Theoretical study of HCX (NH₂) (X= O, S, and Se) analogues in gas phase: Electronic Structure, Natural Bond Orbital (NBO) & Natural Resonance Theory (NRT)

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ABSTRACT

This paper presents a comparative study was carried out on the physical-chemistry properties based on the ab initio calculations in the HCX (NH₂) analogues with 6-311++G (d, p) basis set in gas phase. Natural Bond Orbital (NBO) analysis of these molecules was carried out in order to understand the electronic structures and hybridization of the atoms at the same level of theory. The results showed the stabilization energies related to LpN → σ * C-X (X=O, S, Se) delocalization increase from X=O to X=Se that is in accordance with rise C–X bond length in the order C–Se> C–S > C–O. Also, the order of stabilization energies related to LpX → σ * N-C (X=O, S, Se) delocalization represented nucleophilisity property of selenium compounds is higher than sulfur compounds. The values of atomic charge confirmed these results. In this work, resonance weights derived from the Natural Resonance Theory (NRT), are also used to calculate "natural bond order,"

Keywords: HOMO-LUMO Orbitals; Natural Bond Orbital (NBO); Natural Resonance Theory (NRT); HCX (NH₂) (X=O, S, Se).

1. Introduction

A discrete atom or molecular fragment is a part of the molecule that can vary and it is called substitution. The substitution variation influences on a reaction or property in another part of molecules [1]. Effect of substitution on reactions or properties of molecular structures can obtain information about steric properties and electronic characteristics of substituents. Furthermore, unknown mechanisms and features of some chemical reactions can be evaluated by substitution effects [1].

At this current paper, the structural properties of formamide and its analogs have been evaluated. Formamide (H_2NCOH) meets the required criteria of abundance and diffusion in the Universe. The analysis of the molecular composition of comets-asteroids and of the interstellar clouds shows that the compounds made of the 4 more common and biologically relevant elements H, O, C, and N (excluding He) are isocyanate HNCO and formamide H2NCOH. Formamide was detected in the gas phase of interstellar medium [6], in the long period comet Hale-Bopp, and tentatively in the solid phase of grains around the young stellar object W33A. Also, it is one of the important molecules often used as a model of biological systems such as peptide and DNA structures, Formamide has been used as a softener for fiber and paper and as a solvent for ionic compounds, resins, and plasticizers [2-4]. Thioamide is one of the amides analogues known as a functional group. Thioamides display the multiple bond character along the C-N bond greater than amides and causing in a larger rotational barrier. Thioamide- containing drugs are also used to control thyrotoxicosis [5]. In the thyroid, thioamides can inhibit the enzyme thyroid peroxidase and the synthesis of triiodothyronine (T_3) and thyroxine (T_4) reduce [6-8]. The replacement of sulfur with selenium in the antihypertensive drug such as methimazole, leads to good compound which can inhibit thyroid hormones [6-7]. HCSe (NH_2) compound is another analogue of formamide. Some of compounds consists of selenium are as the efficient intermediates [9-

12]. In this research, molecular structure of HCX (NH$_2$) was evaluated using Natural Resonance Theory (NRT). NRT is a suitable method for demonstration of electron delocalization in molecules. The electron distribution, the chemical reactivity of molecules can predict using NRT. Also, this theory allows the estimation of relative stability of products, reaction intermediates, and reactants [13-15].

2. Computational Details

Computational methods of all computations are performed using software Gaussian [09W] [16] and spectral analysis using software [Gauss View 3.0]. Full optimization of the molecular geometry is obtained at level of MP2 / 6-311++G ** [17-19]. In this study, energy values of the Highest Occupied Molecular Orbital (E$_{HOMO}$), the Lowest Unoccupied Molecular Orbital (E$_{LUMO}$), the gap (ΔE), charge, bond order, bond type, hybridization, resonance, donor-acceptor interactions, were evaluated for HCX(NH$_2$) structures (X=O, S, Se) according to the same level of theory.

Table 1: The structures of HCX(NH$_2$) molecules (X=O, S, Se) were optimized at the MP2/6-311++G (d, p) level of theory. The absolute energies of these molecules are listed in Table 1.

Molecules	ZPE (Hartree/Particle)	Sum of Electronic and Zero point Energies
HCO(NH$_2$)	0.046124	-169.459524
HCS(NH$_2$)	0.044090	-492.029499
H CSe(NH$_2$)	0.043332	-2494.280312

3. Results and Discussion

3.1. Molecular geometry and Stability

We first optimized the studied structures without any symmetry constraints. For this purpose, optimized geometries were used to evaluate the frequencies. The global minimum of the structure was confirmed by gaining all positive frequencies. The optimized molecular structures of analogs HCX (NH_2) (X=O, S, Se) obtained from GAUSSIAN 09 is shown in Fig.1.

Table 2: Calculated structural parameters of HCX (NH_2) (X=O, S, Se) by MP2/6-311++G (d, p) level of theory

Geometry HCX (NH_2) (X=O, S, Se)

| Bond length Value (Å) $NH_2=CHO$		Bond length Value (Å) $NH_2=CHS$		Bond length Value (Å) $NH_2=CHSe$	
N1-C2	1.3688	N1-C2	1.355	N1-C2	1.349
C2-O3	1.2163	C2-S3	1.630	C2-Se3	1.779
C2-H4	1.1045	C2-H4	1.093	C2-H4	1.091
N1-H5	1.0097	N1-H5	1.010	N1-H5	1.011
N1-H6	1.0074	N1-H6	1.008	N1-H6	1.009
Value (°) Bond angle		Value (°) Bond angle		Value (°) Bond angle	
∠N1C2O3	124.747	∠N1C2S3	126.008	∠N1C2Se3	125.831
∠H4C2O3	122.823	∠H4C2S3	121.638	∠H4C2Se3	121.078
∠H5N1H6	117.885	∠H5N1H6	118.426	∠H5N1H6	118.644
Value (°) Dihedral angle		Value (°) Dihedral angle		Value (°) Dihedral angle	
∠ H5-N1-C2-O3	-12.360	∠ H5-N1-C2-S3	-8.107	∠ H5-N1-C2-Se3	-6.6187
∠H4-C2-N1-H5	169.915	∠H4-C2-N1-H5	173.883	∠H4-C2-N1-H5	175.080
∠O3-C2-N1-H6	-165.753	∠S3-C2-N1-H6	-170.688	∠Se3-C2-N1-H6	-172.051
∠H4-C2-N1-H6	16.522	∠H4-C2-N1-H6	11.301	∠H4-C2-N1-H6	9.589
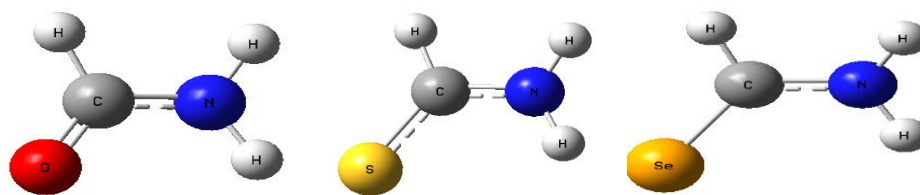
Fig.1. Optimized molecular structures studied by MP2/6-311++G**

