

## Structural Properties, Natural Bond Orbital, Theory Functional Calculations (DFT) and Energies for the 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan Compound

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**Abstract:** A theoretical study on molecular structure, vibrational spectra and energies of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan is reported. The molecular geometry and vibrational frequencies and energies in the ground state are calculated by using DFT levels of theory with 3-21G and LANL2DZ basis sets. The calculated HOMO and LUMO energies also confirm that charge transfer occurs within the molecule. The geometries and normal modes of vibrations obtained from B3LYP/ 3-21G and LANL2DZ calculations are in good agreement with the experimentally observed data. B3LYP/ LANL2DZ calculation results indicated that some selected bond length and bond angles values for the  $C_{14}H_{10}N_6O$ .

**Key words:** Furazan Derivatives • LANL2DZ • Molecular Geometry • HOMO • LUMO • B3LYP level

### INTRODUCTION

1,2,5-oxadiazole, or Furazan, is a heterocyclic aromatic organic compound. Compounds based on the furazan ring have attractive properties as organic energetic materials. First, the aromaticity of the ring stabilizes the backbone. Secondly, the planarity of the ring permits better crystal packing, resulting in high density. Third, the oxygen atom in the ring is not bonded to either carbon or hydrogen and is able to engage in redox chemistry when bonding to carbon in the eventual decomposition products. 1,2,5-oxadiazole, is an heterocyclic aromatic organic compound consisting of a five-atom ring containing 1 oxygen and 2 nitrogen atoms. The furazan ring system is also found in the steroid furazabol. Furazan and its derivatives are obtained from the oxime derivatives of 1,2-diketones.

Furazan was first prepared and characterized in 1964 by melting glyoxime with succinic anhydride in 57% yield. A series of furazans that have been synthesized have been found to be powerful explosives. More specifically, the work done by *Coburn*<sup>15</sup> at the Los Alamos Laboratory in New Mexico in 1968 has been crucial in setting the foundation for this research. *Coburn* saw the structure of furazan and realized that furazan

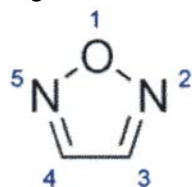
derivatives could have potential as explosive compounds due to their nitrogen rich structures. He went on to synthesize many different furazan compounds. A key compound that *Coburn* used as an intermediate for each of these compounds was diaminofurazan.

**Furazan Derivatives:** 3,4-Dimethylfurazan: (b.p. 154–159°C) is prepared by dehydrating dimethylglyoxime. A variety of related derivatives are known, including diphenyl- and methylethylfurazan.

Carboxylic acid derivatives: Potassium permanganate oxidizes 3,4-dimethylfurazan first to methylfurazancarboxylic acid and then to furazandicarboxylic acid. By warming oxyfurazan acetic acid with excess of potassium permanganate, oxyfurazancarboxylic acid is obtained. It crystallizes as prisms (m.p. 175°C). Furazancarboxylic acid (m.p. 107°C) is prepared by oxidation of furazanpropionic acid with potassium permanganate. It dissolves in base to give nitrosocyanacetate.

Diaminofurazan: The energetic precursor, diaminofurazan, can be prepared by heating diaminoglyoxime with potassium hydroxide followed by cooling to give white crystals. Like many other furazans, diaminofurazan forms stable complexes with copper(II) salts [1-6].

During this study we report the optimized geometries, assignments and electronic structure calculation for the title compound. 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan is a Furazan derivative. The molecular formula of furazan are  $C_{14}H_{10}N_6O$ . in this paper, 1,2-diketones. 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan ( $C_{14}H_{10}N_6O$ ) optimized geometries and frequencies of the stationary point and energies in the ground state using DFT (B3LYP) methods with LANL2DZ and 3-21G basis set. The calculated HOMO and LOMO energies and Bond length and bond angles values.



**Computation:** The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. All computational are carried out using Gaussian 09w program. The optimization is complete when the numerical process converges, that is to say, when forces are zero. Energy minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints. The molecular structure, frequencies and energy of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan in the ground state is computed by performing the DFT with the 3-21G and LANL2DZ basis sets.

## RESULTS AND DISCUSSION

**Molecular Geometry:** The molecular structure and atom numbering of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan are shown in (Figure 1).

