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## Atropisomerism at C–N bonds: Structural conformations and vibrational spectral study of Iminothiazoline Derivatives with density functional theoretical optimizations

F.Z. MIMOUNI<sup>1,2\*</sup>, A. RAHMOUNI<sup>3</sup>, H. DJERADI<sup>1,2</sup>, N. BELBOUKHARI<sup>1</sup>, A. CHERITI<sup>2</sup>

<sup>1</sup> Bioactive Molecules & Chiral Separation Laboratory, Bechar University

<sup>2</sup> Phytochemistry & Organic Synthesis Laboratory, Bechar University

<sup>3</sup> Modelisation & Calcul Methods Laboratory, Saida University

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Corresponding author Email \*Mimouni2401@yahoo.fr

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**Abstract** – The isolation of the pair atropisomers of the both iminothiazoline derivatives and the spectroscopic analytical of the compound have been computed using B3LYP/6-31G(d,p) level to derive the equilibrium geometry, conformational stability, molecular orbital energies and vibrational frequencies was studied in this paper.

**Keywords:** Atropisomer, Iminothiazoline, energy barrier, DFT

### Introduction

The atropisomerism is a natural phenomenon that plays a major role in the pharmaceutical, cosmetic, food and environmental. Thus, the atropisomeric separation is now essential to validate the concepts of molecular interactions at the basis of many therapeutic approaches.

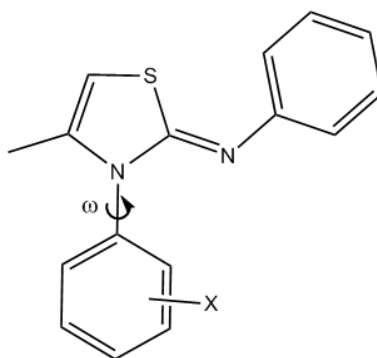
IR spectroscopy combined with quantum chemical computations has recently been used as effective tools in the vibrational analysis of drug molecules, biological compounds and natural products compounds [1-2]

### 1. Experimental

We have previously described the synthesis of the N,N'-diaryl-2-iminothiazoline derivatives and their chiral separation by TLC in the previous paper [3].

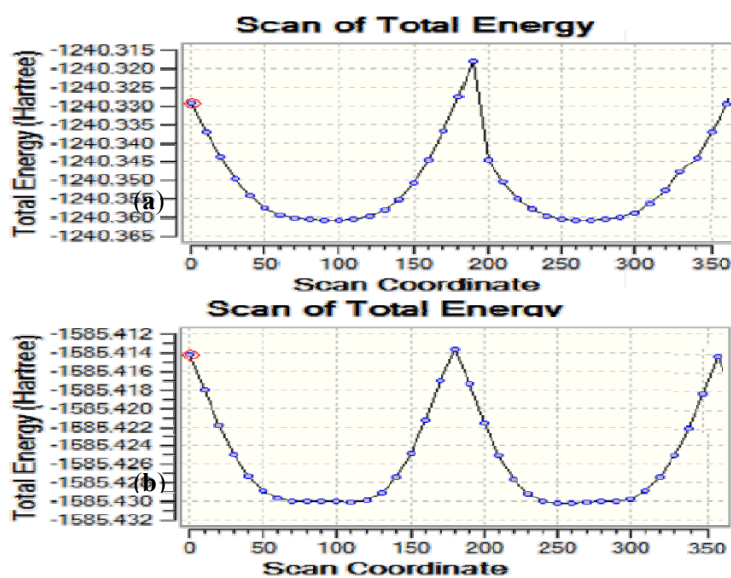
### 2. Computational details

Gaussian 03W and GaussView molecular visualization [4-5] software package was used for all theoretical calculations which were performed with B3LYP method at 6-31G (d,p) basis set level. The study of rotational barriers implies the determination of the potential energy curve and therefore the variation of the energy as a function of the dihedral angle. For these molecules, it requires a careful scan in energy around the dihedral angle  $\omega$ , **Fig. 1**.



**Fig. 1.** Structure of the molecules: (a) x= ortho-OMe  
(b) x= meta-Cl.

The scan varies the dihedral angle by  $10^\circ$  from 0 to  $360^\circ$ , to give two atropisomers (GS), and one transition state (TS) in the rotation. The different energies obtained from the scan are optimized at each dihedral angle. The scan of the iminothiazoline derivatives is in **Fig. 2**.