3.2. *Frontier Molecular Orbital Analysis*

The most important of the frontier molecular orbitals (FMOs) such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbit play a significant role in molecular stability. The HOMO and LUMO energies are quantum mechanical descriptors. The frontier molecular orbitals (FMO) analysis provides precise and valuable information about the reactivity of a system [20-21]. The energy of HOMO implies the ability of a molecule to donate electrons and the energy of LUMO describes the electron accepting ability of a molecule. The energy gap between HOMO-LUMO indicates chemical reactivity, global Hardness (η) and global softness (σ) [21- 22]. The HOMO and LUMO pictures are shown in Fig. 2.
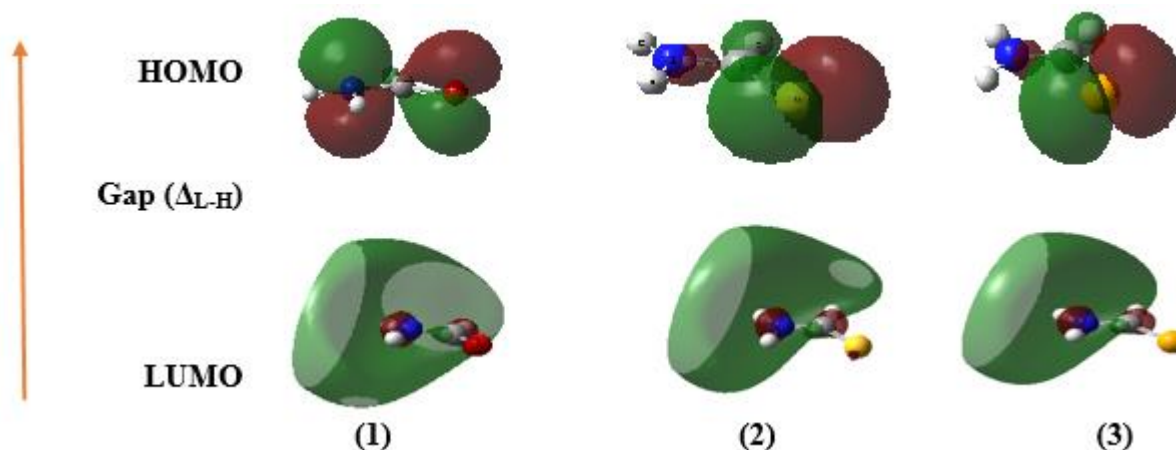

Fig. 2. HOMO - LUMO of orbitals of the HCX (NH$_2$) (X=O, S, Se) molecules with MP2/6-311++G**, respectively.

The energy difference between HOMO and LUMO called as H-L gap for HCO (NH$_2$), HCS (NH$_2$) and H CSe (NH$_2$) are 12.528, 9.928 and 9.245eV, respectively. The greater the LUMO -HOMO gap indicates larger stability with lesser chemical reactivity and vice versa. Thus, our calculations indicate that the H CSe (NH$_2$) is more reactive than other compounds. In fact, this decrease of H-L gap can be due to the decrease of the stability of H CSe (NH$_2$) structure that increases the orbital overlap between HOMO and LUMO [22].

Table.3. the energy values of the HOMO and LUMO of the HCX (NH$_2$) (X=O, S, Se) with MP2/6-311++G**.

Molecule	HOMO (eV)	LUMO (eV)	Gap (Δ_{L-H}) (eV)
H CO (NH$_2$) (1)	-0.42578	0.03462	0.46040
H CS (NH$_2$) (2)	-0.33459	0.03027	0.36486
H CSe (NH$_2$) (3)	-0.31084	0.02892	0.33976

The chemical properties of the molecules can be directly correlated to their electronic structures [23]. The quantum chemical parameters provide information about the chemical reactivity of our studied molecules. A hard molecule has a large energy gap (Eg) and a soft molecule has a small energy gap (Eg.) [24-25]. The η (Reaction Index), μ (Chemical potential) and σ (total softness) can be determined as follows [26-27]:

$$[\eta = (I-A)/2] \qquad (1)$$

$$[\mu = - (I+A)/2 = -\chi] \qquad (2)$$

$$[\sigma = 1/2\eta] \qquad (3)$$

Where A and I are ionization potential and electron affinity (EA), respectively. χ is also electronegativity. According to Koopman's theory ionization energy (IE = -EHOMO) and electron affinity (EA =-ELUMO) are generally [28]:

$$\eta = (E_{LUMO} - E_{HOMO})/2 \qquad (4)$$

$$\mu = (E_{HOMO} + E_{LUMO})/2 \qquad (5)$$

Table 4. MP2/6-311++G**calculated thermodynamic parameters [H, G (in a. u.) and S (in *Cal mol^{-1}K^{-1}*)] at 25°C and 1 atm pressure and quantum molecular descriptors for the analogs HCX (NH$_2$) (X=O, S, Se)

Geometry Molecular Descriptors	HCO(NH$_2$)	HCS(NH$_2$)	H CSe (NH$_2$)
H (a.u.)	-169.4550	-492.0248	-2494.27548
G (a.u.)	-169.4839	-492.0550	-2494.30711
S (*cal mol^{-1}K^{-1}*)	60.658	63.614	66.573
ε_{HOMO} (eV)	-0.4258	-0.3346	-0.3108
ε_{LUMO} (eV)	0.0346	0.0303	0.0289
$\Delta E_{(L-H)=}$ energy gap (Eg.) (eV)	0.4604	0.3649	0.3397
IP = -E$_{HOMO}$ (eV)	0.4258	0.3346	0.3108
EA = -E$_{LUMO}$ (eV)	-0.0346	-0.0303	-0.0289
(I-A)/2 (eV) = η	0.2302	0.1824	0.1699
(I+A)/2 (eV) = χ	-0.1898	-0.1370	-0.1409
μ = -χ (eV)	0.1898	0.1370	0.1409
σ = 1/η (eV^{-1})	4.3440	5.4259	5.8892
ω = χ^2/2η (eV)	0.0041	0.0017	0.0016
Dipole moment (μD) (Debye)	4.267	4.717	5.046

These values of dipole moment shows the considered molecules are highly polarized in nature. Ionization potential (IP) is a basic description of the chemical reactivity of atoms and molecules. The high IP value pertains to strong stability, thus HCSe (NH$_2$) has lower IP energy than other two molecules. According to the calculations performed in these molecules the hardness (η) corresponds to the gap between the HOMO and LUMO orbital. The hardness (η), the amount of energy in the gap also decreases. The electrophilicity index ($\omega = \chi^2/2\eta$) contains information about both electron transfer (chemical potential) and stability (hardness) and is a better descriptor of global chemical reactivity [29- 31]. The higher value of electrophilicity index displays the high capacity of the molecule to accept electrons, it seems that closely related to electronegativity, i.e. Electrophilicity index measures the propensity or capacity of a species to accept electrons. It is a mea sure of the stabilization in energy after a

system accepts additional amount of electronic change from the environment [30] .The electrophilicity index for structures **1, 2** and **3** are 0.0041, 0.0017, and 0.0016 eV, respectively. The structure **1** has the highest electrophilicity index; therefore it has high capacity for acceptance electrons. Also, the electrophilicity seems to depend on ionization potential (EA) [31], Table 4 shows the similar trend of the decrease of values in EA and ω. Dipole moment *(μD)* is a suitable measure for the asymmetric nature of the molecular structure [32]. Dipole moment of structures **1, 2** and **3** are 4.267, 4.717 and 5.046 Debye. Therefore structure **3** has the highest value of dipole moment (5.046 Debye) which refers high asymmetry in the structure and irregularly arranged which gives rise to the increased dipole moment. Analysis of data respects that by replacing atoms from O to Se in HCX (NH_2) structure, bond length of C-X (X=O, S, Se) increases, total dipole moment and hardness decrease. Thus the separation of charge has direct influence on reactivity [33-34]. When dipole moment increases, the hardness decreases and reactivity rises. These results were shown in table 5 and Figure 3.