All calculations were carried out using the computer program Gaussian 09. The optimized structural parameters of  $C_{14}H_{10}N_6O$  calculated by the DFT (B3LYP) levels with the 3-21G and LANL2DZ basis sets are listed in (Table 1).

**Vibrational Analysis:** Vibrational spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, reaction kinetics. The calculated data of the vibrational spectrum of  $C_{14}H_{10}N_6O$  is given in (Table 2).

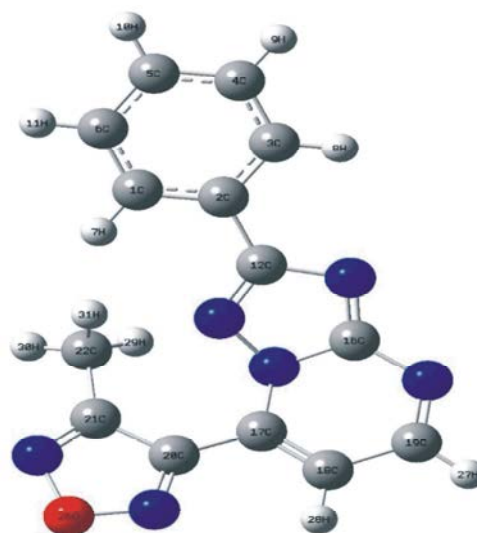


Fig. 1: Molecular structure and atom number in with use van der waals radii.

Table 1: Optimized geometrical parameters for  $C_{14}H_{10}N_6O$  at DFT (B3LYP) levels with the 3-21G and LANL2DZ basis sets

Geometrical parameters	DFT (B3LYP)	
	3-21G	LANL2DZ
<b>Bond lengths (Å)</b>		
$N_{14}-C_{12}$	1.3712	1.3790
$N_{13}-N_{15}$	1.3984	1.3814
$N_{15}-C_{17}$	1.3647	1.3769
$C_{16}-N_{23}$	1.3423	1.3563
$C_{17}-C_{20}$	1.4628	1.4704
$C_{21}-C_{22}$	1.4950	1.4984
$N_{24}-O_{26}$	1.4437	1.4183
$N_{25}-O_{26}$	1.4683	1.4401
<b>Bond angle (°)</b>		
$C_2-C_{12}-N_{14}$	122.2419	123.1090
$C_2-C_{12}-N_{13}$	122.0412	122.1172
$N_{13}-N_{15}-C_{17}$	128.9101	127.9927
$N_{14}-C_{16}-N_{23}$	130.9736	130.6469
$N_{15}-C_{17}-C_{20}$	122.4142	120.8886
$C_{18}-C_{17}-C_{20}$	121.4034	123.0612
$C_{17}-C_{20}-N_{24}$	118.8401	119.0282
$C_{22}-C_{21}-N_{25}$	121.9099	121.3687
$C_{20}-N_{24}-O_{26}$	104.9530	105.3390
$C_{21}-N_{25}-O_{26}$	105.1451	105.7084
<b>Dihedral angle(°)</b>		
$C_6-C_1-C_2-C_{12}$	-179.9958	-179.9228
$O_3-C_2-C_{12}-N_{14}$	2.8054	3.7807
$C_1-C_2-C_{12}-N_{13}$	2.7243	3.7212
$C_{12}-N_{14}-C_{16}-N_{23}$	-178.0686	-178.2185
$C_{12}-N_{13}-N_{15}-C_{17}$	177.9006	178.4109
$N_{13}-N_{15}-C_{17}-C_{20}$	2.2058	1.3278
$C_{19}-C_{18}-C_{17}-C_{20}$	-179.5431	-179.2988
$C_{17}-C_{20}-N_{24}-O_{26}$	-176.0613	-177.2464
$C_{22}-C_{21}-N_{25}-O_{26}$	177.2845	177.6779

The angle  $C_{22}-C_{21}-N_{25}$  ( $121.9099^\circ$ ) is significantly greater than  $C_{17}-C_{20}-N_{24}$  ( $118.8401^\circ$ ). The bond length  $N_{25}-O_{26}$  ( $1.4683 \text{ \AA}$ ) greater than bond length  $N_{24}-O_{26}$  ( $1.4437 \text{ \AA}$ ).

