The C=N-OH in-plane and out-of-plane bending vibrations occurred at (848, 505, 458, 306, and107) and (604, 499, 402, 129, 61) cm<sup>-1</sup> respectively, Table2.

### Thiophene ring vibrations

Generally the C-C stretching vibrations in aromatic compounds were noticed through the region of 1430–1650 cm<sup>-1</sup>. The five member ring heteroaromatic compounds with two double bonds in the ring usually indicated two ring stretching bands near 1590 and 1400 cm<sup>-1</sup>. In this molecule, the C=C asymmetric stretching vibrations occurred at 1566, 1542, and the C-C symmetric stretch at 1480 cm<sup>-1</sup>.

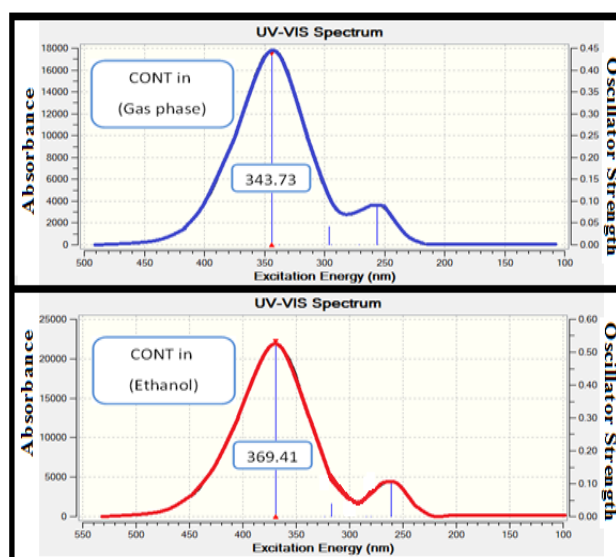
The most vibrational ring modes are affected by the substitutions in the aromatic ring. Since the presence of electron withdrawing group increases the bond order, thus the force constant rises and hence the wave number of absorption increases. In most cases, mesomeric effect works along with the inductive effect, and cannot be ignored the conjugation due to the thiophene ring which lowers the absorption frequency<sup>19</sup>. The in plane and out of plane bending vibrations observed in (1143, 757, 657, and 209) and (604, 340, and 201) cm<sup>-1</sup>respectively. Kwiatkowski et al<sup>20</sup> reported that C-S stretching vibration existed at 839 and 608 cm<sup>-1</sup>. In this work the stretching of the C-S bond in the thiophene ring identified at 824 and 505 cm<sup>-1</sup>, and the C-S-C stretching, and bending vibration recorded at (757), and (458, and 306) cm<sup>-1</sup>.

### Electronic properties

#### Electronic absorption spectra

The calculations contain the electronic absorption spectra (UV), and molecular orbital energies, the energy difference ( $\Delta E = E_f - E_i$ ), absorption wavelengths ( $\lambda$  max), and oscillator strengths ( $f$ ) based on the optimized geometry in ethanol, and gas phase with major contributions, presented in Tables 3 and Figure 2.

In the UV region with high extinction coefficients, all molecules allow strong  $\pi$ - $\pi^*$  and  $\sigma$ - $\sigma^*$  transition<sup>21, 22</sup>. According to the Frank–Condon principle, the maximum absorption peak ( $\lambda$  max) in an UV spectrum corresponds to the vertical excitation. For the examined molecule the UV spectrum showed two peaks. The peak with maximum absorption intensity in both gas phase, and ethanol as a solvent evaluated at 343.73 and 369.41 nm with an oscillator strength of 0.4379, and 0.5336 consequently.



**Figure 2:** The theoretical electronic spectra for CONT molecule in gas phase and ethanol.

This peak corresponds to the electronic transition from the HOMO to LUMO with 100% major contribution. The second peak with the lower absorption intensity appeared at 256.15 nm,  $f = 0.0864$  (in gas phase), and 260.73 nm,  $f = 0.1092$  (in Ethanol). During the transferring

from gas phase to polar solvent (ethanol) a red shift was observed, this shift was higher in the first peak than the second. Therefore it can be concluding that the transition is  $\pi-\pi^*$ .

