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DFT study of 2,6-dicyanooxane, 2,6-dicyanothiane, 2,6-dicyanoselenane and their corresponding isodicyano isomers

Peyvand Ghanbarpour

Department of Chemistry, College of Science, Arak Branch, Islamic Azad University, Arak, Iran.

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Abstract: Conformational preference, structural, thermodynamic and electrostatic parameters of 2,6-dicyanooxane, 2,6-dicyanothiane, 2,6-dicyanoselenane and their corresponding isodicyano isomers were Studied by means LC-WPBE, LC-BLYP, B3LYP, M06-2X and MP2 methods with the 6-311+G** basis set, natural bond orbital (NBO) interpretation and atoms in molecules theory (AIM). All levels of theory used in this work showed that the axial-equatorial conformations of theses compounds are most stable compared to their corresponding axial-axial and equatorial-equatorial forms.

Keywords: DFT-B3LYP, NBO, 2,6-Dicyanooxane, 2,6-Dicyanothiane, 2,6-Dicyanoselenane.

Introduction

Heterocycles are an important class of organic compounds largely represented in nature and in daily life applications. The knowledge of their properties and chemical behavior is crucial for understanding their functions in biological systems and predicting their features in new materials. Often, heterocyclic compounds are able to undergo chemical transformation into other, more stable, heterocycles [1]. Nowadays, with the development of continuously more affordable and reliable quantum chemical methods heterocyclic properties can be described on the basis of theoretical calculations [2].In this way many researches focused on the tetrahydropyran as a heterocylic compound and derivation′ s [3-7].

The classical anomeric effect was for long time considered an intriguing phenomenon that nonetheless played a key role in determining the structure and reactivity of carbohydrates and related organic compounds.

Over the past half-century or so modern experimental and theoretical methods and the sustained efforts of several groups worldwide have yielded a clearer picture of the anomeric effect. It is now recognised as representing a fundamental and dominant stereoelectronic interaction that determines structure and energetics in both ground and transition states [8–12]. One of the most important recent developments in computational chemistry is the rise of the use of density functional theory (DFT) [13-22]. The introducing of gradient-corrected (nonlocal) functionals and hybrid approaches has quickly led to the development of new mathematical expressions for exchange and correlation terms which are useful in calculating geometries, energies, vibrational frequencies and other important molecular properties [23-26]. It appears that new DFT methods may give equal or greater accuracy and efficiency for medium-sized or larger molecular systems at lower computational costs than ab initio [27]. Many studies have been done on determination factors of conformation preference in heterocylic compounds [28-30]. In 2010 Mo performed the reaserches on the

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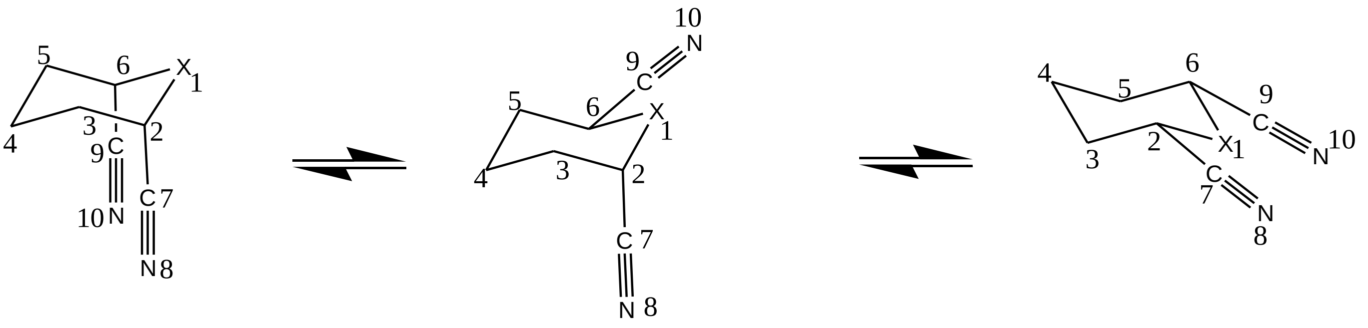
*Corresponding author. Tel: +98 (863 366 3041); E-mail: peyvandghanbarpour@yahoo.com

conformation preference of dimethoxymethane, substituted tetrahydropyrans, and reference molecules (dimethyl ether, tetrahydropyrans and substituted cyclohexanes). He concluded that hyperconjugative interactions are not responsible for the anomeric effect and he interpreted the result in terms of electrostatic interactions [31]. There is no general consensus about the actual origin of the conformation preference, but the factors of multiple steric (i.e. Pauli exchange) and stereoelectronic interactions (associated with dipole–dipole interactions and donor–acceptor electron delocalization) are discussed as a possible factor [32-34]. There are no published data about impacts of the structural parameters, hyper-conjugative anomeric effect (HCAE), dipole–dipole interactions , and steric repulsions on the conformational preferences in compounds **1-6**, accordingly in the present work, we investigate the impacts of the above mentioned factors on the conformational behaviors of compounds **1-6** by means of the long-range corrected density functional (LC-BLYP [35], LC-ωPBE [36]), hybrid meta exchange–correlation functional(M06-2X) [37] hybrid density functional (B3LYP) [38-40] theory based methods, second-order M□ller–Plesset perturbation theory (MP2) calculations [41,42] with 6-311+G** [43-46] basis set on all atoms ,natural bond orbital (NBO) interpretation [47] and AIM analysis [48].

