



## Theoretical Study of Structural and Electronic Properties in 2-imino Methyl phenol: Exchange , correlation energy and NBO analysis

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### ABSTRACT

Imines are a functional group or chemical compound with a carbon-nitrogen double bond. An amine can be processed through increasing nucleophilic substitution reaction of a ketone or aldehyde with ammonia or an amine leading to formation of a hemiaminal -C (OH) (NHR)-. This hemiaminal converts to an imine with losing water. The imines synthesis reaction is as an equilibrium reaction. Imines are used in chemical and pharmaceutical industries. in this study Exchange and Correlation energies of 2-imino methyl phenol with the formula of  $C_7H_7NO$  are calculated by using the DFT methods with 3-21G, 6-31G , 6-311G and 6-21G basis sets. the optimized structure and electronic properties calculations for the studied molecule have been performed using Gaussian 09 program . A mathematical equation of second grade was exploited for the correlation and exchange energy with the number of primitives. The Natural Bonding Orbital (NBO) analysis were performed on the  $C_7H_7NO$  at the B3LYP/ 6-31G level of theory . The chemical reactivity of the  $C_7H_7NO$  have been investigated at B3LYP/6-31G(d) level of theory .The band gap energy, total energy (E), chemical hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ), and Global electrophilicity index ( $\omega$ ), ionization potential (IP) and electron affinity (EA) for the  $C_7H_7NO$  have been calculated for the chemical activity of the above molecules.

**Keywords:** DFT Calculation , 2-imino methyl phenol ( $C_7H_7ON$ ) , Primitive , NBO analyses , Exchange and Correlation Energy

## Introduction

Imines are a functional group or chemical compound with a carbon-nitrogen double bond. An amine can be processed through increasing nucleophilic substitution reaction of a ketone or aldehyde with ammonia or an amine leading to formation of a hemiaminal -C (OH) (NHR)-. This hemiaminal converts to an imine with losing water. The imines synthesis reaction is as an equilibrium reaction. Imines are used in chemical and pharmaceutical industries. . [1-3]

In this study, the structural properties of imine with the formula of  $C_7H_7NO$  are calculated by using the DFT methods with 3-21G, 6-31G , 6-311G and 6-21G basis sets. Then mathematical equations for correlation and exchange energies for this molecule have been calculated comparing to Primitive numbers. The band gap energy, total energy (E), chemical hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ), and Global electrophilicity index ( $\omega$ ), ionization potential (IP) and electron affinity (EA) for  $C_7H_7NO$  have been calculated by using B3LYP/6-31g .

## METHODS

All computational on  $C_7H_7NO$  are carried out using Gaussian 09 program at the restricted LSDA , B3LYP , PBEPBE , HF , MP2 levels in 3-21G, 6-31G , 6-311G and 6-21G basis sets . Exchange and Correlation energies in the above mentioned basis sets were calculated and the curve for correlation and exchange energies according to the number of primitives was drawn using Excell 2013 and the mathematical equation between them was obtained . Energy minimum molecular geometries were located by minimizing energy. Natural bonding orbital (NBO) analysis were performed on the  $C_7H_7NO$  at the B3LYP/6-31G level of theory .

## RESULTS AND DISCUSSION

### Molecular properties:

The structure of  $C_7H_7NO$  is shown in figure 1. All computational are carried out using Gaussian 09 program. Theoretical calculation of bond lengths for the  $C_7H_7NO$  was determined by optimizing the geometry . (Table 1)