**Table 3:** The absorption wavelength, energies, oscillator strengths, and major contribution for the CONT molecule.

TD-DFT/(B3LYP)/6-311++G(2d,2p)							
Gas				Ethanol			
$\lambda(\text{nm})$	$E(\text{eV})$	$f$	Major Contribution (%)	$\lambda(\text{nm})$	$E(\text{eV})$	$f$	Major Contribution (%)
343.73	3.6071	0.4379	H→L(100%)	369.41	3.3563	0.5336	H→L(100%),
337.85	3.6698	0.0000	H-2→L(79%), H-2→L+1(20%)	323.46	3.8331	0.0000	H-3→L(82%), H-3→L+1(17%)
296.36	4.1836	0.0419	H-1→L(100%)	317.17	3.9091	0.0391	H-1→L(100%)
294.24	4.2137	0.0005	H-5→L(68%), H-5→L+1(17%), H-3→L(13%)	284.23	4.3621	0.0010	H-5→L(52%), H-5→L+1(11%) H- 2→L(35%)
271.52	4.5663	0.0004	H-5→L(13%), H-3→L(68%) H- 3→L+1(18%)	280.14	4.4258	0.0001	H-5→L(52%), H-2→L(51%), H-2→L+1
256.15	4.8402	0.0864	H-6→L(29%), H→L+1(70%)	260.73	4.7553	0.1092	H-4→L(35%), H→L+1(64%)

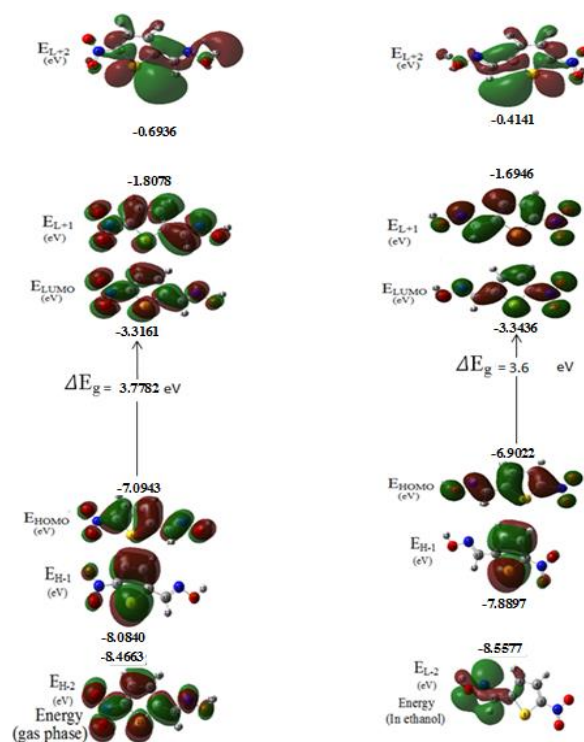
### Molecular Orbital

Both the HOMO and LUMO are the important orbitals, which take a part in chemical stability<sup>23</sup>. The HOMO performs the ability to donate an electron, while the LUMO act as an electron acceptor, demonstrating the ability to gain an electron. It is well known that the smaller the HOMO - LUMO energy gap ( $\Delta E_g$ ) express the charge transfer interactions take place within the molecule<sup>24</sup>. From Figure 3, the calculated  $\Delta E_g$  in gas phase was 3.7782 eV which is larger than the value in solvent ethanol 3.6 eV, this may be due to bathochromic shift. The occurrence of the lower LUMO energy value (-3.3161 in gas phase, and -3.3436 eV in ethanol), and the raise of the HOMO energy value (-7.0943 in gas phase, and -6.9022 eV in ethanol) is due to the conjugation in this molecule<sup>19</sup>.

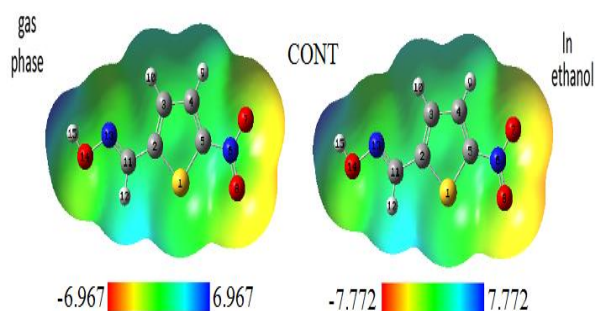
### Molecular Electrostatic Potential (MEP)