Results and discussion

Structural parameters:

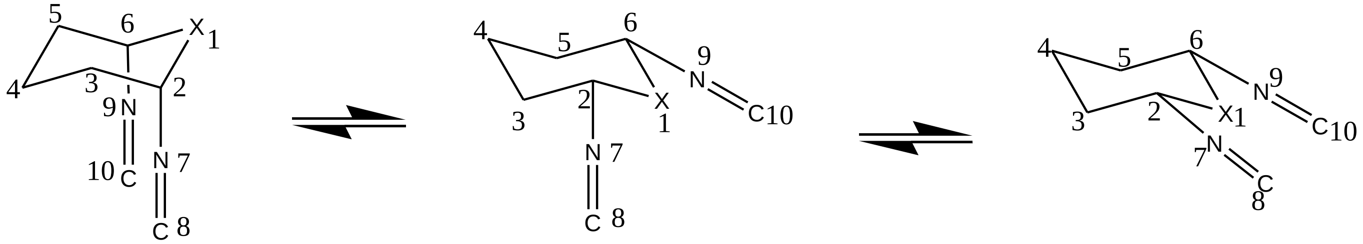
The structural parameters [bond lengths (r), bond angles (θ), torsion angles (ϕ) and their differences: Δr, Δθ and Δϕ parameters] for the axial-axial, axial-equatorial and equatorial-equatorial conformations of compounds **1**–**3** and **4-6**, as calculated at the LC-wPBE/6-311+G**, B3LYP/6-311+G**, LC-BLYP/6-311+G**, M06-2X/6-311+G** and MP2/6-311+G** levels of theory, are summarized in Table **1**. The $\sigma_{M1\text{-}C2}$ bond lengths in the axial- equatorial conformations of compounds of **1- 6** are shorter than the $\sigma_{M1\text{-}C6}$ bond lengths.Also the $\sigma_{C2\text{-}CN}$ and $\sigma_{C2\text{-}NC}$ bond lengths in the axial-equatorial conformations of compounds **1- 6** are longer than $\sigma_{C6\text{-}CN}$ and $\sigma_{C6\text{-}NC}$ bond lengths. The hyper-conjugative interactions between the non-bonded lone pairs of the six-membered rings [LPM, M = O, S, Se] and the $\sigma^*_{C2\text{-}CN}$ and $\sigma^*_{C2\text{-}NC}$ anti-bonding orbitals ($LP_{ax}M_1 \rightarrow \sigma^*_{C2\text{-}CN}$) and ($LP_{ax}M_1 \rightarrow \sigma^*_{C2\text{-}NC(ax)}$) are responsible for decrease the $\sigma_{M1\text{-}C2}$ bond lengths by increasing their double bond characters. Also the mentioned hyper-conjugative interactions cause to increase $\sigma_{C2\text{-}CN}$ and $\sigma_{C2\text{-}NC}$ bond lengths compared to the $\sigma_{C6\text{-}CN}$ and $\sigma_{C6\text{-}NC}$ bond lengths in axial-equatorial conformations of compounds **1- 6**.



Ax-Ax Ax-Eq Eq-Eq

X = O(1), S(2), Se(3)

Scheme 1: Schematic representation of the axial- axial, axial-equatorial and equatorial-equatorial conformations of compounds **1**–**3**.



Ax-Ax Ax-Eq Eq-Eq

X = O(4), S(5), Se(6)

Scheme 2: Schematic representation of the axial- axial, axial-equatorial and equatorial-equatorial conformations of compounds **4**–**6**.

The evidence which illustrates the importance of the hyperconjugative interaction impacts on the structural parameters is the decrease of the $\Delta[\theta_{6\text{-}1\text{-}2(ax,eq)}-\theta_{6\text{-}1\text{-}2(eq,eq)}]$ and $\Delta[\phi_{6\text{-}1\text{-}2\text{-}3(ax,eq)}-\phi_{6\text{-}1\text{-}2\text{-}3(eq,eq)}]$ parameters ongoing from the axial-equatorial conformations of compound **1** to compound **3** and from compound **4** to compound **6**. Note that the strong $LP_{ax}M_1\rightarrow\sigma^*_{C2\text{-}CN(ax)}$and $LP_{ax}M_1\rightarrow\sigma^*_{C2\text{-}NC(ax)}$ electron delocalizations in the axial-equatorial conformations of compounds **1-3** and **4-6**, respectively, increase the double bond characters of the M_1–C_2 bonds compared M_1-C_6 and $\theta_{6\text{-}1\text{-}2}$, decreasing the ($\phi_{6\text{-}1\text{-}2\text{-}3}$) torsion angle values in the axial-equatorial conformation compared to those in their corresponding equatorial-equatorial forms.

Natural Bond Orbital analyses (NBO):

A second-order perturbation theory analysis was performed on the NBOs to estimate the stabilization energy of donor–acceptor orbital interactions. In this way, the anomeric effect was analyzed and a quantitative measure of the energy associated with orbital interactions was estimated. The calculation results for all conformations of the compounds **1-6** are given in Table **5** and **6**. The results show that the summation of stabilizing interactions in the axial- axial forms is higher than those in the other forms.