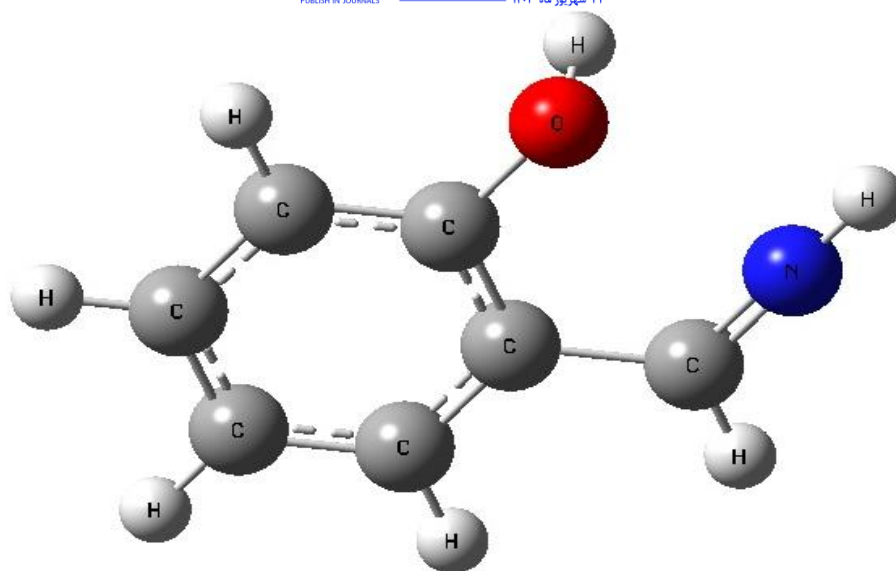


Fig. 1: The theoretical optimized possible geometric structure of  $C_7H_7NO$

Table 1: Calculated bond lengths ( $\text{\AA}$ ) for the  $C_7H_7NO$

BOND	bond lengths ( $\text{\AA}$ )	BOND	bond lengths ( $\text{\AA}$ )
C1-C2	1.395160	C2-H8	1.099656
C1-C6	1.394829	C4-O11	1.43
C2-C3	1.3947123	O11-H12	0.96
C3-C13	1.54	C5-H9	1.099761
C3-C4	1.2954262	C6-H10	1.099604
C4-C5	1.394825	C13-H14	1.07
C5-C6	1.395138	C13-N15	1.293600
C1-H7	1.099610	N15-H16	1.000000

### Exchange and Correlation Energy calculated:

The total optimized energy of  $C_7H_7NO$  at the RHF and RMP2 levels in 3-21G, 6-31G, 6-311G and 6-21G basis sets are calculated using gaussian 09. Correlation energy are calculated with equation 1. The results of these calculations are shown in tables 2 and 3. [4-9]

$$E_{\text{correlation}} = E_{\text{RMP2}} - E_{\text{RHF}} \quad (1)$$

To calculate the exchange energy, total optimized energy of  $C_7H_7NO$  at the restricted LSDA, B3LYP, PBEPBE, HF, MP2 levels in 3-21G, 6-31G, 6-311G and 6-21G basis sets are calculated. The average of energy differences in different levels is equal to exchange energies in the mentioned levels. The results of the exchange energy are shown in table 4 and 5.

The number of the primitives in 3-21G, 6-31G, 6-311G and 6-21G basis sets are 156, 226, 269 and 183 respectively. The correlation and exchange energies diagram in relation with the primitives number is drawn using Excell 2013 and using fitting method mathematical equations are exploited. The results are shown in the Figures 2 and 3.

Table 2 : The correlation energy calculated for  $C_7H_7NO$  at 3-21G, 6-31G, 6-311G and 6-21G basis sets

Basis set	$E_{HF} (au)^a$	$E_{MP2}(au)$	$E_{corr.}(au)=E_{MP2}-E_{HF}$
3-21g	-396.147	-396.981	-0.834
6-31g	-398.215	-399.054	-0.838
6-311g	-398.297	-399.196	-0.899
6-21g	-397.891	-398.725	-0.833

au :atomic unit

Table 3 : The primitive number and correlation energy calculated for  $C_7H_7NO$

Basis set	Primitive NO.	$E_{corr.}(au)$
3-21g	156	-0.834
6-31g	226	-0.838
6-311g	269	-0.899
6-21g	183	-0.833