**Fig. 2.** Theoretical DFT energy scans of the molecules (a) and (b)

### 3. Results and discussion

A typical energy scan (**Fig. 2**) contains two minima, one around  $\omega = -100^\circ$ , and the other around  $\omega = 100^\circ$  for (a), and one around  $\omega = -110^\circ$ , and the other around  $\omega = 110^\circ$  for (b), the scans in energy represent the variation of the energy as a function of a frozen dihedral angle  $\omega$ , therefore, the structures obtained during this scan are not optimized structures.

#### 3.1. Geometry optimization

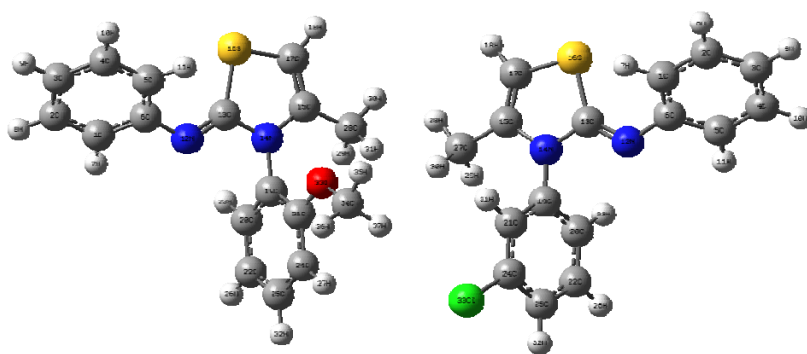
The geometries of the atropisomers are optimized independently of the dihedral angle  $\omega$  using the structure of the ground states (GS) obtained during the scan. The results presented in **Table 1**.

**Table 1:** Minimum energy barriers of phenyl rotation computed at B3LYP/6-31G (d,p) level of compounds (a) and (b).

<i>Atropisomer</i>	<b>Ra-(a)</b>	<b>Sa-(a)</b>	<b>Ra-(b)</b>	<b>Sa-(b)</b>
$\omega^\circ$	-98.16762	97.73809	108.80587	-108.60443
Energy (Hartree)	-1240.36078855	-1240.36078942	-1585.43005205	-1585.43005168
$\Delta E$ (Kcal/mol)	0.000546	0.000000	0.000000	0.000232
Dipole moment (Debye)	4.7640	4.7626	3.2734	3.2818

The optimization of the ground states (GS) gives two groups of atropisomers (GS), the difference in energy between this two groups is negligible compared to the value of the rotational barrier. Therefore the values of the energy of the two groups of atropisomers are equivalent.

Calculated geometric parameters and definitions of the natural coordinates for the molecules are summarized in the **Table 2**.



**Fig. 3.** Optimized molecules (a) and (b) in stable state with B3LYP/6-31G(d,p)

The bond length and bond angles parameters of the optimized molecular structure of the both atropisomers of (a) and (b) are the same, for the dihedral angles, there are four dissimilar around the N14—C19 bond like the previous Table shows.

### 3.2. Atomic charges

Atomic charges of 4Me, 3N-(2'-OMe), N2-imino  $\Delta$ 4 thiazoline (a) and 4Me, 3N-(3'-Cl), N2-imino  $\Delta$ 4 thiazoline (b), calculated by DFT method 6-31G(d,p) levels of calculation, are shown in **Table 3**. As can be seen from the table, all obtained magnitudes are in agreement each other. The magnitudes of the carbon atomic charges are found to be either positive or negative at the basis set. These magnitudes are changing between (-0.380 and 0.386) for (a) and (-0.375 and 0.368) for (b). Carbon that is close to S-atom has the minimum charge magnitude. The heterocyclic N-atom has the minimum charge magnitude -0.562, -0.574 for (a) and (b) respectively. All the magnitudes of the hydrogen atomic charges are positive; the maximum values are for hydrogen atoms of the methyl. For O-atom, the magnitude of charge is -0.525 and for Cl-atom is -0.014.