We deleted electron delocalizations [*ie.* $LP_{M1}\rightarrow\pi^*_{C\equiv N}$, $LP_{M1}\rightarrow\sigma^*_{C\equiv N}$, $LP_{M1}\rightarrow\pi^*_{N\equiv C}$, $LP_{M1}\rightarrow\sigma^*_{N\equiv C}$, M = O, S, Se] from the Fock matrixes of the axial-axial, axial-equatorial and equatorial- equatorial conformations (Tables **7** and **8**). The NBO analysis show that the hyper-conjugative anomeric effect (HCAE) have not determinant impacts on the conformation preferences in compounds **1-6**.

Based on results, the $HCAE_{total}$ associated with the HC-endo-AEs and HC-exo-AEs in the axial-axial, axial-equatorial and equatorial-equatorial conformations $\Sigma(HCAE)_{ax,ax}-\Sigma(HCAE)_{ax,eq}$ parameters decrease ongoing from compound **1** to compound **3** but increase from compound **4** to compound **5** and decrease compound **5** to compound **6**. Also $\Sigma(HCAE_{eq,eq}-\Sigma(HCAE)_{ax,eq}$ decrease ongoing from compound **1** to **2** but increase compound **2** to compound **3**, and decrease from compound **4** to compound **5** and increase compound **5** to compound **6**. The variations of $\Sigma(HCAE)_{ax,ax}-\Sigma(HCAE)_{ax,eq}$ parameter on going from compounds **1** to **2** and $\Sigma(HCAE_{eq,eq}-\Sigma(HCAE)_{ax,eq}$ parameter ongoing from compounds **4** to **5** correlate very well with the differences energies between the axial–axial, equatorial-equatorial and axial-equatorial conformations of compounds **1-2** and **4-5**,respectively. But the variations of HCAE values from compound **2** to **3** and also from compound **5** to compound **6** do not justify solely their variations of the axial-equtorial conformation preferences between conformations of the mention compounds.

Table 1. B3LYP/6-311+G**, LC-ωPBE6-311+G**(a), LC-BLYP/6-311+G**(b), M06-2X/6-311+G**(c) and MP2/6-311+G**(d) calculated bond lengths (Å) for the conformations of compounds **1**-**6**.