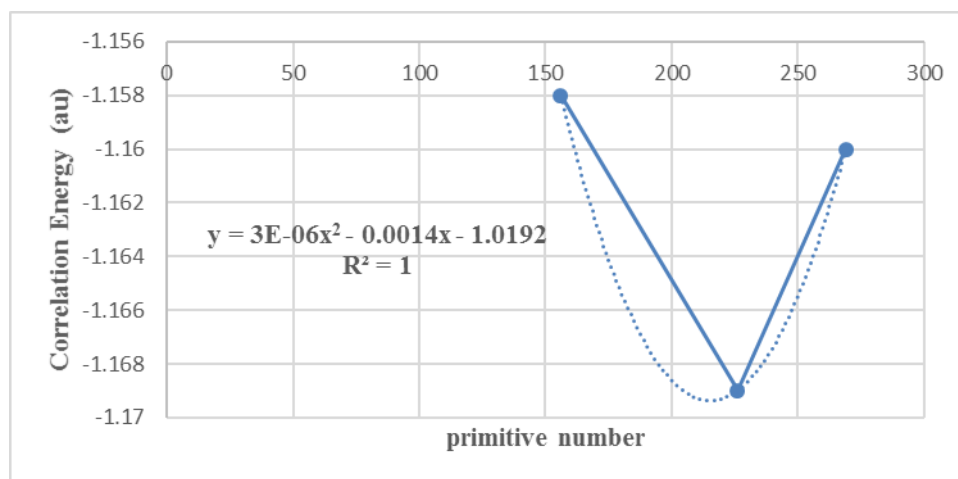


Figure2 : The Correlation Energy of the  $C_7H_7NO$  system as a primitive number at different levels of theory with 3-21G,6-31G,6-311G and 6-21G basis sets ( ..... Calculated data ,        fitted )



Table4:The exchange energy calculated for  $C_7H_7NO$  at 3-21G,6-31G,6-311G and 6-21G basis sets

method	total energy (au)				energy difference (au)			
	3-21g	6-31g	6-311g	6-21g	3-21g	6-31g	6-311g	6-21g
LSDA	-396.445	-398.525	-398.640	-398.193	-2.185	-2.211	-2.195	-2.203
B3LYP	-398.630	-400.736	-400.835	-400.396				
MPW1PW91	-398.532	-400.637	-400.725	-400.297	-0.098	-0.099	-0.110	-0.099
B3LYP	-398.630	-400.736	-400.835	-400.396				
PBEPBE	-398.142	-400.257	-400.352	-400.396	-0.488	-0.479	-0.483	0.000
B3LYP	-398.630	-400.736	-400.835	-400.396				
PBEPBE	-398.142	-400.257	-400.352	-400.396	-0.390	-0.380	-0.373	0.099
MPW1PW91	-398.532	-400.637	-400.725	-400.297				
LSDA	-396.445	-398.525	-398.640	-398.193	-2.087	-2.112	-2.085	-2.104
MPW1PW91	-398.532	-400.637	-400.725	-400.297				
LSDA	-396.445	-398.525	-398.640	-398.193	-1.697	-1.732	-1.712	-2.203
PBEPBE	-398.142	-400.257	-400.352	-400.396				
Average =Exchange Energy(au)					-1.158	-1.169	-1.160	-1.085

Table 5 : The primitive number and exchange energy calculated for C<sub>7</sub>H<sub>7</sub>NO

Basis set	Primitive NO.	Eexch. (au)
3-21g	156	-1.158
6-31g	226	-1.169
6-311g	269	-1.160
6-21g	183	-1.085

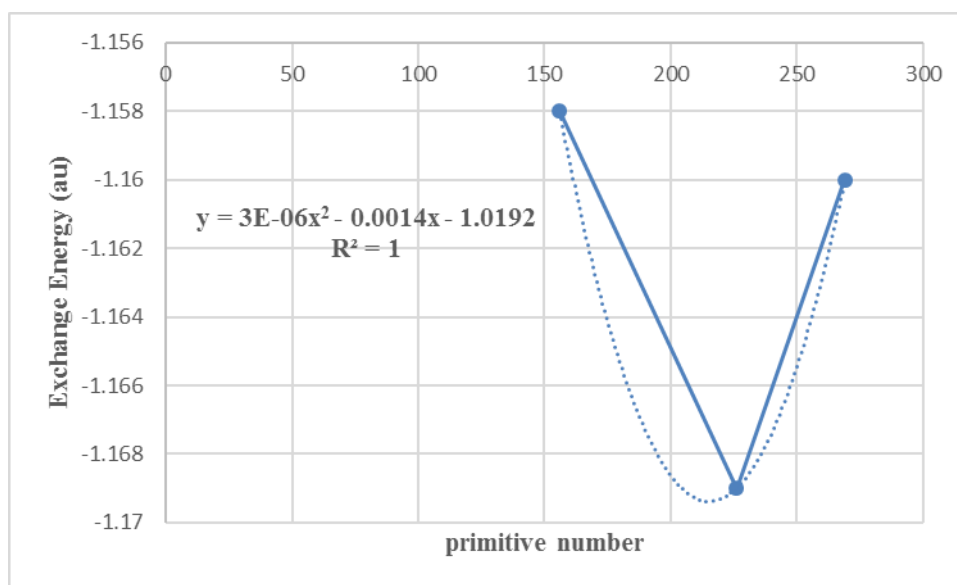


Figure3 : The Exchange Energy of the C<sub>7</sub>H<sub>7</sub>NO system as a primitive number at different levels of theory  
With 3-21G,6-31G,6-311G and 6-21G basis sets ( ..... Calculated data , fitted )

### NBO study on the structure of the C<sub>7</sub>H<sub>7</sub>NO:

NBO calculation are carried out using Gaussian 09 program at the B3LYP/6-31G level [8-9].