**Table 2:** Selected optimized dihedral angle parameters of compounds (a) and (b) with B3LYP/6-31G (d,p).

<b>4Me, 3N-(2'-OMe), N2-imino <math>\Delta^4</math> thiazoline (a)</b>			
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub>	-179.7317	C <sub>15</sub> -N <sub>14</sub> -C <sub>13</sub> -N <sub>12</sub>	177.3107
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	-0.3801	S <sub>16</sub> -C <sub>13</sub> -N <sub>12</sub> -C <sub>6</sub>	-6.2486
C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub> -C <sub>4</sub>	-1.4029	C <sub>17</sub> -C <sub>15</sub> -N <sub>14</sub> -C <sub>19</sub>	-177.6217
C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub> -H <sub>11</sub>	177.0702	C <sub>17</sub> -C <sub>15</sub> -N <sub>14</sub> -C <sub>13</sub>	-0.4128
C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> -N <sub>12</sub>	178.0083	H <sub>18</sub> -C <sub>17</sub> -S <sub>16</sub> -C <sub>13</sub>	179.7265
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>10</sub>	-178.9209	C <sub>19</sub> -C <sub>21</sub> -O <sub>33</sub> -C <sub>34</sub>	175.7525
C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	179.4135	C <sub>20</sub> -C <sub>22</sub> -C <sub>25</sub> -H <sub>32</sub>	179.9744
C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	-0.8271	C <sub>20</sub> -C <sub>22</sub> -C <sub>25</sub> -C <sub>24</sub>	0.0256
C <sub>6</sub> -C <sub>5</sub> -C <sub>4</sub> -C <sub>3</sub>	0.2279	C <sub>20</sub> -C <sub>19</sub> -N <sub>14</sub> -C <sub>15</sub>	<b>-102.1794/102.0059</b>
C <sub>6</sub> -C <sub>5</sub> -C <sub>4</sub> -H <sub>10</sub>	179.8293	C <sub>20</sub> -C <sub>19</sub> -N <sub>14</sub> -C <sub>13</sub>	<b>80.7377/-81.1003</b>
H <sub>7</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	-0.4120	C <sub>20</sub> -C <sub>19</sub> -C <sub>21</sub> -C <sub>24</sub>	0.5866
H <sub>7</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	179.3473	C <sub>20</sub> -C <sub>19</sub> -C <sub>21</sub> -O <sub>33</sub>	179.7348