Table 5. Relationship between bond lengths of C-X, hardness and dipole moments in HCX (NH_2) (X=O, S, Se)

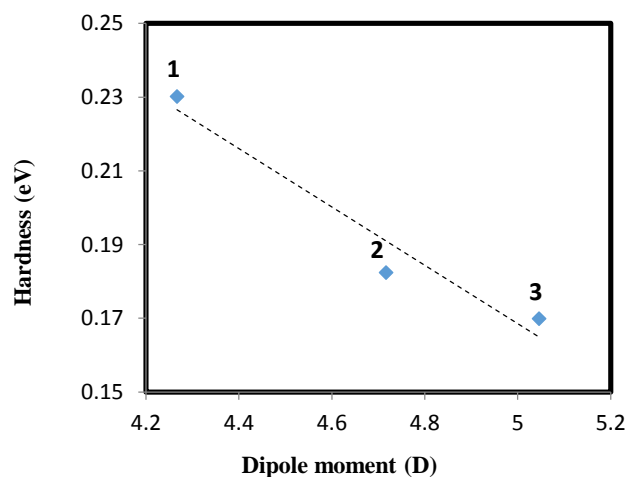| Molecule	C-X bond length (Å)	hardness (η, eV)	dipole moments (μD)
H CO (NH_2) (1)	1.2163	0.2302	4.267
H CS (NH_2) (2)	1.630	0.1824	4.717
H CSe (NH_2) (3)	1.779	0.1699	5.046

Fig.3. Relationship of Hardness and dipole moment showing a linear correlation represented by:
$$y = -0.0791x + 0.5642 \; with \; R^2 = 0.9451$$

3.3. Vibrational frequency and IR spectrum analysis

The molecular vibrations can be identified using infrared spectroscopy (IR) [35]. The second derivative of the molecular energy plays an important role calculation of the vibrational frequencies. In Gaussian calculation, the Hessian matrix or second derivative matrix can give information about a maximum, minimum, or saddle point [36]. Infrared spectroscopy can be evaluated not only chemical structure but also the peaks of functional groups for the targeted systems [37].

The molecular structures of analogs $HCX (NH_2)$ (X=O, S, Se) belong to C1 group pointe symmetry. The molecules considered consist of 6 atoms and have 12 normal modes of vibration of the same. A species under C1 Symmetry (3N-6). IR spectra of the variation of frequency of the studied systems are presented in Fig.4.

The lowest possible quantum state of molecule can never have zero oscillation energy, that is, vibrations of bonding atoms can never be completely zero at rest in relation to each other. The energy of the zero point, $E_{ZPE,}$ depends on the vibrational frequency and the bond strength in a chemical bond and atomic masses [38]. When reduced the mass by changing the

atomic mass of the individual atoms in the molecule, then the frequency also changes. As a result, take place changing in force constant [39].

Reducing vibrating frequencies from molecules 1 through 3 represents a reduction in bond energy. Consequently, the studied HOMO-LUMO energy gap reveals that reducing vibrating frequencies is closely related to the increase the length of the bond from molecules 1 through 3.
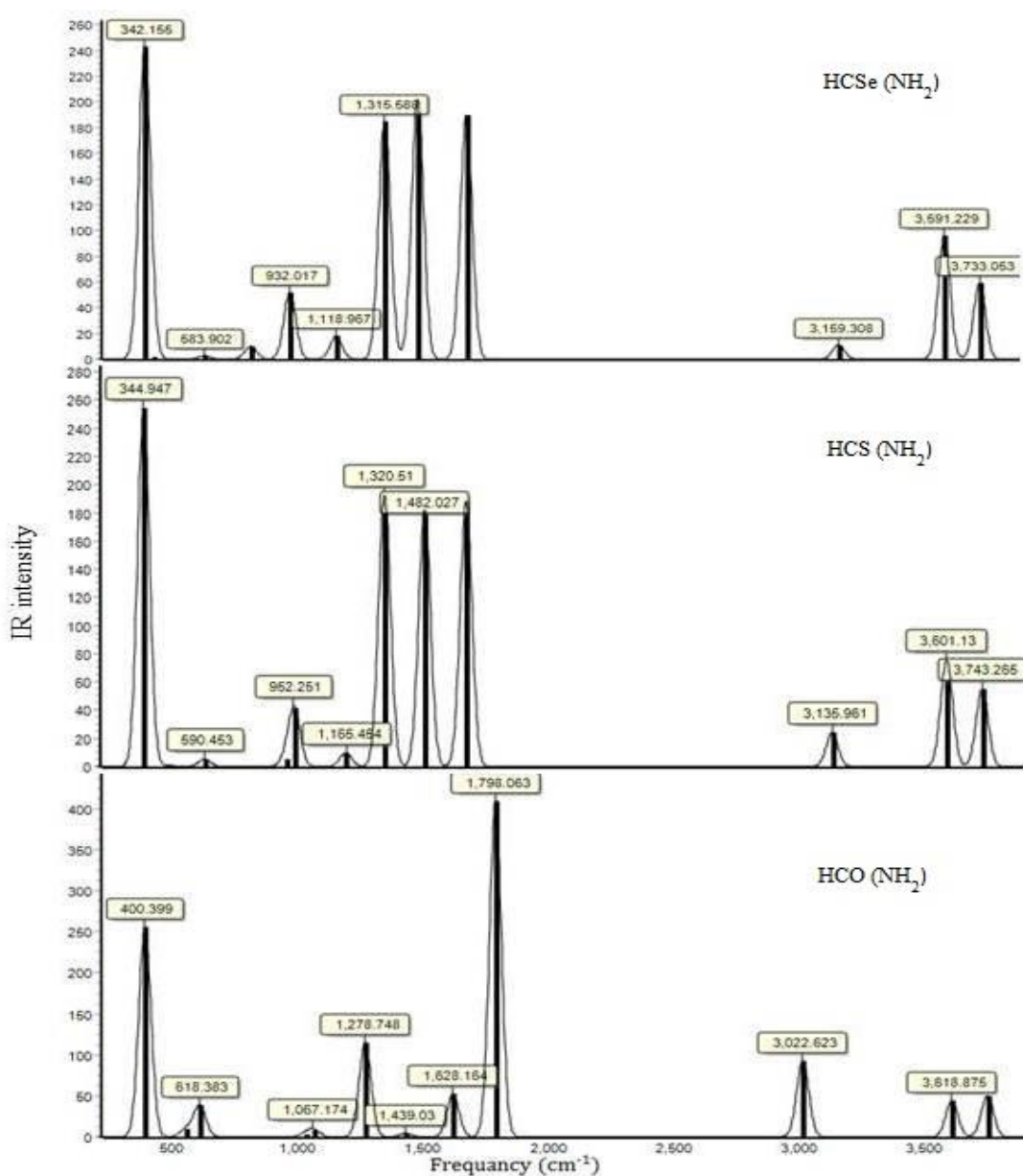

Fig.4. IR spectrum of the HCX (NH$_2$) (X=O, S, Se)

Table 6. *ZPE*(Hartree/Particle), *Harmonic frequencies* (cm^{-1}), *Energy gap* (Eg.) (eV), *force constants* (mDyne/A), and *reduced masses*(AMU) in MP2/6-311++G**method.

