A theoretical study an influence of oxygen group elements to rotational barrier of 2-(2'-pyridyl)-1,3,4-oxa(thia, selena and tellura) diazoles

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A THEORETICAL STUDY AN INFLUENCE OF OXYGEN GROUP ELEMENTS TO ROTATIONAL BARRIER OF 2-(2’-PYRIDYL)-1,3,4-OXA (THIA, SELENA AND TELLURA) DIAZOLES

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Abstract

Surveying of the references shows that selenium and tellurium containing compounds will be one of the most promising heterocycles in the future. Therefore, the influence of oxygen group elements – O, S, Se and Te to rotational barrier heights of 2-(2'-pyridyl)-1,3,4-oxa (thia, selena and tellura) diazoles were investigated by DFT/def2-TZVP method and also by DFT/6-311G(d) method only for O, S and Se series. And also, their thermodynamic parameters (∆H, ∆G) were calculated in gas phase. Furthermore, some model compounds with conjugated C=C-C=C, N=C-C=C and N=C-C=N fragments with neighbouring chalcogen atoms were considered. It was found that, a rising of barrier heights in the case of 2-(2'-pyridyl)-1,3,4-oxa(thia, selena and tellura)diazoles and also, in the model compounds with N=C-C=N fragment by increasing atomic number of chalcogen atom. By going from O to Te the rising of HOMO level and decreasing of HOMO-LUMO energetic gap were observed. It was found that, turning of pyridyl ring to ±30° from the coplanar cis (cyn) structure due to the lone pair electron repulsion of nitrogen atoms of N=C-C=N fragment in the case of S, Se and Te containing considered compounds. This is also leads to stability of the trans (anti) structure relatively to cis (cyn) structure and the trans-cis energy difference is increasing by going O to Te. And also, the trans structure is becoming more stable due to the hydrogen bond between nitrogen atom of chalcogenazole ring and H atom of pyridine ring in orto position.

Keywords: n-rotational barrier, barrier heights, 5-(pyridine-2'-yl)-1,3,4-chalcogenadiazoles, theoretical study, DFT.

Introduction

It is well known, that oxygen has very different chemical behavior relatively to other chalcogens. At the same time, the chemical property of selenium and tellurium is similar to sulphur [1]. Oxa- and thiadiazoles greatly expanded the arsenal of heterocyclic compounds. However, selenadiazoles and telluridiazoles are little-studied heterocycles. This may be due to the instability of these compounds. For example, 1,3,4-selenadiazole is stable only at 0°C in a dark place and in vacuum [2]. Surveying of the references shows that absence of data on the synthesis of 1,3,4-tellurudiazole.
Chalcophenes – the first chalcogens-containing compounds, chemical and spectral property of which was subjected to a comparative study by experimental and theoretical methods. The nature of the frontier molecular orbitals of furan, thiophene, selenophene, and tellurophene by experimental and theoretical methods has been studied in [3], [4], and periodic changes in the energies of occupied and vacant MOs in the series of furan, thiophene, selenophene and tellurophen have been observed. The increase in the reactivity of the C5 carbon atom in the series of furan, thiophene, selenophene and tellurophene is shown in [5]. In the series of $C_6H_5XCH_3$ anisoles (X - O, S, Se, Te), an increase in the p-donor properties of the heteroatom and the order of the CAr.-X bond and, consequently, an increase in $p\pi$-conjugation were observed [6]. Antioxidative properties of 2-Phenylsulfenyl-, 2-phenylselenenyl- and 2-phenyltellurenyl-1-naphthol have been evaluated in comparison with 2-benzyl-1-naphthol and for 2-Phenyltellurenyl-1-naphthol obtained a significantly lower oxidation potential than other three compounds [7]. Besides, for all compounds found an ability to inhibit stimulated LTB4 biosynthesis in human neutrophils and highly potent 5-lipoxygenase inhibitor with minimum IC50-value was determined for 2-phenyltellurenyl-1-naphthol [7]. At another publication [8] provided antioxidant activity and the role of organoselenium compounds in the human organism. Wide range of biological activities organoselenium and organotellurium compounds described by Nogueira and Rocha [9].

Above mentioned data shows a growing interest in various types of organic compounds of selenium and tellurium with chemical and pharmacological points of view.