**Table 2:** Selected optimized dihedral angle parameters of compounds (a) and (b) with B3LYP/6-31G (d,p) (continued).

H <sub>7</sub> -C <sub>1</sub> -C <sub>6</sub> -N <sub>12</sub>	<b>-2.1614</b>	C <sub>21</sub> -C <sub>19</sub> -N <sub>14</sub> -C <sub>15</sub>	<b>78.9922/-79.15577</b>
H <sub>7</sub> -C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub>	-178.4669	C <sub>21</sub> -C <sub>19</sub> -N <sub>14</sub> -C <sub>13</sub>	<b>-98.0907/ 97.7381*</b>
H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub>	0.0265	C <sub>21</sub> -O <sub>33</sub> -C <sub>34</sub> -H <sub>37</sub>	63.9826
H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	179.3780	C <sub>21</sub> -O <sub>33</sub> -C <sub>34</sub> -H <sub>36</sub>	-58.5205
H <sub>9</sub> -C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	-179.9744	C <sub>21</sub> -O <sub>33</sub> -C <sub>34</sub> -H <sub>35</sub>	-177.2675
H <sub>9</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>10</sub>	0.4307	C <sub>22</sub> -C <sub>20</sub> -C <sub>19</sub> -N <sub>14</sub>	-179.2934
<b>4Me, 3N-(3'-Cl), N2-imino <math>\Delta^4</math> thiazoline (b)</b>			
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub>	179.9744	C <sub>17</sub> -S <sub>16</sub> -C <sub>13</sub> -N <sub>12</sub>	175.7969
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	-0.6410	S <sub>16</sub> -C <sub>13</sub> -N <sub>12</sub> -C <sub>6</sub>	5.6603
C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub> -C <sub>4</sub>	-1.7311	S <sub>16</sub> -C <sub>17</sub> -N <sub>15</sub> -C <sub>27</sub>	-178.7599
C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub> -H <sub>11</sub>	178.4893	S <sub>16</sub> -C <sub>17</sub> -C <sub>15</sub> -C <sub>27</sub>	-0.1304
C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> -N <sub>12</sub>	177.4999	H <sub>18</sub> -C <sub>17</sub> -S <sub>16</sub> -C <sub>13</sub>	178.31001
C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub>	1.3205	C <sub>19</sub> -N <sub>14</sub> -C <sub>13</sub> -S <sub>16</sub>	-178.6885
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	0.2318	C <sub>15</sub> -N <sub>14</sub> -C <sub>13</sub> -S <sub>16</sub>	2.8100
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>10</sub>	-179.4088	C <sub>17</sub> -S <sub>16</sub> -C <sub>13</sub> -N <sub>14</sub>	-2.3375
C <sub>1</sub> -C <sub>6</sub> -N <sub>12</sub> -C <sub>13</sub>	49.3184	C <sub>17</sub> -C <sub>15</sub> -N <sub>14</sub> -C <sub>13</sub>	-1.8456
C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	-0.1473	C <sub>17</sub> -C <sub>15</sub> -N <sub>14</sub> -C <sub>19</sub>	179.7071
C <sub>6</sub> -C <sub>5</sub> -C <sub>4</sub> -C <sub>3</sub>	0.9698	C <sub>20</sub> -C <sub>19</sub> -N <sub>14</sub> -C <sub>15</sub>	<b>107.0321/ -106.76254</b>
N <sub>14</sub> -C <sub>19</sub> -C <sub>21</sub> -C <sub>24</sub>	<b>-108.6044 /108.8059*</b>	H <sub>31</sub> -C <sub>21</sub> -C <sub>24</sub> -Cl <sub>33</sub>	1.2617
C <sub>13</sub> -N <sub>14</sub> -C <sub>19</sub> -C <sub>20</sub>	<b>-71.3404/ 71.55401</b>	H <sub>26</sub> -C <sub>22</sub> -C <sub>20</sub> -H <sub>23</sub>	-0.5449
N <sub>14</sub> -C <sub>19</sub> -C <sub>20</sub> -H <sub>23</sub>	1.3680	H <sub>31</sub> -C <sub>21</sub> -C <sub>24</sub> -C <sub>25</sub>	-178.4090
N <sub>14</sub> -C <sub>15</sub> -C <sub>27</sub> -H <sub>30</sub>	-176.4442	H <sub>31</sub> -C <sub>21</sub> -C <sub>19</sub> -N <sub>14</sub>	-2.0139
N <sub>14</sub> -C <sub>13</sub> -N <sub>12</sub> -C <sub>6</sub>	63.8111	H <sub>31</sub> -C <sub>21</sub> -C <sub>19</sub> -C <sub>20</sub>	178.1330
C <sub>15</sub> -N <sub>14</sub> -C <sub>19</sub> -C <sub>21</sub>	<b>-72.8217/ 73.08692</b>	H <sub>32</sub> -C <sub>25</sub> -C <sub>22</sub> -C <sub>20</sub>	179.6457
N <sub>14</sub> -C <sub>15</sub> -C <sub>27</sub> -H <sub>28</sub>	-176.0963	H <sub>32</sub> -C <sub>25</sub> -C <sub>22</sub> -H <sub>26</sub>	-0.1277
N <sub>14</sub> -C <sub>15</sub> -C <sub>27</sub> -H <sub>29</sub>	-56.2854	Cl <sub>33</sub> -C <sub>24</sub> -C <sub>25</sub> -H <sub>32</sub>	0.0578

**Table 3:** Atomic charges for optimized geometry of (a) and (b).

Compound (a)				Compound (b)			
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C1	-0.094	C20	-0.059	C1	-0.099	H18	0.128
C2	-0.093	C21	0.385	C2	-0.097	C19	0.223
C3	-0.088	C22	-0.106	C3	-0.097	C20	-0.044
C4	-0.098	H23	0.103	C4	-0.093	C21	-0.054
C5	-0.101	C24	-0.146	C5	-0.092	C22	-0.101
C6	0.233	C25	-0.081	C6	0.230	H23	0.111
H7	0.080	H26	0.090	H7	0.094	C24	-0.111
H8	0.078	H27	0.092	H8	0.082	C25	-0.058
H9	0.075	C28	-0.374	H9	0.078	H26	0.105
H10	0.078	H29	0.131	H10	0.081	C27	-0.369
H11	0.093	H30	0.120	H11	0.080	H28	0.126
N12	-0.555	H31	0.138	N12	-0.551	H29	0.136
C13	0.312	H32	0.091	C13	0.305	H30	0.134
N14	-0.562	O33	-0.525	N14	-0.574	H31	0.121
C15	0.386	C34	-0.084	C15	0.368	H32	0.115
S16	0.195	H35	0.131	S16	0.206	Cl33	-0.014
C17	-0.380	H36	0.122	C17	-0.375	-	-
H18	0.122	H37	0.112	-	-	-	-
C19	0.180	-	-	-	-	-	-