Molecules	ZPE (Hartree/Particle)	Harmonic frequencies (cm^{-1})	Energy gap (Eg.) (eV)	force constants (mDyne/A)	reduced masses (AMU)
HCO(NH$_2$)	0.046124	400.2190	0.4604	0.1135	1.2030
HCS(NH$_2$)	0.044090	344.4349	0.3649	0.0834	1.1936
HCSe(NH$_2$)	0.043332	341.3776	0.3397	0.0818	1.1920

3.4. Natural Bond Orbital (NBO)

NBO program under Gaussian 09 software package was used to perform the Mulliken population analysis by the natural bond orbital method at MP2 method with 6-311++G (d, p) basis set. With the help of second-order perturbation theory, the donor and acceptor occupancies with their interaction energies received during the process were reported.

Natural bond orbital studies, provides a resourceful method for analyzing intra- and intermolecular bonding and interaction among bonds in the molecule. The NBO analysis is an appropriate source for analyzing charge transfer or conjugative interaction in molecular system [40]. In Weinhold's NBO calculation, hyperconjugation has a stabilizing effect that arises from delocalization of electron density from filled (bonding or lone pair) Lewis type NBO to another neighboring electron deficient orbital (non-Lewis type NBO, such as antibonding or Rydberg) when these orbitals are aptly oriented [weinhold,2017]. For each donor NBO (i) and acceptor NBO (j), stabilization energy can be described by means of second-order perturbation interaction energy E (2) and estimated by the following equation:

$$E(2) = \Delta E_{ij} = q_i \frac{F^2_{(ij)}}{\varepsilon_j - \varepsilon_i} \qquad (6)$$

Where q$_i$ is the donor orbital occupancy ε_i and ε_j are diagonal elements (orbital energies) and F$_{(i,j)}$ is the off-diagonal NBO Fock matrix elements. The larger the E(2) value, the more drastic is the interaction between the ''filled'' (donor) Lewis-type NBOs and ''empty''

(acceptor) non-Lewis NBOs [weinhold,2001, 2012, Reed]. The natural bonding orbital (NBO) analysis is an effective method for studying the intra- and inter-molecular bonding and also it is a measure of hyper conjugation [41-42].

The values of the larger E(2) reveals that interactions between electron donors and electron orbital receptors are more severe. The perturbation energies of donor- acceptor interactions (E2) are shown in Table 7. The NBO analysis indicated that energies of $LP_{(2)O3} \rightarrow \sigma^*_{N1-C2}$ and $LP_{(1)N1} \rightarrow \pi^*_{C2-O3}$ interactions are the most important interactions in $NH_2=CHO$ molecule, that related to the resonance in the molecules. These are donor- acceptor electrons such as the LP (1) N atom of electron donating group to the anti-bonding acceptor π^*(C-O) that energy of the interaction is shown as $\varepsilon_{LP(1)N1 \rightarrow \pi^*(C2-O3)} = 25.50$ Kcal/mol. The larger energy shows the hyper conjugation between the electron donating nitrogen and the carboxyl group. These interactions give stronger stabilization to the $NH_2=CHO$ structure.

Table 5 listed donor and acceptor natural orbitals. The natural orbitals are classed as the Lewis—type orbitals (σ, π or lone pair), the valence non-Lewis orbitals and the Rydberg orbitals [Gangadharan R. P.,2014]. The main natural bond orbitals (NBO) analysis showed that total stabilization energy for LP (1) N $\rightarrow$ π^* or σ^* delocalization increases with increasing p character (hybrid on Nitrogen) of considering atoms lone pair [43], i.e. Compounds that form C-X (X=O, S, and Se) -bonds can illustrate $SP^{6.02}$, $SP^{50.54}$ and $Sp^{99.99}$ hybrid, respectively. In contrast, the occupancy of the LP (1) N decreases with increasing p character of the lone pair of considering atoms and their occupancies are 1.74045, 0.75838, and 1.46176, respectively [Table 7]. As well as, elements of Sixth group (Group 6A) including O has pretty high electronegativity that of the charge value increases along with electronegativity because the nature of the intense electron withdrawing of O atom leads to an increase in self-centered electrons

Table 7. NBO analysis results for molecules 1, 2, and 3 at MP2/6-311++G** level

Molecules	Donor NBO	Acceptor NBO	q i→j a.u.	E(2) kcal/mol	E(j)-E(i) a.u.	F(i.j) a.u.
	LP (2) O3	σ* N1 - C2	1.93786	29.68	1.15	0.167
HCO (NH$_2$)	LP (1) N1	π*C2 – O3	1.71264	25.50	0.91	0.139
	LP (1) N1	σ*C2 – O3	1.74045	19.17	1.04	0.130
	LP (2) S 6	σ* N1 - C2	0.93496	9.11	1.02	0.123
HCS (NH$_2$)	LP (1) N1	σ*C 2 – S6	0.75838	47.61	1.03	0.063
	LP (2) Se 6	σ* N1 - C2	1.89125	14.37	1.01	0.109
HCSe(NH$_2$)	LP (1) N1	σ*C2 – Se6	1.46176	114.02	0.46	0.204

The transfer of charges from the lone-pair (LP(1)N1) to the anti-bonding orbital π*(C2-O3) increase the population at π*(C2-O3) accounting for the stabilization of 25.50 Kcal.mol^{-1} which in this molecule energy of charge corresponds to the gap between the HOMO and LUMO orbital energies. Also, the results show that the NCX angle from O to Se does not have the same trend, which is consistent with the LpX → σ * N-C transitions in NBO analysis. Stabilization energies

LUMO

HOMO
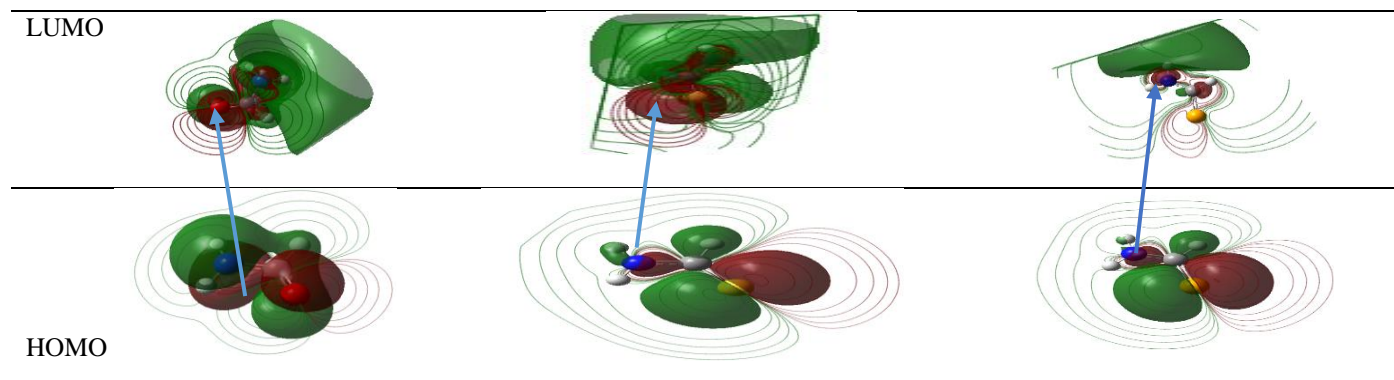
LP1 N1→π*C2-O3	LP1 N1→σ*C2-S6	LP1 (1)N→σ*C2-Se 6
LP2 O3→π* N1 - C2	LP2 S6→σ* N1 - C2	LP2 Se6→σ* N1 - C2
sp$^{24.31}$(96.02%) →sp$^{6.02}$ (85.21%)	sp$^{1.48}$(53.29%)→ sp$^{50.54}$(97.56%)	sp$^{73.23}$(98.62%)→ sp$^{99.99}$(99.40%)
sp$^{99.99}$(99.90%) →sp$^{1.66}$(62.39%)	sp$^{99.99}$(99.88%)→ sp$^{1.48}$(59.71%)	sp$^{99.99}$(99.81%)→ sp$^{1.45}$(59.08%)
NH_2=CHO	NH_2=CHS	NH_2=CHSe