One of promising class of heterocyclic compounds are chalcogenadiazoles. Their oxygen and sulfur derivatives, namely 1,3,4-Oxadiazoles and 1,3,4-thiadiazoles have a wide spectrum of biological activity among chalcogenadiazoles [1], [10], [11]. One of them, 2-pyridyl-1,3,4-oxadiazoles, object of our study is of great interest from the chemical and pharmacological points of view [11].

In the recently work [12], we observed a difference in relative energy between cis and trans planar structures of 2-methylthio-5-(pyridyl)-1,3,4-oxadiazole and 5-(pyridyl) -1,3,4-oxadiazol-2-thione by theoretical methods. This led to us to study an influence of chalcogens to rotational barrier in a series of related compounds. Therefore, in the present work we considered rotational barrier of pyridyl fragment around single bond in series of 2-(pyridin-2'-yl)-1,3,4-oxadiazole, -1,3,4-thiadiazole, -1,3,4-selenadiazole and -1,3,4-telluradiazoles (Scheme 1). Before theoretical investigations of our main compounds - POD, PTD, PSD and PTeD, we analyzed some model compounds (Scheme-2), which contains conjugated system with presence of chalcogen atoms (MC1-MC4). Some model compounds contain nitrogen atom in the conjugate system ($N=C-C=C$) in the ring or outside of the ring and also, in the both side of the conjugated system ($N=C-C=N$) to study the effect of the nitrogen atom to the rotational barrier. Furthermore, to study influence of additional double bond and also, to build conjugated five-membered ring system, we considered model compounds MC5-MC8 (Scheme-2).
X = O, 2-(Pyridin-2'-yl)-1,3,4-oxadiazole (POD)
X = S, 2-(Pyridin-2'-yl)-1,3,4-thiadiazole (PTD)
X = Se, 2-(Pyridin-2'-yl)-1,3,4-selenadiazole (PSD)
X = Te, 2-(Pyridin-2'-yl)-1,3,4-telluradiazole (PTeD)

Scheme-1. Cis (left) and trans (right) geometric structures of POD, PTD, PSD and PTeD

Scheme-2. Considered model structures

1 Computations

The standard 6-311G(d) basis set available for O, S and Se in Gaussian 03 [13] program package. The def2-TZVP method is developed by Ahlrichs group [14] can be employed for O, S, Se and including Te containing compounds. Therefore, calculations were carried out using Gaussian-03 and ORCA 4.0.0 [15] quantum-chemical program packages. The Hybrid method of Becke [16] with three parameters and correlation functions of Lee, Yang and Parr [17] was chosen as a DFT (B3LYP) method in Gaussian calculation by 6-311G(d) basis set and also, in ORCA calculation by the def2-TZVP method. Geometries of studied compounds by ORCA were built using the ORCA modified Avogadro [18] program package. The GaussView 3.09 program was used to build structures for Gaussian calculations. The procedure of dihedral scan in both program packages started from cis structures, e.g., 0°C to 360°C with 10°C step size.
2 Results and discussions

2.1 DFT/6-311G(d) calculations of Model Compounds

The Potential curve of MC1, in the case of X – O is very similar to the potential energy curve of butadiene-1.3 [19] and potential minima has at 20°C and at 180°C which belongs to the gauche and trans structure. The coplanar structure at 0B° belongs to the cis structure and its energy higher than the structure at 20°C only to 0.5 kJ/mol. The trans structure is stable, than the gauche and cis structures approximately to 12 kJ/mol. But, rotational barrier of the model compound MC1 (X-O) differs from barrier heights of butadiene-1,3, it is higher and equal to 31.6 kJ/mol (Fig.1). In the case of single bond systems, like ethane and butane, the origin of barrier caused by mainly steric effects [20], [21]. In addition, in the conjugated systems, the mesomeric effect also plays an important role and carries a large contribution to the value of rotation barrier [20], [22]. Due to the steric effect of the extreme hydrogen atoms of the cis conjugated system by increasing the atomic number of the chalcogen atom observed deviation from the coplanar structure to ±40°. The structure similar to gauche structure of butadiene become more stable than cis structure of MC1 (X-S and Se). However, the rotation barrier is reduced by approximately 10 kJ/mol, in the case of X-S and X-Se of MC1 (Fig.1).