	1			2			3			4			5			6		
Geometry	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
Bond lengths (Å)																		
r_{1-2}	1.413	1.426	1.430	1.853	1.852	1.859	2.005	2.004	2.011	1.420	1.413	1.425	1.848	1.846	1.861	2.001	1.999	2.012
	1.413[a]	1.410[a]	1.413[a]	1.813[a]	1.812[a]	1.818[a]	1.949[a]	1.949[a]	1.955[a]	1.405[a]	1.399[a]	1.409[a]	1.809[a]	1.807[a]	1.821[a]	1.946[a]	1.946[a]	1.957[a]
	1.407[b]	1.404[b]	1.406[b]	1.810[b]	1.808[b]	1.815[b]	1.944[b]	1.944[b]	1.950[b]	1.399[b]	1.393[b]	1.402[b]	1.805[b]	1.804[b]	1.816[b]	1.941[b]	1.940[b]	1.951[b]
	1.417[c]	1.413[c]	1.417[c]	1.833[c]	1.832[c]	1.838[c]	1.976[c]	1.977[c]	1.982[c]	1.409[c]	1.402[c]	1.412[c]	1.829[c]	1.828[c]	1.840[c]	1.975[c]	1.974[c]	1.984[c]
	1.427[d]	1.425[d]	1.427[d]	1.827[d]	1.826[d]	1.831[d]	1.978[d]	1.979[d]	1.983[d]	1.416[d]	1.410[d]	1.421[d]	1.821[d]	1.820[d]	1.832[d]	1.974[d]	1.973[d]	1.984[d]
r_{2-3}	1.538	1.538	1.537	1.543	1.542	1.541	1.540	1.540	1.538	1.533	1.533	1.532	1.537	1.537	1.532	1.535	1.535	1.530
	1.525[a]	1.525[a]	1.524[a]	1.529[a]	1.529[a]	1.528[a]	1.529[a]	1.529[a]	1.527[a]	1.520[a]	1.521[a]	1.519[a]	1.524[a]	1.524[a]	1.521[a]	1.524[a]	1.524[a]	1.520[a]
	1.519[b]	1.519[b]	1.517[b]	1.524[b]	1.524[b]	1.522[b]	1.523[b]	1.524[b]	1.521[b]	1.514[b]	1.515[b]	1.512[b]	1.519[b]	1.519[b]	1.514[b]	1.518[b]	1.518[b]	1.513[b]
	1.532[c]	1.532[c]	1.531[c]	1.536[c]	1.536[c]	1.534[c]	1.535[c]	1.536[c]	1.533[c]	1.527[c]	1.527[c]	1.525[c]	1.531[c]	1.531[c]	1.526[c]	1.530[c]	1.530[c]	1.525[c]
	1.532[d]	1.532[d]	1.530[d]	1.537[d]	1.537[d]	1.535[d]	1.537[d]	1.537[d]	1.534[d]	1.527[d]	1.527[d]	1.525[d]	1.531[d]	1.532[d]	1.527[d]	1.531[d]	1.533[d]	1.526[d]
r_{3-4}	1.532	1.533	1.534	1.533	1.533	1.533	1.534	1.534	1.534	1.531	1.533	1.535	1.532	1.532	1.534	1.533	1.533	1.534
	1.520[a]	1.522[a]	1.523[a]	1.522[a]	1.522[a]	1.522[a]	1.522[a]	1.523[a]	1.522[a]	1.519[a]	1.521[a]	1.523[a]	1.521[a]	1.521[a]	1.522[a]	1.521[a]	1.522[a]	1.523[a]
	1.515[b]	1.517[b]	1.517[b]	1.516[b]	1.517[b]	1.516[b]	1.517[b]	1.517[b]	1.517[b]	1.514[b]	1.516[b]	1.517[b]	1.515[b]	1.516[b]	1.516[b]	1.516[b]	1.517[b]	1.517[b]
	1.532[c]	1.529[c]	1.529[c]	1.528[c]	1.529[c]	1.528[c]	1.528[c]	1.529[c]	1.529[c]	1.526[c]	1.528[c]	1.530[c]	1.527[c]	1.528[c]	1.528[c]	1.528[c]	1.528[c]	1.529[c]
	1.529[d]	1.530[d]	1.531[d]	1.529[d]	1.530[d]	1.530[d]	1.530[d]	1.531[d]	1.531[d]	1.528[d]	1.529[d]	1.531[d]	1.528[d]	1.529[d]	1.530[d]	1.529[d]	1.531[d]	1.531[d]
r_{4-5}	1.532	1.535	1.534	1.533	1.534	1.533	1.534	1.535	1.534	1.531	1.535	1.535	1.532	1.534	1.534	1.533	1.535	1.534
	1.520[a]	1.523[a]	1.523[a]	1.522[a]	1.523[a]	1.522[a]	1.522[a]	1.523[a]	1.522[a]	1.519[a]	1.523[a]	1.523[a]	1.521[a]	1.523[a]	1.522[a]	1.521[a]	1.523[a]	1.523[a]
	1.515[b]	1.517[b]	1.517[b]	1.516[b]	1.517[b]	1.516[b]	1.517[b]	1.518[b]	1.517[b]	1.514[b]	1.517[b]	1.517[b]	1.515[b]	1.517[b]	1.516[b]	1.516[b]	1.518[b]	1.517[b]
	1.527[c]	1.529[c]	1.529[c]	1.528[c]	1.529[c]	1.528[c]	1.528[c]	1.529[c]	1.529[c]	1.526[c]	1.529[c]	1.530[c]	1.527[c]	1.529[c]	1.528[c]	1.528[c]	1.529[c]	1.529[c]
	1.529[d]	1.531[d]	1.531[d]	1.529[d]	1.531[d]	1.530[d]	1.530[d]	1.532[d]	1.531[d]	1.528[d]	1.531[d]	1.531[d]	1.528[d]	1.531[d]	1.530[d]	1.529[d]	1.532[d]	1.531[d]
r_{5-6}	1.538	1.538	1.537	1.543	1.541	1.541	1.540	1.539	1.538	1.533	1.531	1.532	1.537	1.533	1.532	1.535	1.530	1.530
	1.525[a]	1.524[a]	1.524[a]	1.529[a]	1.529[a]	1.528[a]	1.529[a]	1.528[a]	1.527[a]	1.520[a]	1.518[a]	1.519[a]	1.524[a]	1.521[a]	1.521[a]	1.524[a]	1.520[a]	1.520[a]
	1.519[b]	1.518[b]	1.517[b]	1.524[b]	1.523[b]	1.522[b]	1.523[b]	1.522[b]	1.521[b]	1.514[b]	1.512[b]	1.512[b]	1.519[b]	1.515[b]	1.514[b]	1.518[b]	1.514[b]	1.513[b]
	1.532[c]	1.531[c]	1.531[c]	1.536[c]	1.535[c]	1.534[c]	1.535[c]	1.534[c]	1.533[c]	1.527[c]	1.525[c]	1.525[c]	1.531[c]	1.527[c]	1.526[c]	1.530[c]	1.526[c]	1.525[c]
	1.532[d]	1.531[d]	1.530[d]	1.37[d]	1.536[d]	1.535[d]	1.537[d]	1.536[d]	1.534[d]	1.527[d]	1.524[d]	1.525[d]	1.531[d]	1.528[d]	1.527[d]	1.531[d]	1.528[d]	1.526[d]
r_{6-1}	1.431	1.435	1.430	1.853	1.860	1.859	2.005	2.010	2.011	1.420	1.432	1.425	1.848	1.862	1.861	2.001	2.011	2.012
	1.431[a]	1.417[a]	1.413[a]	1.813[a]	1.819[a]	1.818[a]	1.949[a]	1.955[a]	1.955[a]	1.405[a]	1.415[a]	1.409[a]	1.809[a]	1.821[a]	1.821[a]	1.946[a]	1.956[a]	1.957[a]
	1.407[b]	1.411[b]	1.406[b]	1.810[b]	1.815[b]	1.815[b]	1.944[b]	1.949[b]	1.950[b]	1.399[b]	1.408[b]	1.402[b]	1.805[b]	1.817[b]	1.816[b]	1.941[b]	1.949[b]	1.951[b]
	1.417[c]	1.421[c]	1.417[c]	1.833[c]	1.838[c]	1.838[c]	1.976[c]	1.982[c]	1.981[c]	1.409[c]	1.419[c]	1.412[c]	1.829[c]	1.840[c]	1.840[c]	1.975[c]	1.984[c]	1.984[c]