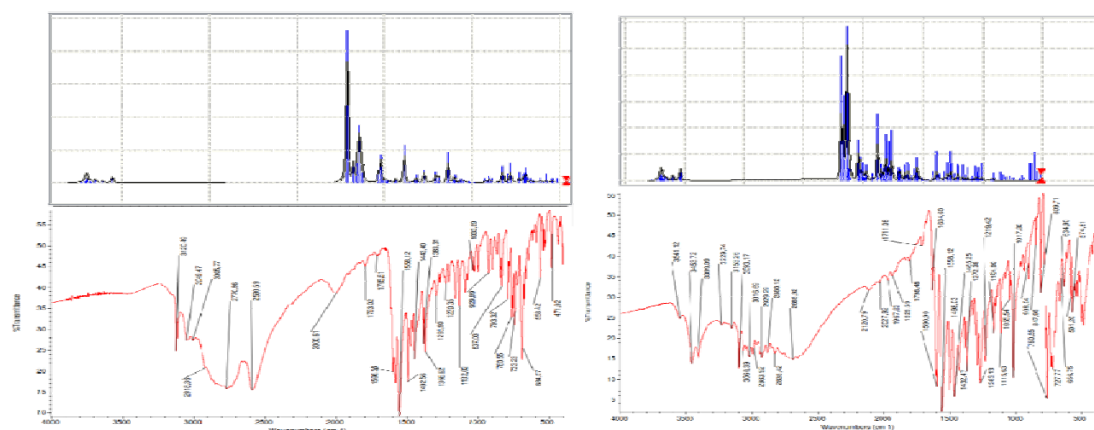
### 3.3. Vibrational frequencies

We have performed a frequency calculation analysis to obtain the spectroscopic signature of iminothiazoline derivatives in this study. Vibrational frequencies have been calculated using B3LYP/6-31G (d,p) method. The theoretical spectrum was scaled with **0.967** (for wavenumbers under  $1800\text{ cm}^{-1}$ ) and **0.955** (for those over  $1800\text{ cm}^{-1}$ ). Then all scaled frequencies have been compared with experimental values.

The existence of the thiazole ring in a structure can easily be determined owing to the relation of C–H and C=C–C ring vibrations. The aromatic C–H stretching vibrations appear in the region  $3453.72\text{--}2929.29\text{ cm}^{-1}$  for (a) and  $3049.77\text{--}3005.77\text{ cm}^{-1}$  for (b); also, methyl group frequencies occur at  $3229.74\text{--}2688.92\text{ cm}^{-1}$  for (a), these vibrations observed theoretically in the same range, for (b) are observed at  $2770.86\text{--}2590.59\text{ cm}^{-1}$  experimentally and at  $3146.67\text{--}3048.90\text{ cm}^{-1}$  for B3LYP/6-31G (d,p).

The Imine bands are most characteristic bands of the IR spectrum, the bands identified at  $1711.08$  and  $1793.02\text{ cm}^{-1}$  are assigned to C=N stretching vibration for (a) and (b) derivatives respectively. According to our calculation, these bands observed in  $1686.49$ ,  $1712.11\text{ cm}^{-1}$ .