Fig. 1. Rotational barrier of MC1-MC4 calculated by DFT/6-311G(d) method

The presence of a nitrogen atom in the ring, in the case of MC2, promotes the formation of an intramolecular H-bond with the nitrogen atom and the hydrogen atom of the vinyl fragment. However, this does not lead to a stability of cis structure relative to trans structure. The trans structure (MC2, X-O) is lower in energy
relatively to cis structure approximately to 5-6 kJ/mol and trans$\rightarrow$ cis barrier heights are similar to MC1. The presence of the nitrogen atom outside of the ring (MC3) or simultaneously in the ring and outside of the ring (MC4) leads to significant changes in the potential curve of MC3 and MC4. The barrier heights increase by going down from O to Te in the periodic table. In the case of X-O (MC3), the barrier heights decrease comparing to oxygen derivatives of MC2 and MC1. In the cis structure of MC3, intramolecular H-bond between nitrogen atom and H atom of double bond of the ring. Maybe this leads to a slight stability of the cis structure relative to trans in the case of X – O. However, despite of this, in the case of X-S and X-Se (MC3), the trans structure becomes more optimal relative to the cis structure approximately to 13 kJ/mol. Also, similar trans$\leftrightarrow$ cis barrier heights were obtained for sulphur and selenium analogues of MC4 comparing to MC3. But the energy difference between trans and cis structures rise to 25 kJ/mol. In the case of X – O, the energy difference between trans and cis structures is only 10 kJ/mol and the barrier height is equal to 24 kJ/mol. Whereas, it is equal to 33.5 kJ/mol for sulphur and selenium analogues of MC4.

![Fig. 2. Rotational barrier of MC5-MC8 calculated by DFT/6-311G(d) method](image)

Presence of additional double bond in the five-membered ring in the case of MC5-MC8 lead to the ring to $\pi$-electron excessive system. Therefore, a rising of barrier heights will be observed. The potential curve graphs of MC5-MC8 is given in Fig.2. According to DFT/6-311G(d) data, additional double bond in the case of MC5 relatively to MC1 lead to very small changes in barrier heights and lead to decrease of the relative energy difference between trans and cis structures from approximately
13 kJ/mol till 5 kJ/mol in the case of X-O, S and Se. It should be noted that, there is absence the minimum in the potential curve MC5 related to the gauche structure (compare Fig 2. MC5 and Fig.1. MC1). Similar changes were found in the case of MC6 by introducing additional double bond to five-membered ring relatively to MC2 decreased the relative energy difference of trans to cis structures and become approximately equal in X-O, X-S and X-Se. The potential curve graph of MC7 is very close to potential curve graph of MC3. The cis structure of MC7 in the case of X-O, become more stable relatively to MC3(X-O). Only, in the case of MC8, it was found that the rising of barrier heights about 10 kJ/mol relatively to MC4. According to observed data, in the example of model compounds a rising of barrier heights in the series X-O, S and Se were observed in the case of MC3, MC4 and MC8. But, in the case of MC3 increasing conjugation through additional double bond (case MC7) lead to approximately equal barrier heights for all X-O, S and Se compounds. The MC4 and MC8 has the characteristic group - N=C-C=N similar to 2-(Pyridin-2'-yl)-1,3,4-oxa(thia, selena and tellura)diazoles. The cis and trans structures of cyclic systems may be also named as cyn and anti structures [23].

2.2 2-(Pyridin-2'-yl)-1,3,4-oxa(thia and selena)diazoles.

These compounds free of steric effects and consist of two units, which considered as π-electron deficient and π-electron excessive systems, respectively. The chalcogen atom is the key heteroatom in π-electron excessive system [1]. By increasing the atomic number of chalcogens, the electron-donating ability of chalcogenadiazole ring increases and, consequently, the mesomer effect between two conjugated systems connected by single C-C bond increases. Because of this, the coplanar structure corresponds to POD, PTD, PSD and PTeD. However, potential curve of the compounds carried out by DFT method show coplanar structure only for POD in both cis and trans structures. But, the last structure has advantages over first structure in energy approximately 10 kJ/mol. By going from POD to PSD, according to DFT/6-311G(d) results show a rising of trans to cis barrier heights and also rising up relative energy difference between them (trans-cis). The rising of barrier heights in series POD-PSD confirms an increase of the mesomeric effect between two rings. In the case of PSD, insignificant stability of a structure at ±40°C than cis structure was observed. This structure is similar to the gauche structure of butadiene and MC1 (Fig.4).