	1.427 [d]	1.431 [d]	1.427 [d]	1.827 [d]	1.831[d]	1.831[d]	1.978[d]	1.981[d]	1.983[d]	1.416[d]	1.426 [d]	1.421 [d]	1.821[d]	1.832[d]	1.832[d]	1.974[d]	1.981[d]	1.984[d]
$r_{2\text{-}C\equiv N}$	1.480	1.481	1.466	1.463	1.463	1.458	1.457	1.456	1.453	-	-	-	-	-	-	-	-	-
	1.478 [a]	1.479 [a]	1.465 [a]	1.463 [a]	1.463 [a]	1.458 [a]	1.459 [a]	1.458 [a]	1.455 [a]	-	-	-	-	-	-		-	-
	1.472 [b]	1.473 [b]	1.459 [b]	1.458 [b]	1.457[b]	1.452[b]	1.453[b]	1.453[b]	1.499[b]	-	-	-	-	-	-	-	-	-
	1.484 [c]	1.484 [c]	1.469 [c]	1.466 [c]	1.465 [c]	1.461 [c]	1.461 [c]	1.461 [c]	1.457 [c]	-	-	-	-	-	-	-	-	-
	1.481 [d]	1.481 [d]	1.470 [d]	1.466 [d]	1.466[d]	1.462[d]	1.461[d]	1.461[d]	1.458[d]	-	-	-	-	-	-	-	-	-
$r_{6\text{-}C\equiv N}$	1.480	1.466	1.466	1.463	1.457	1.458	1.457	1.453	1.453	-	-	-	-	-	-	-	-	-
	1.478 [a]	1.465 [a]	1.465 [a]	1.463 [a]	1.458 [a]	1.458 [a]	1.459 [a]	1.455 [a]	1.455 [a]	-	-	-	-	-	-		-	-
	1.472 [b]	1.458 [b]	1.459 [b]	1.458 [b]	1.452[b]	1.452[b]	1.453[b]	1.449[b]	1.449[b]	-	-	-	-	-	-	-	-	-
	1.484 [c]	1.469 [c]	1.469 [c]	1.466 [c]	1.460 [c]	1.461 [c]	1.461 [c]	1.457 [c]	1.457 [c]	-	-	-	-	-	-	-	-	-
	1.481 [d]	1.467 [d]	1.470 [d]	1.466 [d]	1.461[d]	1.462[d]	1.461[d]	1.458[d]	1.458[d]	-	-	-	-	-	-	-	-	-
$r_{C\equiv N(ax)}$	1.153	1.153	-	1.153	1.154	-	1.154	1.154	-	-	-	-	-	-	-	-	-	-
	1.146 [a]	1.146 [a]	-	1.146 [a]	1.146 [a]	-	1.146 [a]	1.147 [a]	-	-	-	-	-	-	-		-	-
	1.138 [b]	1.138 [b]	-	1.138 [b]	1.139[b]	-	1.139[b]	1.139[b]	-	-	-	-	-	-	-	-	-	-
	1.148 [c]	1.148 [c]	-	1.149 [c]	1.149 [c]	-	1.149 [c]	1.150 [c]	-	-	-	-	-	-	-	-	-	-
	1.176 [d]	1.176 [d]	-	1.177 [d]	1.177[d]	-	1.178[d]	1.178[d]	-	-	-	-	-	-	-	-	-	-
$r_{C\equiv N(eq)}$	-	1.152	1.152	-	1.153	1.153	-	1.154	1.154	-	-	-	-	-	-	-	-	-
	-	1.145 [a]	1.145 [a]	-	1.146 [a]	1.146 [a]	-	1.146 [a]	1.146 [a]	-	-	-	-	-	-		-	-
	-	1.137 [b]	1.137 [b]	-	1.138[b]	1.138[b]	-	1.139[b]	1.138[b]	-	-	-	-	-	-	-	-	-
	-	1.147 [c]	1.147 [c]	-	1.148 [c]	1.148 [c]	-	1.149 [c]	1.149 [c]	-	-	-	-	-	-	-	-	-
	-	1.175 [d]	1.175 [d]	-	1.176[d]	1.176[d]	-	1.177[d]	1.177[d]	-	-	-	-	-	-	-	-	-
$r_{2\text{-}N=C}$	-	-	-	-	-	-	-	-	-	1.438	1.443	1.418	1.425	1.428	1.418	1.419	1.422	1.415
	-	-	-	-	-	-	-	-	-	1.433 [a]	1.438 [a]	1.415 [a]	1.423 [a]	1.426 [a]	1.417 [a]	1.420 [a]	1.422 [a]	1.416 [a]
	-	-	-	-	-	-	-	-		1.428[b]	1.432 [b]	1.409 [b]	1.419[b]	1.422[b]	1.412[b]	1.416[b]	1.418[b]	1.411[b]
	-	-	-	-	-	-	-	-	-	1.437 [c]	1.443 [c]	1.419 [c]	1.429 [c]	1.428 [c]	1.418 [c]	1.420 [c]	1.423 [c]	1.417 [c]
	-	-	-	-	-	-	-	-	-	1.435[d]	1.440 [d]	1.416 [d]	1.425[d]	1.428[d]	1.419[d]	1.421[d]	1.422[d]	1.417[d]
$r_{6\text{-}N=C}$	-	-	-	-	-	-	-	-	-	1.438	1.418	1.418	1.425	1.418	1.418	1.419	1.415	1.415
	-	-	-	-	-	-	-	-	-	1.433 [a]	1.415 [a]	1.415 [a]	1.423 [a]	1.417 [a]	1.416 [a]	1.420 [a]	1.416 [a]	1.416 [a]
	-	-	-	-	-	-	-	-	-	1.428[b]	1.410 [b]	1.409 [b]	1.419[b]	1.412[b]	1.412[b]	1.416[b]	1.411[b]	1.411[b]
	-	-	-	-	-	-	-	-	-	1.437 [c]	1.419 [c]	1.419 [c]	1.425 [c]	1.419 [c]	1.418 [c]	1.420 [c]	1.417 [c]	1.417 [c]
	-	-	-	-	-	-	-	-	-	1.435[d]	1.417 [d]	1.416 [d]	1.425[d]	1.419[d]	1.419[d]	1.421[d]	1.417[d]	1.417[d]
$r_{N=C(ax)}$	-	-	-	-	-	-	-	-	-	1.172	1.172	-	1.172	1.172	-	1.173	1.172	-
	-	-	-	-	-	-	-	-	-	1.166 [a]	1.165 [a]	-	1.166 [a]	1.165 [a]	-	1.166 [a]	1.165 [a]	-
	-	-	-	-	-	-	-	-	-	1.157[b]	1.157 [b]	-	1.157[b]	1.157[b]	-	1.158[b]	1.157[b]	-