### Frontier molecular orbital:

Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability. The HOMO represents the ability to donate an electron , LUMO as an electron acceptor represents the ability to obtain an electron .The HOMO and LUMO energy were calculated by B3LYP/ 6-31G method . Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures. The large LUMO-HOMO gap is often concerned as a molecule stability condition . The LUMO-HOMO energies and energy gap were also calculated at the B3LYP/6-31G and the values are listed in table 6 , respectively.

Table 6 : Global chemical reactivity indices for C<sub>7</sub>H<sub>7</sub>NO at the level of B3LYP/6-31G theory

	B3LYP/6-31g
E total /hartree	-400.736
E HOMO/ev	-0.17968
E LUMO/ ev	-0.03742
E gap / ev	0.14226

### Chemical reactivity [4-6]:

The chemical reactivity descriptors calculated using DFT are ; total energy (E), chemical hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ), and Global electrophilicity index ( $\omega$ ). Chemical hardness is associated with the stability and reactivity of a chemical system. In a molecule it measures the resistance to change in the electron distribution or charge transfer. On the basis of frontier molecular orbitals, chemical hardness corresponds to the gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) . Chemical hardness is approximated using equation 2 . where  $\epsilon_{\text{LUMO}}$  and  $\epsilon_{\text{HOMO}}$  are the LUMO and HOMO energies. The larger the LUMO– HOMO energy gap, the harder and more stable/less reactive the molecule . Table 7 contains the computed chemical hardness value for C<sub>7</sub>H<sub>7</sub>NO .

$$\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) / 2 \quad (2)$$

Electronic chemical potential is defined as the negative of electronegativity of a molecule and determined using equation 3.

$$\mu = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}) / 2 \quad (3)$$

Physically,  $\mu$  describes the escaping tendency of electrons from an equilibrium system. The values of  $\mu$  for C<sub>7</sub>H<sub>7</sub>NO is presented in table 7. The greater the electronic chemical potential, the less stable or more reactive is the molecule. Global electrophilicity index ( $\omega$ ), introduced by Parr, is calculated using the electronic chemical potential and chemical hardness as shown in equation 4 .

$$\omega = \mu^2 / 2\eta \quad (4)$$

Electrophilicity index measures the propensity or capacity of a species to accept electrons [9,4]. It is a measure of the stabilization in energy after a system accepts additional amount of electronic charge from the environment[ 7]. The electrophilicity value (table 7) for C<sub>7</sub>H<sub>7</sub>NO is 0.08283 eV .

The HOMO and LUMO orbital energies are related to gas phase ionization potential (IP ) and electron affinity (EA) of C<sub>7</sub>H<sub>7</sub>NO according to the Koopmans' theorem through equations 5 and 6 . The ionization potential (IP) and electron affinity (A) values for C<sub>7</sub>H<sub>7</sub>NO are presented in table 7.

$$\text{EA} = -\epsilon_{\text{LUMO}} \quad (5)$$

$$\text{IP} = -\epsilon_{\text{HOMO}} \quad (6)$$

Table 7 :Global chemical reactivity indices for B<sub>12</sub>N<sub>12</sub> at the level of B3LYP/6-31G theory

E <sub>total</sub> /hartree	-400.736
E <sub>HOMO</sub> /ev	-0.17968
E <sub>LUMO</sub> / ev	-0.03742
E <sub>gap</sub> / ev	0.14226
μ / ev	-0.10855
η / ev	0.07113
ω / ev	0.08283
EA/ev	0.03742
IP/ev	0.17968

## CONCLUSION

DFT calculations are carried out using Gaussian 09 program. The structure of the molecule C<sub>7</sub>H<sub>7</sub>NO is totally optimized. A mathematical equation of second grade was exploited for the correlation and exchange energy with the number of primitives .

The electronic properties (IP, EA, μ, η, ω, E<sub>gap</sub>) are calculated by using B3LYP/6-31g and the values of these are 0.17968 ( ev ), 0.03742 (ev) , -0.10855 (ev) , 0.07113 (ev), 0.08283 (ev) and 0.14226 (ev) respectively .Therefore C<sub>7</sub>H<sub>7</sub>NO shows poor conductivity.

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