**Fig.3. Potential curve of POD series by DFT/6-311G(d) and DFT/def2-TZVP**

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The DFT/def2-TZVP method also show the minimum at $\pm 30^\circ C$ in the case of PTD, PSD and PTeD. The energy difference between cis structure and structures at $\pm 30^\circ C$ or at $\pm 40^\circ C$ is very small, equal to 0.5 - 1 kJ/mol.

![Image of molecular structures](image)

**Fig. 4.** The cis structure of POD and the structure of PSD at $B \pm 40B^\circ$ and calculated by DFT/6-311G(d)

### 2.3 DFT/def2-TZVP calculations of 2-(Pyridin-2'-yl) - 1,3,4-oxa(thia, selena and tellura)diazoles.

This method allowed us to calculate and compare results including tellurium derivative - PTeD. The data of this method is completely consistent with the results of DFT/6-311G(d) method results obtained using Gaussian program package. It also shows the rising barrier heights and the relative energy differences between trans and cis structures in series of POD, PTD, PSD and PTeD (Fig.3). Only, barrier heights lay a few below relatively to DFT/6-311G(d) barrier heights approximately to 3 kJ/mol.

It should be noted that replacement of oxygen atom to other chalcogens brings to reduction of $\alpha$ (C-X-C) angle in the cis (Table.1) and trans structures (Table 2). Also, the length of C-X bond is increased. For example, according to DFT/def2-TZVP results the length of C-O (POD), C-S (PTD), C-Se (PSD), and C-Te (PTeD) is equal to 1.37, 1.75, 1.91, and 2.12 Å, respectively. These changings lead to decreasing of $\beta$ (C2'-C2-N3) valent angle. While, the changes at $\gamma$(N1'-C2'-C2) valent angle is not significant. As a result, the distance between pyridine and chalcogenadiazole nitrogen atoms changes from 2.89 to 2.78 Å. Some geometrical characteristics is listed in table 1 and also the table contains the information about the HOMO, LUMO energies and the energy difference between them.
Table 1. Some geometrical and energetical characteristics of the cis structure of POD, PTD, PSD and PTeD by DFT/6-311G(d) and DFT/def2-TZVP*

<table>
<thead>
<tr>
<th></th>
<th>POD</th>
<th>PTD</th>
<th>PSD</th>
<th>PTeD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{LUMO}$, eV</td>
<td>-1.965 (-1.880)</td>
<td>-2.113 (-2.132)</td>
<td>-2.196 (-2.189)</td>
<td>-2.276</td>
</tr>
<tr>
<td>$E_{HOMO}$, eV</td>
<td>-7.183 (-7.388)</td>
<td>-7.078 (-7.132)</td>
<td>-7.043 (-7.066)</td>
<td>-6.797</td>
</tr>
<tr>
<td>$\Delta E(L-H)$, eV</td>
<td>5.218 (5.507)</td>
<td>4.965 (5.000)</td>
<td>4.847 (4.877)</td>
<td>4.521</td>
</tr>
<tr>
<td>$l(X-C)$</td>
<td>1.37 (1.37)</td>
<td>1.75 (1.77)</td>
<td>1.91 (1.92)</td>
<td>2.12</td>
</tr>
<tr>
<td>$l(N \cdots N)$</td>
<td>2.89 (2.90)</td>
<td>2.81 (2.80)</td>
<td>2.80 (2.78)</td>
<td>2.78</td>
</tr>
<tr>
<td>$\alpha(C - X - C)$, $^\circ$</td>
<td>102.19 (102.01)</td>
<td>86.67 (85.95)</td>
<td>81.55 (81.20)</td>
<td>75.82</td>
</tr>
<tr>
<td>$\beta(C'2 - C2 - N3)$, $^\circ$</td>
<td>129.76 (129.87)</td>
<td>124.41 (124.28)</td>
<td>123.97 (123.83)</td>
<td>122.82</td>
</tr>
<tr>
<td>$\gamma(N1' - C2' - C2)$, $^\circ$</td>
<td>116.38 (116.29)</td>
<td>116.57 (116.20)</td>
<td>116.62 (116.28)</td>
<td>116.82</td>
</tr>
</tbody>
</table>

*DFT/6-311G(d) data given in brackets. $l(N \cdots N)$ is distance between pyridine and chalcogenadiazole nitrogen atoms.