	-	-	-	-	-	-	-	-	-	1.169[c]	1.168[c]	-	1.169[c]	1.169[c]	-	1.169[c]	1.169[c]	-
	-	-	-	-	-	-	-	-	-	1.189[d]	1.188[d]	-	1.189[d]	1.189[d]	-	1.190[d]	1.190[d]	-
$r_{N=C(eq)}$	-	-	-	-	-	-	-	-	-	-	1.171	1.172	-	1.172	1.172	-	1.173	1.173
	-	-	-	-	-	-	-	-	-	-	1.165[a]	1.165[a]	-	1.165[a]	1.165[a]	-	1.166[a]	1.166[a]
	-	-	-	-	-	-	-	-	-	-	1.157[b]	1.157[b]	-	1.157[b]	1.157[b]	-	1.158[b]	1.158[b]
	-	-	-	-	-	-	-	-	-	-	1.168[c]	1.168[c]	-	1.169[c]	1.169[c]	-	1.169[c]	1.169[c]
	-	-	-	-	-	-	-	-	-	-	1.187[d]	1.187[d]	-	1.188[d]	1.188[d]	-	1.190[d]	1.189[d]
$\Delta[r_{1-2(ax,eq)}-r_{1-2(ax,ax)}]$		-0.005			-0.001			-0.001			-0.007			-0.002			-0.002	
		-0.003[a]			-0.001[a]			0.000[a]			-0.006[a]			-0.002[a]			0.000[a]	
		-0.003[b]			-0.002[b]			0.000[b]			-0.006[b]			-0.001[b]			-0.001[b]	
		-0.004[c]			-0.001[c]			0.001[c]			-0.007[c]			-0.001[c]			-0.001[c]	
		-0.002[d]			-0.001[d]			0.001[d]			-0.006[d]			-0.001[d]			-0.001[d]	
$\Delta[r_{1-2(ax,eq)}-r_{1-2(eq,eq)}]$		-0.004			-0.007			-0.007			-0.012			-0.015			-0.013	
		-0.003[a]			-0.006[a]			-0.006[a]			-0.01[a]			-0.014[a]			-0.011[a]	
		-0.0024[b]			-0.007[b]			-0.006[b]			-0.009[b]			-0.012[b]			-0.011[b]	
		-0.004[c]			-0.006[c]			-0.005[c]			-0.010[c]			-0.012[c]			-0.010[c]	
		-0.002[d]			-0.005[d]			-0.004[d]			-0.011[d]			-0.012[d]			-0.011[d]	
$\Delta[r_{2-C\equiv N(ax,eq)}-r_{2-C\equiv N(ax,ax)}]$		0.001			0.000			-0.001			-			-			-	
		0.001[a]			0.000[a]			-0.001[a]			-			-			-	
		0.001[b]			-0.001[b]			0.000[b]			-			-			-	
		0.000[c]			-0.001[c]			0.000[c]			-			-			-	
		0.000[d]			-0.006[d]			0.000[d]			-			-			-	
$\Delta[r_{2-C\equiv N(ax,eq)}-r_{2-C\equiv N(eq,eq)}]$		0.015			0.005			0.003			-			-			-	
		0.014[a]			0.005[a]			0.003[a]			-			-			-	
		0.014[b]			0.005[b]			0.004[b]			-			-			-	
		0.010[c]			0.006[c]			0.004[c]			-			-			-	
		0.013[d]			0.004[d]			0.003[d]			-			-			-	
$\Delta[r_{2-N=C(ax,eq)}-r_{2-N=C(ax,ax)}]$		-			-			-			0.005			0.003			0.003	
		-			-			-			0.005[a]			0.003[a]			0.002[a]	
		-			-			-			0.004[b]			0.003[b]			0.002[b]	
		-			-			-			0.006[c]			0.003[c]			0.003[c]	
		-			-			-			0.005[d]			0.003[d]			0.001[d]	
$\Delta[r_{2-N=C(ax,eq)}-r_{2-N=C(eq,eq)}]$		-			-			-			0.025			0.010			0.007	