Fig.5. HOMO-LUMO plot of NH_2=CHX(X=O, S, Se)

related to LpX → σ * N-C delocalization for HCX (NH_2) (X=O, S, Se) are 29.68, 9.11 and 14.37 Kcal.mol^{-1}, respectively. This trend is similar to the changes of bond order in C–X. The LpX →σ * N-C donor-acceptor interactions seem to effect on π bonds in C–N [27]. Previous research has shown that the nucleophilicity of selenium is higher than that of sulfur, so it is more active and reactive [Kaur,2007; Wei,2010; Reich, 2016]. The electronegativity of X atoms is a significant factor of reactivity. Equation 7 can be used to predict electronegativity (EN) of X atom in molecule [Wei, 2010]. The equation 7 was proposed by Luo and Benson where r is the covalent radius in Angstrom for atom (table 4) and n is the number of valence electrons.

$$EN = \frac{n}{r} \qquad (7)$$

According equation 7 and bond length of C–X in table 4, the electronegativity of X atom (X=O, S, and Se) decreases in the order O> Se > S. This is in accordance with trend electronegativity of structures and LpX → σ * N-C delocalization. Table 4 shows that the electronegativity of HCX (NH_2) structures also has a similar trend to E(2) of LpX → σ * N-C delocalization. Also, the stabilization energies related to LpN → σ * C-X (X=O, S, Se) delocalization for HCX (NH_2) are 19.17, 47.61 and 114.02 Kcal.mol^{-1}, respectively. Oxygen has high electronegativity and low polarizability [Kaur,2007;], therefore the E(2) values for

X=O can be smaller. A strong LpN → σ * C-X electron delocalization tends to weaken C-X bond and it can decrease the bond length character of the C–N bond, because there is an overlapping between LpN non-bonding and σ * C-X antibonding orbitals. Also, it is noteworthy that the increase in the size of the atoms (X=O, S, Se) weakens C-X bond.

3.5. Determine the Value of Resonance

Resonance weights derived from the Natural Resonance Theory (NRT), are used to calculate "natural bond order," "natural atomic valency," and other atomic and bond indices reflecting the resonance composition of the wave function. Using the data in the Table 5 below, the resonance structures and the resonance percentage in these compounds can be shown. There are commands in the output file to draw resonant structures. According to the Table 8, if we want to draw the resonance of structure 1, a bond between C-N can be added and a bond removed from C-O, and a pair of nonbonding electrons must be removed from N atom and placed on the O atom.

Table 8. Resonance values and order of resonant structures

```
        Resonance
 RS     weight(%)                    Added(Removed)
---------------------------------------------------------------
 1*(4)   66.33
 2*(2)   27.62     N  1- C  2, ( C  2- O  3), ( N  1),  O  3
 3 (2)    1.97     C  2- O  3, ( C  2- H  4), ( O  3),  H  4
 4 (2)    1.88    ( N  1- C  2),  C  2- O  3,  N  1, ( O  3)
 5        0.87     N  1- C  2, ( C  2- H  4), ( N  1),  H  4
 6        0.35     N  1- C  2, ( N  1- H  5), ( C  2- H  4),  H  5
 7 (2)    0.29     N  1- C  2, ( N  1- H  6), ( C  2- O  3),  O  3
 8        0.20     N  1- C  2, ( N  1- H  6), ( C  2- O  3),  H  6
 9        0.17     N  1- C  2,  N  1- C  2, ( N  1- H  5), ( C  2- O  3),
                  ( C  2- H  4), ( N  1),  O  3,  H  5
10-13     0.32
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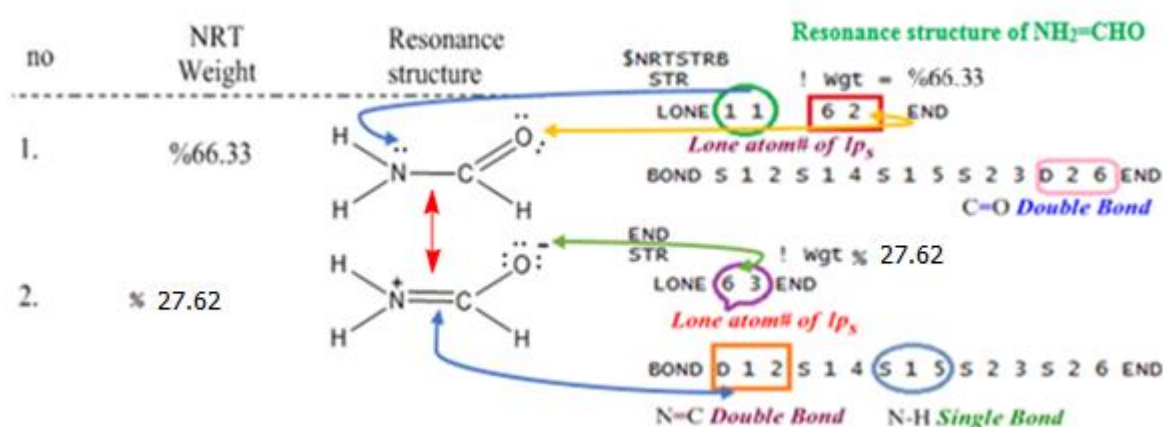