Table 2: DFT (B3LYP) with 3-21G And LANL2DZ level calculated vibrational frequencies of C<sub>14</sub>H<sub>10</sub>N<sub>6</sub>O (cm<sup>-1</sup>).

DFT (B3LYP)			
3-21G		LANL2DZ	
Frq(cm <sup>-1</sup> )	IR	Frq(cm <sup>-1</sup> )	IR
163.33	3.6106	77.77	1.4079
262.35	5.0606	131.74	3.6897
367.02	12.0144	363.19	9.8245
491.29	10.5103	478.68	13.3439
632.61	12.8571	632.89	14.7394
669.63	69.9033	661.12	87.8285
764.15	19.6929	882.18	34.7696
850.66	34.2759	841.45	18.6162
983.55	25.1495	954.83	28.3565
1049.25	17.5002	1013.83	33.8138
1202.45	140.0170	1036.89	27.4157
1209.14	20.4603	1199.46	40.6622
1315.45	43.4512	1232.91	120.2869
1469.44	66.1996	1313.88	34.1632
1518.78	30.5423	1462.09	37.3327
1596.20	39.7232	1545.01	76.5145
1624.28	137.0568	1683.55	195.3549
3273.16	27.1146	3388.22	29.8200

The calculated infrared spectra for different basis sets of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan are presented in (Figure 2).

In the spectrum of C<sub>14</sub>H<sub>10</sub>N<sub>6</sub>O, the strong IR absorption are due to N-N, C-H, C-N, N-O, bonds and phenyl ring.

**Raman Analysis:** Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational and other low-frequency modes in a system [7]. The Raman effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. For the spontaneous Raman effect, which is a form of light scattering, a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength. The Raman effect, which is a light scattering phenomenon, should not be confused with absorption (as with fluorescence) where the molecule is excited to a discrete (not virtual) energy level.

In this we have carried out computed chemical shift calculations of present molecule. The Raman spectrum of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan are showed in (Figure 3).

**NMR Analysis:** NMR spectroscopy is a useful technique for identifying and analyzing organic compounds. In this we have carried out computed chemical shift calculations of present molecule. The NMR spectrum of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl) are showed in (Figure 4).

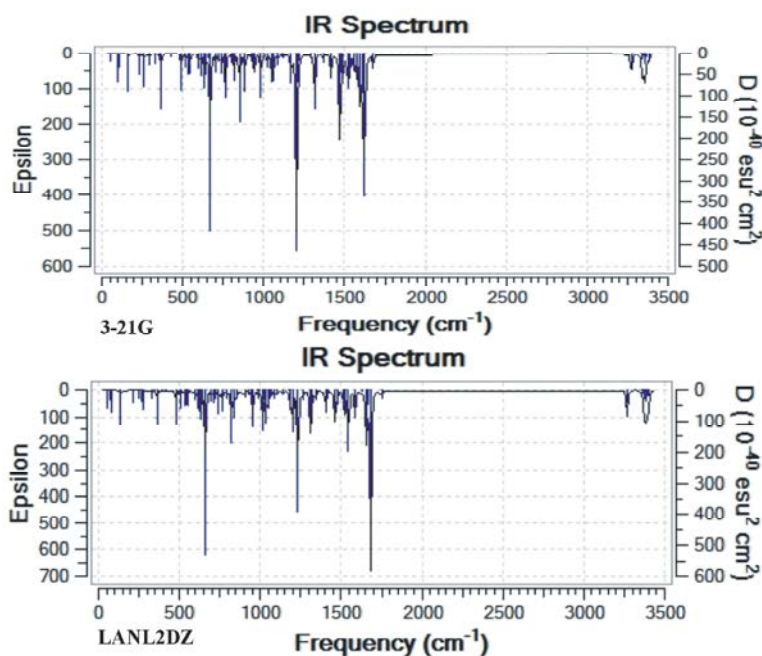


Fig. 2: Calculated infrared spectra of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan. First calculated by DFT (B3LYP)/3-21G and second calculated by DFT (B3LYP)/LANL2DZ.