	-	-	-	0.023^{a}	0.009^{a}	0.006^{a}
	-	-	-	0.023^{b}	0.010^{b}	0.007^{b}
	-	-	-	0.024^{c}	0.010^{c}	0.006^{c}
				0.024^{d}	0.009^{d}	0.005^{d}
$\Delta[r_{1\text{-}2(ax,eq)}-r_{1\text{-}6(ax,ax)}]$	-0.005	-0.001	-0.001	-0.007	1.848	-0.002
	-0.003^{a}	-0.001^{a}	0.000^{a}	-0.006^{a}	1.809^{a}	0.000^{a}
	-0.003^{b}	-0.002^{b}	0.000^{b}	-0.006^{b}	1.805^{b}	-0.001^{b}
	-0.004^{c}	-0.001^{c}	0.001^{c}	-0.007^{c}	1.829^{c}	-0.001^{c}
	-0.002^{d}	-0.001^{d}	0.001^{d}	-0.006^{d}	1.821^{d}	-0.001^{d}
$\Delta[r_{1\text{-}2(ax,eq)}-r_{1\text{-}6(eq,eq)}]$	-0.004	-0.007	-0.007	-0.012	-0.015	-0.013
	-0.003^{a}	-0.006^{a}	-0.006^{a}	-0.010^{a}	-0.014^{a}	-0.011^{a}
	-0.002^{b}	-0.007^{b}	-0.006^{b}	-0.009^{b}	-0.012^{b}	-0.011^{b}
	-0.004^{c}	-0.006^{c}	-0.004^{c}	-0.010^{c}	-0.012^{c}	-0.010^{c}
	-0.002^{d}	-0.005^{d}	-0.004^{d}	-0.011^{d}	-0.012^{d}	-0.011^{d}

Table 2. B3LYP/6-311+G**, LC-ωPBE6-311+G**$^{(a)}$, LC-BLYP/6-311+G**$^{(b)}$, M06-2X/6-311+G**$^{(c)}$ and MP2/6-311+G**$^{(d)}$ calculated Bond angles (°)for the conformations of compounds **1-6**.

	1			**2**			**3**			**4**			**5**			**6**		
Geometry	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
Bond angles (degree)																		
$\theta_{1\text{-}2\text{-}3}$	112.6	111.7	111.7	112.7	112.7	112.4	112.3	111.7	112.2	113.1	112.2	111.3	113.0	112.5	112.4	112.4	112.0	112.2
	112.8^{a}	111.8^{a}	111.6^{a}	112.9^{a}	112.3^{a}	112.5^{a}	112.5^{a}	112.0^{a}	112.3^{a}	113.1^{a}	112.2^{a}	111.3^{a}	113.1^{a}	112.6^{a}	112.4^{a}	112.7^{a}	112.2^{a}	112.3^{a}
	112.5^{b}	111.6^{b}	111.4^{b}	112.9^{b}	112.4^{b}	112.6^{b}	112.5^{b}	112.0^{b}	112.4^{b}	112.9^{b}	112.0^{b}	111.2^{b}	113.2^{b}	112.7^{b}	112.6^{b}	112.7^{b}	112.3^{b}	112.4^{b}
	112.7^{c}	111.8^{c}	111.5^{c}	112.7^{c}	112.3^{c}	112.5^{c}	112.4^{c}	111.8^{c}	112.2^{c}	113.1^{c}	112.3^{c}	111.2^{c}	113.0^{c}	112.5^{c}	112.4^{c}	112.4^{c}	112.0^{c}	112.1^{c}
	112.5^{d}	111.6^{d}	111.6^{d}	112.6^{d}	112.1^{d}	112.4^{d}	112.1^{d}	111.6^{d}	112.1^{d}	113.4^{d}	112.4^{d}	111.6^{d}	113.3^{d}	112.8^{d}	112.6^{d}	112.7^{d}	112.3^{d}	112.3^{d}
$\theta_{2\text{-}3\text{-}4}$	111.0	110.8	110.8	113.7	113.2	112.2	114.6	114.1	113.1	111.1	111.0	109.5	113.8	113.5	112.2	114.6	114.4	113.1
	110.5^{a}	110.3^{a}	109.2^{a}	112.9^{a}	112.6^{a}	111.7^{a}	113.7^{a}	113.4^{a}	112.5^{a}	110.6^{a}	110.5^{a}	109.1^{a}	113.1^{a}	112.8^{a}	111.7^{a}	113.9^{a}	113.7^{a}	112.4^{a}
	110.5^{b}	110.4^{b}	109.3^{b}	113.0^{b}	112.7^{b}	111.8^{b}	113.8^{b}	113.4^{b}	112.6^{b}	110.7^{b}	110.5^{b}	109.3^{b}	113.1^{b}	112.9^{b}	111.8^{b}	113.9^{b}	113.7^{b}	112.6^{b}
	110.2^{c}	110.1^{c}	109.1^{c}	112.8^{c}	112.5^{c}	111.6^{c}	113.6^{c}	113.3^{c}	112.5^{c}	110.4^{c}	110.3^{c}	109.0^{c}	112.9^{c}	112.7^{c}	111.6^{c}	113.7^{c}	113.5^{c}	112.4^{c}