```
        Resonance
 RS     weight(%)                    Added(Removed)
---------------------------------------------------------------
 1*(2)   64.03
 2*      30.07     N  1- C  2, ( C  2- S  6), ( N  1),  S  6
 3        1.52    ( N  1- C  2),  C  2- S  6,  N  1, ( S  6)
 4        1.49    ( C  2- H  3),  C  2- S  6,  H  3, ( S  6)
 5        0.75     N  1- C  2, ( C  2- H  3), ( N  1),  H  3
 6        0.45     N  1- C  2, ( N  1- H  4), ( C  2- H  3),  H  4
 7        0.43     N  1- C  2, ( N  1- H  5), ( C  2- S  6),  S  6
 8        0.41     N  1- C  2, ( N  1- H  5), ( C  2- S  6),  H  5
 9        0.26     N  1- C  2,  N  1- C  2, ( N  1- H  5), ( C  2- S  6),
                  ( C  2- S  6), ( N  1),  S  6,  S  6
10        0.23     N  1- C  2,  N  1- C  2, ( N  1- H  4), ( C  2- H  3),
                  ( C  2- S  6), ( N  1),  H  4,  S  6
11        0.18     N  1- C  2,  N  1- C  2, ( N  1- H  5), ( C  2- S  6),
```
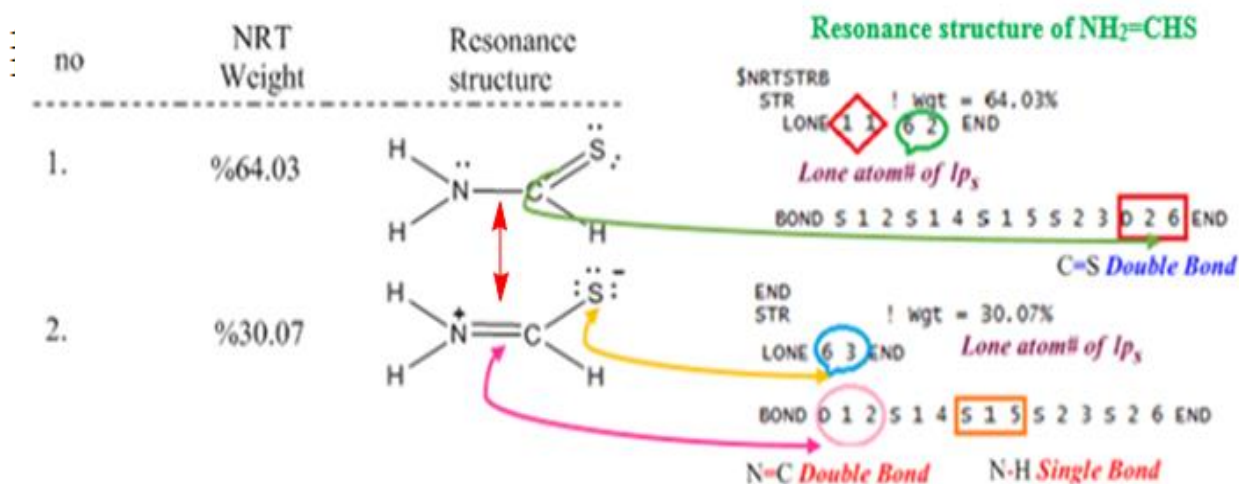
```
         Resonance
  RS    Weight(%)                        Added(Removed)
-------------------------------------------------------------------------------
  1*(2)   59.95
  2*      34.96     N  1- C   2, ( C   2-Se   6), ( N   1), Se   6
  3        1.20   ( N   1- C   2),   C   2-Se   6,   N   1, (Se   6)
  4        1.11   ( C   2- H   3),   C   2-Se   6,   H   3, (Se   6)
  5        0.65     N  1- C   2, ( C   2- H   3), ( N   1),   H   3
  6        0.44     N  1- C   2, ( N   1- H   5), ( C   2-Se   6),   H   5
  7        0.44     N  1- C   2, ( N   1- H   4), ( C   2- H   3),   H   4
  8        0.36     N  1- C   2, ( N   1- H   5), ( C   2-Se   6), Se   6
  9        0.27     N  1- C   2,   N  1- C   2, ( N   1- H   4), ( C   2- H   3),
                  ( C   2-Se   6), ( N   1),   H   4, Se   6
 10        0.25     N  1- C   2,   N  1- C   2, ( N   1- H   5), ( C   2-Se   6),
                  ( C   2-Se   6), ( N   1),   H   5, Se   6
 11        0.16     N  1- C   2,   N  1- C   2, ( N   1- H   5), ( C   2-Se   6),
                  ( C   2-Se   6), ( N   1), Se   6, Se   6
 12        0.11     N  1- C   2, ( N   1- H   4), ( C   2- H   3),   H   3
 13-15     0.08
```
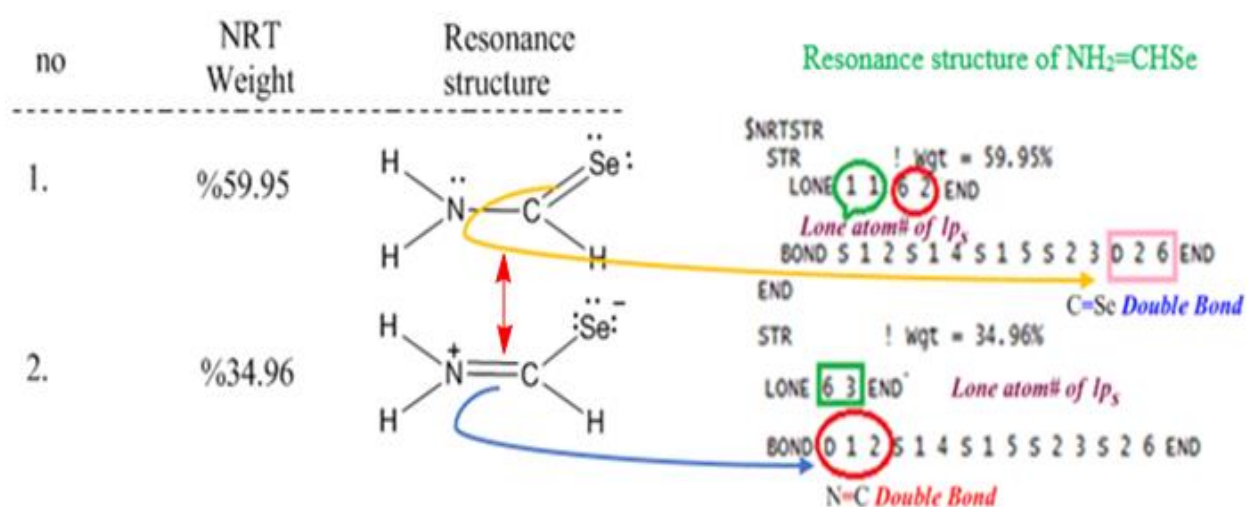

3.6. Natural Bond Order

One another application of NBO output is determining Bond order and evaluation of covalence and ionic properties along with their percentage. According to results of Table 6 are presented bond orders and theirs structures from molecules 1 through 3. When ionic and polar compounds are described, there is a particular difficulty in Pauling-Whelan resonance theory, for this reason covalent and ionic resonance structures need to be attributed to molecules that are described by a single Lewis structure formula. To solve this problem, the polarity of the bond must be indicated by ''ionic-covalent resonance''. It must be considered that the Heitler-London VB pair function explains homopolar bonds ''pure covalent'' bonding [44-46].
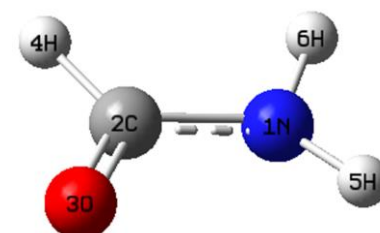
```
Natural Bond Order:  (total/covalent/ionic)

    Atom      1      2      3      4      5      6
    ----    ------ ------ ------ ------ ------ ------
 1.  N  t  0.7298 1.2836 0.0000 0.0000 0.9932 0.9933
        c    ---  0.7836 0.0000 0.0000 0.5956 0.6078
        i    ---  0.5000 0.0000 0.0000 0.3976 0.3856