MEP calculations are useful in describing the molecular geometry and its physiochemical properties<sup>25</sup>. Its provide information about the net electrostatic effect at any point surrounding a molecule in space, which generated due to the total charge distribution of the molecule. The electrostatic potential surface displays the reactive positions and charge density (positive, negative and neutral area in terms of color scaling). The MEP negative charge decreases according to the following order red > orange > yellow > green > blue<sup>26</sup>. The red color represents the zone of maximum negative electrostatic potential (electrophilic attack). The blue color indicates the maximum positive zone (nucleophilic attack). The green represents the area close to neutral. So the MEP

aids to determine the reactivity, hydrogen bonding interactions, and the relative polarity for molecules<sup>27</sup>. Figure 4 indicated that the negative region was mainly localized on the oxygen atoms (belong to NO<sub>2</sub> group O<sub>7</sub>, and O<sub>8</sub>) whereas the nucleophilic reactivity of the molecule was localized on the proton of C=N-OH group.



**Figure 3:** The energy values with molecular orbital geometry in gas phase, and ethanol.



**Figure 4:** The Molecular Electrostatic Potentials.

### NMR spectroscopy

The predicted chemical shift  $\delta$  for all the atoms were listed in Table 4. Since the theoretical calculations were carried out in the isolated gas phase, therefore the theoretical chemical shift values expected to be slightly deviated from the experimental results. Usually the high shielding show downfield, and vice versa<sup>28</sup>. The sulfur nucleus  $S_1$  in thiophene ring showed higher chemical shift

value (200.7 ppm). The  $\delta$  value for the protons belong to thiophene ring presented at (2.7, and 4.0) ppm in gas phase, and (3.1, and 6.3) ppm in DMSO. The  $H_{15}$  which directly bonded with oxygen atom in the OH group (deshielding) demonstrated an increase in the chemical shift (8.2 ppm), down-field. The proton  $H_{12}$  in imine group also showed a down-field shift 6.2 ppm. Since the chemical shift for  $^{13}C$  nucleus is much higher than the proton, because the electron clouds surrounding  $^{13}C$  nucleus are denser, therefore the shielding affects increases<sup>29</sup>. The  $\delta$  for  $C_2$  nucleus appeared at 139.0 and 132.5 ppm in gas phase and DMSO respectively, due to presence of  $C=N$  group. The  $\delta$  value belong to  $C_5$  nucleus were 64.99 and 68.74 ppm in gas phase, and DMSO respectively, these values were lower than the expected result. The carbon nucleus  $C_{11}$  occurred at high chemical shift of 120.3 ppm, which due to the double bond of  $C=N$ .

**Table 4:** The calculated NMR chemical shifts in ppm for CONT molecule in (gas phase and DMSO solvent).

Atom	Chemical shift (ppm)		Atom	Chemical shift (ppm)		Atom	Chemical shift (ppm)	
	Gas phase	DMSO		Gas phase	DMSO		Gas phase	DMSO
S(1)	200.79	181.46	N(6)	270.08	275.83	C(11)	120.28	124.79
C(2)	139.00	132.46	O(7)	676.44	639.07	N(13)	376.59	344.27
C(3)	142.95	144.80	O(8)	620.27	582.88	O(14)	175.23	159.99
C(4)	154.39	154.26	H(9)	2.69	3.11	H(12)	6.15	7.70
C(5)	64.99	68.74	H(10)	3.96	6.27	H(15)	8.19	7.38

### CONCLUSIONS

The present investigation thoroughly analyzed the conformational stability, HOMO–LUMO analyses, MEP, UV spectra, the vibrational spectra, infrared and Raman, and NMR of CONT molecule, based on theoretically calculated used DFT (B3LYP) with 6-311++G(2d,2p) basis set calculations. The total energies of different conformations were obtained. The computational results identify the most stable conformer for (CONT) which was the A form. From the optimize geometry parameters the A conformer is plane molecule because all the dihedral angles are approximately equal zero or 180°. The thiophene ring bond angle of  $S_1-C_2-C_3$  was lower than the bond angle of  $S_1-C_5-C_4$  which due to the smaller nitro group attached at  $C_5$  position. This variation in bond angle depends on the steric effect. The vibrational spectra for the thiophene ring with their reliable assignment revealed that the C=C stretching vibration occurred at a higher wave number. Therefore the substitutions in thiophene ring increase the vibrational modes wave numbers.

The UV electronic spectra illustrated two peaks, one of them more intense. A red shift was recorded in both of them, therefore the transition is  $\pi-\pi^*$ .

The two protons of thiophene ring of CONT molecule, demonstrated lower chemical shift than the other protons, belong to the imine, and OH groups. The occurrence of the deshielding is related to the presence of N, and O atoms.

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