Table 2. Some geometrical and energetical characteristics of the trans structure of POD, PTD, PSD and PTeD by DFT/6-311G(d) and DFT/def2-TZVP*

<table>
<thead>
<tr>
<th></th>
<th>POD</th>
<th>PTD</th>
<th>PSD</th>
<th>PTeD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{LUMO}$, eV</td>
<td>-1.945 (-1.932)</td>
<td>-2.077 (-2.105)</td>
<td>-2.150 (-2.162)</td>
<td>-2.217</td>
</tr>
<tr>
<td>$E_{HOMO}$, eV</td>
<td>-7.145 (-7.171)</td>
<td>-7.026 (-7.077)</td>
<td>-6.994 (-7.023)</td>
<td>-6.700</td>
</tr>
<tr>
<td>$\Delta E(L-H)$, eV</td>
<td>5.2 (5.239)</td>
<td>4.949 (4.972)</td>
<td>4.844 (4.861)</td>
<td>4.483</td>
</tr>
<tr>
<td>$l(X-C)$</td>
<td>1.359 (1.361)</td>
<td>1.737 (1.751)</td>
<td>1.892 (1.898)</td>
<td>2.092</td>
</tr>
<tr>
<td>$l(N \cdots N)$</td>
<td>2.640 (2.629)</td>
<td>2.618 (2.608)</td>
<td>2.620 (2.613)</td>
<td>2.613</td>
</tr>
<tr>
<td>$\alpha(C - X - C)$, $^\circ$</td>
<td>102.2 (102.0)</td>
<td>86.2 (85.5)</td>
<td>81.1 (80.8)</td>
<td>75.3</td>
</tr>
<tr>
<td>$\beta(C'2 - C2 - N3)$, $^\circ$</td>
<td>127.6 (127.5)</td>
<td>124.4 (121.7)</td>
<td>124.4 (124.4)</td>
<td>123.8</td>
</tr>
<tr>
<td>$\gamma(N1' - C2' - C2)$, $^\circ$</td>
<td>117.3 (117.2)</td>
<td>116.2 (116.2)</td>
<td>116.2 (116.1)</td>
<td>116.0</td>
</tr>
</tbody>
</table>

*DFT/6-311G(d) data given in brackets. $l(N\cdots H)$ is distance between H of pyridine ring and chalcogenadiazole nitrogen atoms.

It is well known that, stability and reactivity of related compounds is estimated on the basis of HOMO-LUMO gap [24]. Thermodynamic stable and chemical inert compounds have a high LUMO and low HOMO, and as a result, a large HOMO-LUMO gap. Conversely, a low LUMO and high HOMO leads to a small HOMO-LUMO gap that is characteristic to chemically reactive compounds [24]. Based on HOMO-LUMO gap, we can conclude that a relative reactivity is increased and stability decreased in the series of O→Te in both geometric structures. According to DFT/def2-TZVP results the HOMO-1 is n-type MO and localized mainly in nitrogen atoms of POD, PTD and PTeD (Fig.5). This MO is replaced with HOMO in the case of PSD. The energy of HOMO and HOMO-1 of PSD is equal to -7.043 and -7.047 eV, respectively. Related energy similarity of these MOs is occurred also in the case of PTeD, in which the MOs energy is equal to -6.797 and -6.798 eV, respectively.
Fig. 5. Electron densities on LUMO (L), HOMO (H) and HOMO-1 (H-1) calculated by DFT/def2-TZVP

Fig. 6. Electron densities on LUMO (L), HOMO (H) and HOMO-1 (H-1) calculated by DFT/def2-TZVP

Similar electronic and energetic characteristics also found for trans structures of this compounds (Fig. 6.). For trans structures of these compounds may occur the
H-bond between nitrogen atom of chalcogenazole ring and H atom of pyridine ring in _orto_ position.

On the basis of geometrical, HOMO-LUMO energetic changings the presence of the energetic minimum at ±30° C or at ±40° C in the case of PTD, PSD and PTeD, and its absence in the case of MC4 and MC8 model compounds it can be assumed an existence of lone pair interactions of pyridine and chalcogenadiazoles nitrogen atoms in the case of PTD, PSD and PTeD in their cis structure. Furthermore, the presence of gauche structure due to hydrogen atoms in the case of MC1 is also confirmed a presence an anomeric effect in the cis structure of PTD, PSD and PTeD.