 2.  C  t  1.2836 0.0000 1.7515 0.9649 0.0000 0.0000
        c  0.7836   ---  1.0392 0.8516 0.0000 0.0000
        i  0.5000   ---  0.7123 0.1133 0.0000 0.0000

 3.  O  t  0.0000 1.7515 2.2458 0.0000 0.0000 0.0000
        c  0.0000 1.0392   ---  0.0000 0.0000 0.0000
        i  0.0000 0.7123   ---  0.0000 0.0000 0.0000

 4.  H  t  0.0000 0.9649 0.0000 0.0298 0.0000 0.0000
        c  0.0000 0.8516 0.0000   ---  0.0000 0.0000
        i  0.0000 0.1133 0.0000   ---  0.0000 0.0000

 5.  H  t  0.9932 0.0000 0.0000 0.0000 0.0053 0.0000
        c  0.5956 0.0000 0.0000 0.0000   ---  0.0000
        i  0.3976 0.0000 0.0000 0.0000   ---  0.0000

 6.  H  t  0.9933 0.0000 0.0000 0.0000 0.0000 0.0027
        c  0.6078 0.0000 0.0000 0.0000 0.0000   ---
        i  0.3856 0.0000 0.0000 0.0000 0.0000   ---
```

N1-H6: 0.60 Covalent +0.40 ionic=1.00 Total

N1-C2: 0.78 Covalent +0.50 ionic=1.28 Total
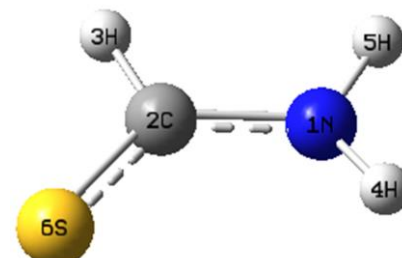
C2-O3:1.04 Covalent +0.71 ionic=1.75 Total


```
Natural Bond Order:  (total/covalent/ionic)

    Atom      1      2      3      4      5      6
    ----    ------ ------ ------ ------ ------ ------
 1.  N  t  0.3498 0.6609 0.0000 0.4958 0.4936 0.0000
        c    ---  0.4155 0.0000 0.2925 0.2975 0.0000
        i    ---  0.2454 0.0000 0.2032 0.1961 0.0000

 2.  C  t  0.6609 0.0000 0.4845 0.0000 0.0000 0.8546
        c  0.4155   ---  0.3956 0.0000 0.0000 0.6005
        i  0.2454   ---  0.0889 0.0000 0.0000 0.2541

 3.  H  t  0.0000 0.4845 0.0121 0.0000 0.0000 0.0000
        c  0.0000 0.3956   ---  0.0000 0.0000 0.0000
        i  0.0000 0.0889   ---  0.0000 0.0000 0.0000

 4.  H  t  0.4958 0.0000 0.0000 0.0034 0.0000 0.0000
        c  0.2925 0.0000 0.0000   ---  0.0000 0.0000
        i  0.2032 0.0000 0.0000   ---  0.0000 0.0000

 5.  H  t  0.4936 0.0000 0.0000 0.0000 0.0030 0.0000
        c  0.2975 0.0000 0.0000 0.0000   ---  0.0000
        i  0.1961 0.0000 0.0000 0.0000   ---  0.0000

 6.  S  t  0.0000 0.8546 0.0000 0.0000 0.0000 1.1424
        c  0.0000 0.6005 0.0000 0.0000 0.0000   ---
        i  0.0000 0.2541 0.0000 0.0000 0.0000   ---
```

N1-H5: 0.30 Covalent +0.20 ionic=0.5 Total

N1-C2: 0.42 Covalent +0.25 ionic=0.67 Total

C2-S6:0.60 Covalent +0.25 ionic=0.85 Total

```
Natural Bond Order:  (total/covalent/ionic)

     Atom      1       2      3       4      5      6
     ----   ------  ------ ------  ------ ------ ------
  1.  N   t 0.6482 1.3730 0.0000  0.9909 0.9879 0.0000
          c   ---   0.8463 0.0000  0.5800 0.5926 0.0000
          i   ---   0.5267 0.0000  0.4110 0.3953 0.0000

  2.  C   t 1.3730 0.0000 0.9733  0.0000 0.0000 1.6537
          c 0.8463   ---   0.7948  0.0000 0.0000 1.0525
          i 0.5267   ---   0.1784  0.0000 0.0000 0.6013

  3.  H   t 0.0000 0.9733 0.0196  0.0000 0.0000 0.0000
          c 0.0000 0.7948   ---   0.0000 0.0000 0.0000
          i 0.0000 0.1784   ---   0.0000 0.0000 0.0000

  4.  H   t 0.9909 0.0000 0.0000  0.0071 0.0000 0.0000
          c 0.5800 0.0000 0.0000    ---   0.0000 0.0000
          i 0.4110 0.0000 0.0000    ---   0.0000 0.0000

  5.  H   t 0.9879 0.0000 0.0000  0.0000 0.0069 0.0000
          c 0.5926 0.0000 0.0000  0.0000   ---   0.0000
          i 0.3953 0.0000 0.0000  0.0000   ---   0.0000