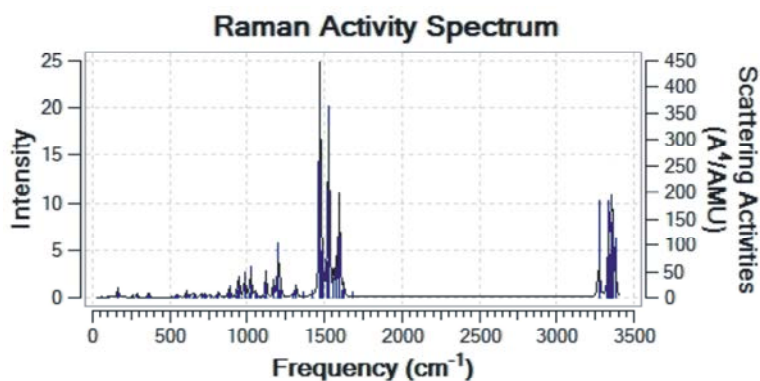


Fig. 3: Calculated Raman spectra of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan by DFT(B3LY)/LANL2DZ.

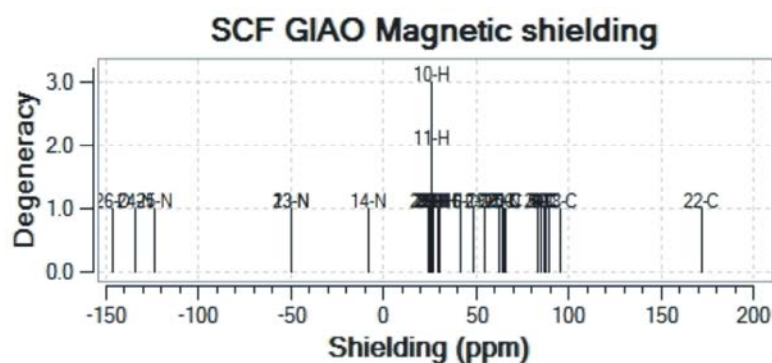


Fig. 4: Calculated NMR spectra of 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan by DFT(B3LY)/LANL2DZ.

**Orbital Analysis:** All the structures allows  $\sigma > \sigma^*$  or  $\pi > \pi^*$  transitions in the UV-Vis region with high extinction coefficients. The frontier orbitals are the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). We concentrate attention on these two orbitals because they are the closest in energy. These orbitals are intimately involved in chemical reactivity, because they are the most available to electrophiles and nucleophiles, respectively. Another key change has to do with the frontier orbitals, the  $\pi$ (HOMO) and  $\pi^*$ (LUMO) orbitals [8-11].

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability.. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity.

Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures. The HOMO and LUMO energy were calculated by DFT with B3LYP method by using 3-21G and LANL2DZ basis sets. In addition, 3D plots of HOMOs and LUMOs are shown in (Figure 5) and the atomic orbital energy of the frontier molecular orbital are given in (Table 3).

**Electron Density Distribution:** The total electron density distribution is a physical property of molecules. The electron density is usually depicted as a comparison of the observed electron density with that predicted by spherical models of the atoms and is called deformation electron density. The total electron density was calculated by DFT/LANL2DZ using SCF density matrix (Figure 6) shown contour maps of total electron density for 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl) furazan. Also in addition (Table 4) given charge atoms of C<sub>14</sub>H<sub>10</sub>N<sub>6</sub>O and the structure atomic charges are shown in (Figure 7).

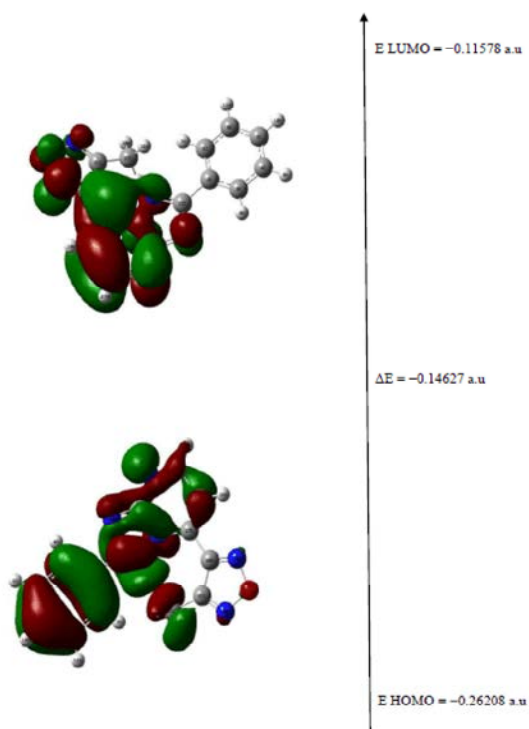


Fig. 5: The atomic orbital compositions of the frontier molecular orbital for 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan.