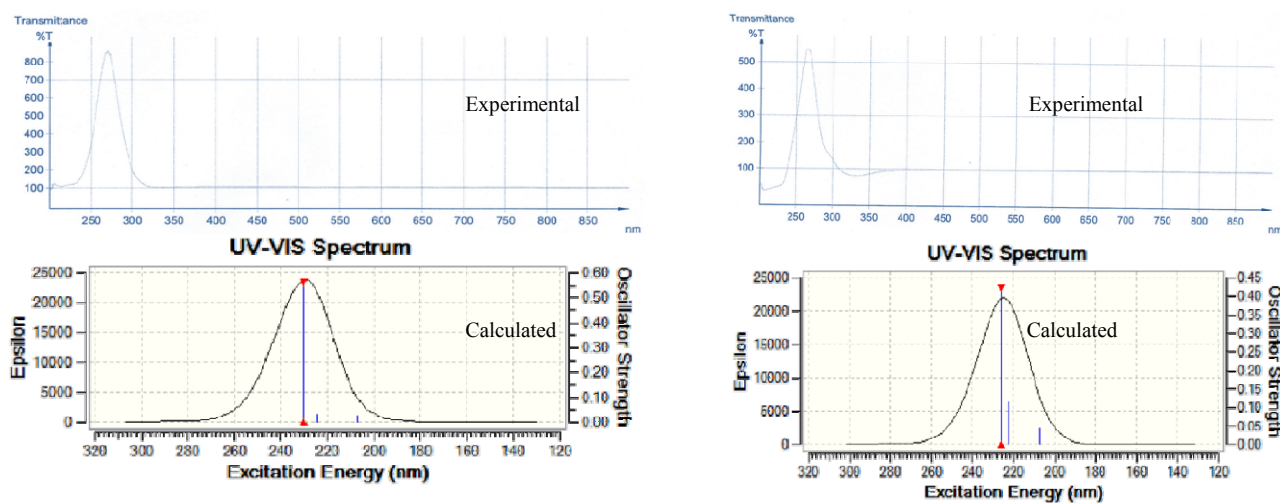
**Fig. 4.** The infrared spectra of (a) and (b)

**Table 4:** Experimental and calculated vibrational frequencies of compounds (a) and (b).

4Me, 3N-(2'-OMe), N2-imino $\Delta^4$ thiazoline (a)			4Me, 3N-(3'-Cl), N2-imino $\Delta^4$ thiazoline (b)		
Assignment	Exp	B3LYP	Assignment	Exp	B3LYP
$\nu$ (C-H) <sub>Hetero</sub>	3541.12	3281.86	$\nu$ (C-H) <sub>Hetero</sub>	3120.49	3277.04
$\nu$ (C-H) <sub>sub-Ar</sub>	3453.72-2983.92	3233.42-3194.04	$\nu$ (C-H) <sub>sub-Ar</sub>	3049.77	3229.14-3223.30
$\nu$ (C-H) <sub>Ar</sub>	3399.09-2929.29	3208.97-3178.70	$\nu$ (C-H) <sub>Ar</sub>	3005.77	3209.10-3175.80
$\nu$ (C-H) <sub>OMe</sub>	3229.74-2836.42	3164.95-3106.26	$\nu_S$ (C-H) <sub>Me</sub>	2770.86	3146.67-3105.06
$\nu$ (C-H) <sub>Me</sub>	3153.26-2688.92	3151.23-3110.19	$\nu_{As}$ (C-H) <sub>Me</sub>	2590.59	3048.90
$\nu$ (C=N)	1711.08	1686.49	$\nu$ (C=N)	1793.02	1712.35
$\nu$ (C=C) <sub>Hetero</sub>	1634.60	1668.43	$\nu$ (C=C) <sub>Hetero</sub>	1705.61	1676.80
$\nu$ (C=C) <sub>Ar</sub>	1590.90-1558.12	1651.10-1486.22	$\nu$ (C=C) <sub>Ar</sub>	1596.36-1492.56	1652.33-1462.11
$\delta$ (CH) <sub>Ar</sub>	1498.03-1465.25	1543.15-1502.63	$\delta$ (CH) <sub>Ar</sub>	1443.40-1366.92	1435.78
$\delta$ (CH) <sub>OMe</sub>	1432.47	1509.52-1498.81	$\nu$ (C-N)	1295.90	1389.53
$\delta$ (CH) <sub>Me</sub>	1372.38	1489.21-1425.65	$\delta$ (CH) <sub>Me</sub>	1132.02-1033.69	1273.93-1059.55
$\nu$ (C-N)	1263.13	1382.88	$\nu$ (C-Cl)	929.8	896
$\nu$ (C-S)	809.71	823.70	$\nu$ (C-S)	733.23	805

### 3.4. UV-Vis spectra analysis

Ultraviolet spectra analysis of both iminothiazoline derivatives has been investigated experimental and theoretical analysis. Absorption maxima ( $\lambda_{max}$ ) of the molecule have been calculated by the DFT method.