  6. Se   t 0.0000 1.6537 0.0000  0.0000 0.0000 2.3394
          c 0.0000 1.0525 0.0000  0.0000 0.0000   ---
          i 0.0000 0.6013 0.0000  0.0000 0.0000   ---
```

N1-H5: 0.59 Covalent +0.40 ionic=0.99 Total

N1-C2: 0.85Covalent +0.53 ionic=1.38 Total

C2-Se6:1.05 Covalent +0.60 ionic=1.65 Total
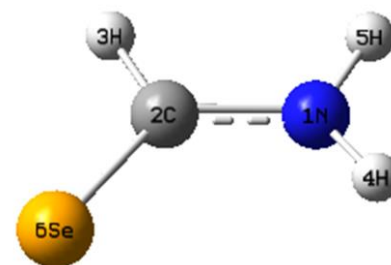
Well known, that one of the most important applications of NBO outputs is to determine the bond order and to determine the ionic or covalent properties and to calculate their percentage. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap. Also, the bond order has a strong relationship with the bond length. Higher bond orders have shorter bond length and consequently, the bond strength will increase. In the studied molecules, the C-X (X = S, and Se) bond order will be weaker than the C–X bond, because the bond strength increases with increasing bond polarity and size. The trend of the C-X (X = S, and Se) bond order is in accordance with electron delocalization of LpX $\rightarrow$ σ * N-C.

3.7. Natural population analysis

-Charges and Charge Transfer (CT)

The calculation of atomic charges plays a quintessence role in the application of quantum chemical calculation in the molecular system [47]. It is observed that atomic charges affected the number of molecular properties. The accrual of charges on the individual atom and the accumulation of electron in the core, valence and Rydberg subshells are presented in Table 9.

Table 9 :Representation of accrual of charges on atoms in HCX (NH$_2$) (X=O, S, Se)

Molecules

	HCO (NH$_2$)			HCS (NH$_2$)			H CSe (NH$_2$)	
Atoms	Number of atom	atomic charges	Atoms	Number of atom	atomic charges	Atoms	Number of atom	atomic charges
N	1	-0.86741	N	1	-0.40823	N	1	0.80842
C	2	0.69311	C	2	0.03416	C	2	0.02694
O	3	-0.69374	H	3	0.08094	H	3	0.16573
H	4	0.08955	H	4	0.20017	H	4	0.40474
H	5	0.39413	H	5	0.19517	H	5	0.39222
H	6	0.38436	S	6	-0.10220	Se	6	-0.18120

From comparison of Table 7 values, it has been found that most electronegative charge of -0.86741 and -0.69374 e is accumulated on N1 and O3 atoms and most electropositive charge of 0.69311 and 0.39413 is collected on C2 and H5 atoms in NH$_2$=CHO molecule. According to electrostatic point of view of the molecule, most electronegative atoms have the inclination to donate an electron, whereas, most electropositive atoms have the tendency to accept an electron.

Table 7 shows that Charge of X atom decreases in the order O> Se> S. This trend represents that the nucleophilicity of selenium is higher than that of sulfur and it is in accordance with trend LpX → σ * N-C delocalization. The charge of N in HCX (NH$_2$) structures decreases from X=O to X=Se that is in accordance with trend LpN → σ * C-X delocalization.

The natural population analysis shows that electrons in the HCX (NH$_2$) (X=O, S, Se) molecule are distributed on the subshell as follows:

Depending on the electronegativity of the atom in the bond, the natural charge is positive or negative and the molecule is neutralized. The electronic population of all atomic orbitals are

specified in this table 9, and the atomic number is estimated according to the total electron population of each atom.

Table 10: Representation of electronic population of all atomic orbitals in HCX (NH_2) (X=O, S, Se)

HCO (NH_2)
Core: 5.99899 (99.9831% of 6) **Valence**: 17.90843 (99.4913% of 18) **Rydberg**: 0.09259 (0.3858% of 24) Total 24.00000

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
N	1	-0.86741	1.99954	5.85232	0.01555	7.86741
C	2	0.69311	1.99968	3.25351	0.05370	5.30689
O	3	-0.69374	1.99977	6.67840	0.01557	8.69374
H	4	0.08955	0.00000	0.90747	0.00298	0.91045
H	5	0.39413	0.00000	0.60335	0.00251	0.60587
H	6	0.38436	0.00000	0.61337	0.00227	0.61564
* Total *		0.00000	5.99899	17.90843	0.09259	24.00000

HCS (NH_2)
Core: 6.99910 (99.9872% of 7) **Valence**: 8.94047 (99.3385% of 9) **Rydberg**: 0.06043 (0.3777% of 16)

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
N	1	-0.40823	0.99974	2.89745	0.01104	3.90823
C	2	0.03416	0.99978	1.94098	0.02508	2.96584
H	3	0.08094	0.00000	0.41749	0.00157	0.41906
H	4	0.20017	0.00000	0.29809	0.00175	0.29983
H	5	0.19517	0.00000	0.30340	0.00143	0.30483
S	6	-0.10220	4.99959	3.08305	0.01956	8.10220
* Total *		0.00000	6.99910	8.94047	0.06043	16.00000

HCSe (NH_2) (X=O, S, Se)

Core: 31.99699 (99.9906% of 32) **Valence**: 17.88839 (99.3799% of 18) **Rydberg**: 0.11462 (0.2292% of 50).

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
N	1	-0.80842	1.99947	5.78453	0.02443	7.80842
C	2	0.02694	1.99956	3.93051	0.04299	5.97306
H	3	0.16573	0.00000	0.83068	0.00359	0.83427
H	4	0.40474	0.00000	0.59223	0.00304	0.59526
H	5	0.39222	0.00000	0.60505	0.00274	0.60778
Se	6	-0.18120	27.99797	6.14539	0.03783	34.18120
* Total *		0.00000	31.99699	17.88839	0.11462	50.00000

Mulliken atomic charges

Mulliken charges determine the electron population of each atom discussed in the basic functions. The Mulliken charges calculated at same basic set are listed in Table 10. The formation of donor and acceptor pairs involving the charge transfer in the molecules can be suggested from the charge distribution over the atoms [48]. In Table 10, Mulliken atomic charges at different atoms for studied molecules computed by MP2 method by 6-311++G ** basis set.

Mulliken atomic charges of molecules

HCO (NH$_2$)			HCS (NH$_2$)			H CSe (NH$_2$)		
N	1	-0.430357	N	1	-0.335002	N	1	-0.278041
C	2	0.233061	C	2	0.036780	C	2	-0.127402
O	3	-0.436900	H	3	0.214407	H	3	0.163167
H	4	0.105151	H	4	0.279246	H	4	0.268536
H	5	0.278277	H	5	0.266917	H	5	0.277317
H	6	0.250769	S	6	-0.462348	Se	6	-0.303577

From Table 1, it is exact to state that in these molecules, C2 and Hs atoms exhibit positive charges while N1, O, S, and Se atoms exhibit negative charges. It can be seen that the C2 and Hs are electron deficient by this the methods. Further, It causes that the population of hydrogen atoms decreases and have a positive charge. In the amides, the carbonyl carbon is electron deficient, and the nitrogen lone pair interacts with the carbon leading to C-N double bond character. In the thioamide, the carbon is not electron deficient, and the uncharged and large sulfur may accept charge density from the nitrogen.

4. Conclusion

In this investigation, we studied the electronic structures of the analogs HCX (NH$_2$) (X= O, S, and Se) molecules by 6-311++G ** at MP2 level of theory and showed:

1. In all the studied molecules, X-N-C bond angles (X=O, S, and Se) are increased with decreasing bond distance C-X.

2. The SeCH (NH$_2$) molecule has the most change in the bond distance due to an increase occupancy value of C-X bonds. The H5—N1—C2—X dihedral angle increases with de-creasing electronegativity of O, S, and Se.

3. The main natural bond orbitals (NBO) analysis showed that total stabilization energy for *LP (1) N1→ π* or σ* C 2 – X6* delocalization increases with increasing *p* character of σ or π* *C 2 – X6* delocalization [15].

4. Variations of the softness (σ) upon the effect show good correlation with Dipole moment (μ) (Debye).

5. The energy gap between orbitals is one of the parameters of controlling the transfer of pure charge in the interacting to the receiver.

6. The studied HOMO-LUMO energy gap demonstrates that decreasing vibrating frequencies is closely related to the increase the length of the bond from molecules 1 through 3.

7. Charge transfer from N to S is important in thioamides whereas charge transfer from N to O is not very important in amides. There appear to be at least two important factors. The sulfur in the C-S bond has a relatively small charge whereas the oxygen of the C=O group has a relatively large negative charge, and consequently, the energetic cost of further polarization is quite large. However, charge cannot be the only factor. The electronegativity of sulfur is close to that of carbon, and so one might expect similar amounts of charge transfer in thioformamide. However, this is not the case, and considerably more charge transfer is found with the thioamide. Thus, there is an important which makes sulfur able to accommodate additional charge transfer. It is likely that the large size of sulfur plays an important role.

Selenium and sulfur share many common chemical properties. From a purely classical electrostatic point of view, it requires less energy to place a given quantity of charge on a large atom than on a small one.

8. The stabilization energies related to LpX → σ * N-C (X=O, S, Se) delocalization represented nucleophilisity property of selenium compounds is higher than sulfur compounds

9. It is found that the resonance between the π electrons on the C$=$X double bond and the nitrogen lone pair significantly stabilizes the planar conformation in HCXNH2 (X = O, S, and Se).

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