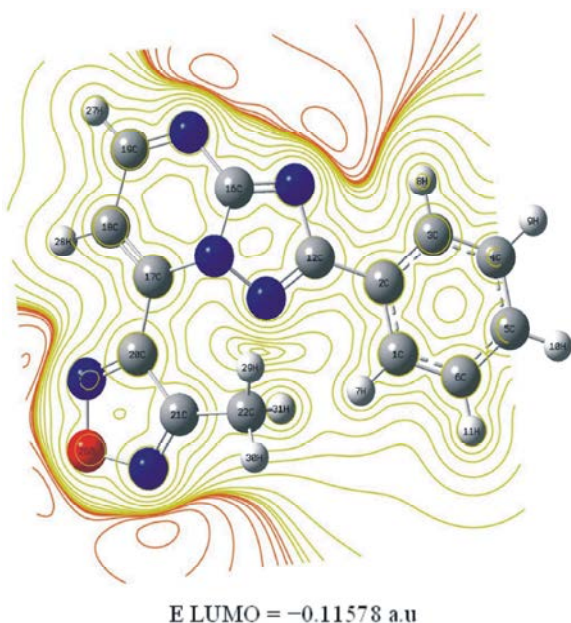


Fig. 6: Contour maps of electron density for 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan in the planes of the molecules. Electron density was calculated at the DFT/LANL2DZ level.

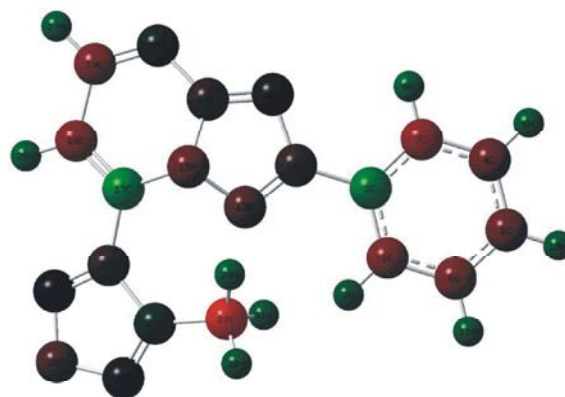


Fig. 7: The structure atomic charges of C14H10N6O with display charge distribution.

Table 3: The atomic orbital energy of the frontier molecular orbital for 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan

DFT/ B3LYP/3-21G	DFT/B3LYP/ LANL2DZ
E LUMO = -0.10094 a.u (First excited state)	E LUMO = -0.11578 a.u (First excited state)
ΔE = -0.15286 a.u (Ground state)	ΔE = -0.14627 a.u (Ground state)
E HOMO = -0.25380 a.u (Ground state)	E HOMO = -0.26208 a.u (Ground state)

Table 4: Charge of C14H10N6O.

Atom NO	Charge
C <sub>2</sub>	0.373
C <sub>12</sub>	-0.087
N <sub>13</sub>	-0.149
N <sub>14</sub>	-0.031
N <sub>15</sub>	-0.204
C <sub>17</sub>	0.414
C <sub>22</sub>	-0.593
C <sub>20</sub>	-0.084
N <sub>24</sub>	-0.021
N <sub>25</sub>	-0.032
O <sub>26</sub>	-0.130

**Natural Bond Orbitals(NBO):** Natural bond orbitals (NBO) describe the molecule by a series of localized bonding orbitals corresponding to a Lewis structure. In quantum chemistry, a natural bond orbital or NBO is a calculated bonding orbital with maximum electron density. Another set of orbitals describes combinations in which electron density is transferred from filled to antibonding orbitals. The NBOs are one of a sequence of natural localized orbital sets that include "natural atomic orbitals" (NAO), "natural hybrid orbitals" (NHO), "natural bonding orbitals" (NBO) and "natural (semi-)localized molecular orbitals" (NLMO). These natural localized sets are intermediate between basis atomic orbitals (AO) and molecular orbitals (MO): Atomic orbital → NAO → NHO →

NBO → NLMO → Molecular orbital Natural (localized) orbitals are used in computational chemistry to calculate the distribution of electron density in atoms and in bonds between atoms. They have the "maximum-occupancy character" in localized 1-center and 2-center regions of the molecule [12]. With a computer program that can calculate NBOs, optimal Lewis structures can be found. An optimal Lewis structure can be defined as that one with the maximum amount of electronic charge in Lewis orbitals (Lewis charge) [13].