**Fig. 5.** UV-Vis experimental and theoretical spectra of (a) in the left and (b) in the right

As can be seen from the **Fig. 5**, intense band corresponding to the  $\pi \rightarrow \pi^*$  electronic transition of aryl groups, the experimental absorption maxima values have been 273 and 275 nm for (a) and (b) respectively. Moreover,  $\lambda_{max}$  are given in an order 225.84, 229.88 nm at B3LYP/6-31G(d,p) calculation level.

### 3.5. Molecular orbital energies

Gaussian molecular visualization program were also used for the simulating the HOMO and LUMO figures of the molecules. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. We can determine how the molecule interacts with other species; hence, they are called the frontier orbital. HOMO, which is the outermost orbital containing electrons, tends to give these electrons as an electron donor. On the other hand, LUMO is the innermost orbital containing free places to accept electrons [6].

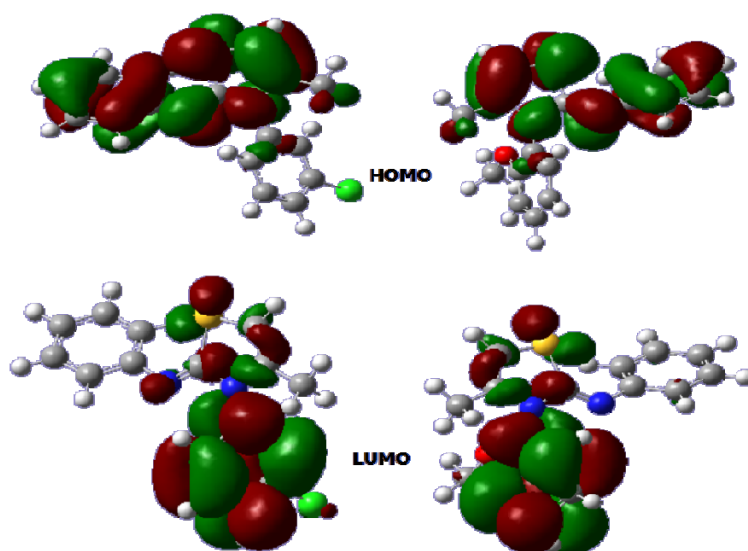
Energy gap between HOMO and LUMO that is an important stability for structures [7] has been calculated using four different methods as presented in **Table 5**.

In addition, 3D plots of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are shown in **Fig. 6**

According to DFT-B3LYP method at 6-31G(d,p) calculation levels, the energy band gap,  $\Delta E$ , between HOMO and LUMO of the molecule was found about 0.161 AU for (a) and 0.157 AU for (b) with little differences between the atropisomers in HOMO energy.

**Table 5:** Selected energy values of complex in its ground state with singlet symmetry at DFT method.

	4Me, 3N-(2'-OMe), N2-imino $\Delta^4$ thiazoline (a)		4Me, 3N-(3'-Cl), N2-imino $\Delta^4$ thiazoline (b)	
	<i>Ra</i>	<i>Sa</i>	<i>Ra</i>	<i>Sa</i>
Lowest MO Eigen value (AU)	-88.89260	-88.89259	-101.55551	-101.55553
Highest MO Eigen value (AU)	4.93348	4.93346	4.85026	4.85031
HOMO (AU)	-0.17725	-0.17726	-0.18769	-0.18766
LUMO (AU)	-0.01617	-0.01617	-0.03064	-0.03064
Energy gap	0.16108	0.16109	0.15705	0.15702



**Fig. 6.** 3D plots of HOMO and LUMO of (a) in the right and (b) in the left.

#### 4. Conclusion

The optimized molecular structures of have been calculated using density functional theory, B3LYP method at 6-31G(d,p) basis set. Besides, the comparison of the experimental and computational results of vibrational frequencies shows a little conformity with each other, which have been also scaled by the appropriate factors obtained from the literature.

In addition, HOMO and LUMO orbitals have been visualized using B3LYP method when shows a different in HOMO energy, Atomic charges are similar between the atropisomers, UV-Vis spectra have been also determined and interpreted.

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