The relative energy (ΔE), ratio (cis/trans) constant, enthalpy (ΔH) and free energy (ΔG) values calculated by both methods in gas phase show an increasing of the stability of anti-conformer by going down from O to Te (Table 3.).

**Table 3. Relative energy and thermodynamic parameters (kJ/mol) of POD, PTD and PSD at 298.15 K in the gas phase**

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔE</th>
<th>ΔH,kJ/mol</th>
<th>ΔG,kJ/mol</th>
<th>TΔS</th>
<th>Keq. (cis/trans)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POD</td>
<td>-11.13 (-10.97)</td>
<td>10.67 (23.53)</td>
<td>10.64 (27.85)</td>
<td>0.03 (-4.32)</td>
<td>1.36·10⁻² (1.3·10⁻⁵)</td>
</tr>
<tr>
<td>PTD</td>
<td>-28.42 (-32.29)</td>
<td>25.05 (28.62)</td>
<td>29.24 (33.98)</td>
<td>-4.19 (-5.36)</td>
<td>7.49·10⁻⁶ (1.1·10⁻⁶)</td>
</tr>
<tr>
<td>PSD</td>
<td>-31.18 (-34.83)</td>
<td>27.84 (31.13)</td>
<td>32.01 (36.46)</td>
<td>-4.17 (-5.33)</td>
<td>2.45·10⁻⁶ (4.0·10⁻⁷)</td>
</tr>
<tr>
<td>PTeD</td>
<td>-35.79</td>
<td>32.17</td>
<td>36.26</td>
<td>-4.09</td>
<td>4.41·10⁻⁷</td>
</tr>
</tbody>
</table>

The obtained data can be confirmed by single crystal XRD data of PTD derivatives, where were found only the anti-conformer, for example, in 2-(Pyridin-2-yl)-1,3-thiazole-4-carboxylic acid hemihydrate [25] and 5-(pyridin-2-yl)-1,3,4-thiadiazol-2-amine [26] the torsion angle is equal to 179.88° C and 178.26° C, respectively. According of this data we can suggest that the trans coplanar structure is characteristic to S, Se and Te containing considered compounds and it is becoming more stable, due to the hydrogen bond between nitrogen atom of chalcogenazole ring and H atom of pyridine ring in _orto_ position.

Overall, the rising of HOMO level and decreasing HOMO-LUMO energetic gap in series of POD, PTD, PSD and PTeD show the particular importance of these compounds with pharmaceutical point of view and our results will be motivating chemist experimenters to synthesis a new derivative of 2-(Pyridin-2'-yl)-1,3,4-oxa(thia)diazole with heavy atoms instead of O and S. Because, the most useful descriptors in QSAR field are energy of frontier orbitals and energetic difference between them [24], [27], [28].

### 3 Conclusion

The influence of oxygen group elements – O, S, Se and Te to rotational barrier heights of 2-(2'-pyridyl)-1,3,4-oxa(thia, selena and tellura)diazoles were investigated by DFT/def2-TZVP method and also by DFT/6-311G(d) method only for O, S and Se series. Furthermore, some model compounds with conjugated C=C-C=C, N=C-C=C and N=C-C=N
fragments with neighbouring chalcogen atoms were considered. It was found that, a rising of barrier heights in the case of 2-(2’-pyridyl)-1,3,4-oxa(thia, selena and tellura)diazoles and also, in the model compounds with N=C-C=N fragment by increasing atomic number of chalcogen atoms. By going from O to Te the rising of HOMO level and decreasing of HOMO-LUMO energetic gap were observed. It was found that, turning of pyridyl ring to $\pm 30^\circ$C from the coplanar cis structure due to the lone pair electron repulsion of nitrogen atoms of N=C-C=N fragment in the case of cis structures of S, Se and Te containing considered compounds. This is also led to stability of the trans structures relatively to cis structures and the trans-cis energy difference is increasing by going O to Te. And also, the trans structure is becoming more stable due to the hydrogen bond between nitrogen atom of chalcogenazole ring and H atom of pyridine ring in *orto* position.

**Acknowledgements**

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**References**