A low amount of electronic charge in Lewis orbitals indicates strong effects of electron delocalization. In resonance structures, major and minor contributing structures may exist. For amides, for example, NBO calculations show that the structure with a carbonyl double bond is the dominant Lewis structure. However, in NBO calculations, "covalent-ionic resonance" is not needed due to the inclusion of bond-polarity effects in the resonance structures [14]. This is similar to other modern valence bond theory methods. The NBO analysis partitions the electron density of the whole molecule out into atomic like orbitals, which are then used to form 2e-2c bonds. NBO Calculated Hybridizations are significant parameters for our investigation.

The structure of the compound has been optimized by using the DFT (B3LYP) method with the 3-21G basis sets, using the Gaussian 09w program. Natural Bond Orbital's (NBOs) are localized few-center orbital's that describe the Lewis-like molecular bonding pattern of electron pairs in optimally compact form.

More precisely, NBOs are an orthonormal set of localized "maximum occupancy" orbital's whose leading  $N/2$  members (or  $N$  members in the open-shell case) give the most accurate possible Lewis-like description of the total  $N$ -electron density. This analysis is carried out by examining all possible interactions between "filled" (donor) Lewis-type NBOs and "empty" (acceptor) non-Lewis NBOs and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to donation of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure. Natural charges have been computed using natural bond orbital (NBO) module implemented in Gaussian 09w.

These quantities are derived from the NBO population analysis. The former provides an orbital picture that is closer to the classical Lewis structure.

Table 5: The NBO Calculated Hybridizations for 3-Methyl-4-(2-phenyl-1,2,4-triazolo-[1,5-a]pyrimidin-7-yl)furazan

DFT/LANL2DZ				
Bond (BD)	Hybridization	E $\sigma$	E $\sigma^*$	$\Delta E$
C2 - C12	sp <sup>2.21</sup> ,sp <sup>1.59</sup>	1.96715	0.03235	1.93480
N13 - N15	sp <sup>3.83</sup> ,sp <sup>2.34</sup>	1.98026	0.02739	1.95287
C19 - N23	sp <sup>1.00</sup> ,sp <sup>1.00</sup>	1.98391	0.01189	1.97202
N15 - C17	sp <sup>1.59</sup> ,sp <sup>2.57</sup>	1.98247	0.04105	1.94342
C17 - C20	sp <sup>1.89</sup> ,sp <sup>1.73</sup>	1.96386	0.03112	1.93247
C20 - C21	sp <sup>1.91</sup> ,sp <sup>2.03</sup>	1.96766	0.06094	1.90672
C21 - C22	sp <sup>1.64</sup> ,sp <sup>2.58</sup>	1.97412	0.01246	1.96166
C20 - N24	sp <sup>99.9</sup> ,sp <sup>99.9</sup>	1.98005	0.02323	1.95682
C21 - N25	sp <sup>2.44</sup> ,sp <sup>1.73</sup>	1.98266	0.02467	1.95799
N25 - O26	sp <sup>6.97</sup> ,sp <sup>4.27</sup>	1.97918	0.06908	1.91010

The NBO analysis involving hybridizations of selected bonds,  $\sigma$  and  $\sigma^*$  energy are calculated at B3LYP methods and LANL2DZ level of theory (Table 5).

## CONCLUSIONS

The theoretical method that better reproduces the experimental data is the B3LYP/3-21G and B3LYP/LANL2DZ calculated molecular geometries, energy and vibrational spectra were performed at this theory level. Calculation results indicated that some selected bond length and bond angles values for the C<sub>14</sub>H<sub>10</sub>N<sub>6</sub>O [15-17].

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