	110.4^{d}	110.1^{d}	109.1^{d}	112.7^{d}	112.2^{d}	111.5^{d}	113.5^{d}	113.1^{d}	112.4^{d}	110.3^{d}	110.1^{d}	109.0^{d}	112.6^{d}	112.3^{d}	111.4^{d}	113.5^{d}	113.0^{d}	112.3^{d}
$\theta_{3\text{-}4\text{-}5}$	109.5	110.5	110.5	112.9	113.8	114.0	113.8	114.7	114.9	109.2	110.3	110.8	112.6	113.6	114.0	113.7	114.6	114.8
	109.0^{a}	110.0^{a}	110.4^{a}	112.3^{a}	113.2^{a}	113.3^{a}	113.3^{a}	114.2^{a}	114.3^{a}	108.7^{a}	109.8^{a}	110.4^{a}	112.1^{a}	113.0^{a}	113.3^{a}	113.1^{a}	114.0^{a}	114.2^{a}
	109.1^{b}	110.1^{b}	110.4^{b}	112.4^{b}	113.3^{b}	113.4^{b}	113.4^{b}	114.2^{b}	114.3^{b}	108.8^{b}	109.9^{b}	110.4^{b}	112.2^{b}	113.1^{b}	113.3^{b}	113.2^{b}	114.1^{b}	114.2^{b}
	108.9^{c}	109.8^{c}	110.2^{c}	112.3^{c}	113.2^{c}	113.3^{c}	113.4^{c}	114.2^{c}	114.4^{c}	108.6^{c}	109.6^{c}	110.2^{c}	112.2^{c}	113.1^{c}	113.3^{c}	113.4^{c}	114.1^{c}	114.3^{c}
	108.7^{d}	109.6^{d}	109.1^{d}	112.1^{d}	113.0^{d}	113.1^{d}	113.3^{d}	114.2^{d}	114.2^{d}	110.3^{d}	109.4^{d}	109.8^{d}	111.7^{d}	112.8^{d}	112.9^{d}	113.0^{d}	113.8^{d}	114.0^{d}
$\theta_{4\text{-}5\text{-}6}$	111.0	109.8	109.8	113.7	112.6	112.2	114.6	113.4	113.1	111.1	109.8	109.5	113.8	112.5	112.2	114.6	113.2	113.1
	110.5^{a}	109.5^{a}	109.2^{a}	112.9^{a}	112.0^{a}	111.7^{a}	113.7^{a}	112.8^{a}	112.5^{a}	110.6^{a}	109.4^{a}	109.1^{a}	113.1^{a}	111.9^{a}	111.7^{a}	113.9^{a}	112.6^{a}	112.4^{a}
	110.5^{b}	109.6^{b}	109.3^{b}	113.0^{b}	112.2^{b}	111.8^{b}	113.8^{b}	112.9^{b}	112.6^{b}	110.7^{b}	109.6^{b}	109.3^{b}	113.1^{b}	112.1^{b}	111.8^{b}	113.9^{b}	112.7^{b}	112.6^{b}
	110.2^{c}	109.4^{c}	109.1^{c}	112.8^{c}	112.0^{c}	111.6^{c}	113.6^{c}	112.8^{c}	112.5^{c}	110.3^{c}	109.4^{c}	109.0^{c}	112.9^{c}	111.9^{c}	111.6^{c}	113.7^{c}	112.7^{c}	112.4^{c}
	110.4^{d}	109.6^{d}	109.1^{d}	112.7^{d}	112.0^{d}	111.5^{d}	113.5^{d}	112.9^{d}	112.4^{d}	110.3^{d}	109.6^{d}	109.0^{d}	112.6^{d}	111.9^{d}	111.4^{d}	113.5^{d}	112.4^{d}	112.3^{d}
$\theta_{5\text{-}6\text{-}1}$	112.6	111.7	111.7	112.7	112.2	112.4	112.3	111.9	112.2	113.1	111.6	111.3	113.0	112.4	112.4	112.4	112.1	112.2
	112.8^{a}	111.8^{a}	111.6^{a}	112.9^{a}	112.3^{a}	112.5^{a}	112.5^{a}	112.1^{a}	112.3^{a}	113.2^{a}	111.7^{a}	111.3^{a}	113.1^{a}	112.4^{a}	112.4^{a}	112.7^{a}	112.2^{a}	112.3^{a}
	112.5^{b}	111.6^{b}	111.4^{b}	112.9^{b}	112.4^{b}	112.6^{b}	112.5^{b}	112.2^{b}	112.4^{b}	112.9^{b}	111.5^{b}	111.2^{b}	113.2^{b}	112.5^{b}	112.6^{b}	112.7^{b}	112.3^{b}	112.4^{b}
	112.7^{c}	111.7^{c}	111.5^{c}	112.7^{c}	112.2^{c}	112.5^{c}	112.4^{c}	112.0^{c}	112.2^{c}	113.1^{c}	111.6^{c}	111.2^{c}	113.0^{c}	112.3^{c}	112.4^{c}	112.4^{c}	112.1^{c}	112.1^{c}
	112.5^{d}	111.7^{d}	111.6^{d}	112.6^{d}	112.2^{d}	112.4^{d}	112.1^{d}	111.8^{d}	112.1^{d}	113.4^{d}	111.9^{d}	111.6^{d}	113.3^{d}	112.5^{d}	112.6^{d}	112.7^{d}	112.2^{d}	112.3^{d}
$\theta_{6\text{-}1\text{-}2}$	117.6	113.7	113.7	101.0	97.3	96.3	97.6	94.0	93.5	118.7	114.4	111.9	101.5	97.7	96.4	97.8	94.4	94.1
	117.1^{a}	113.1^{a}	111.3^{a}	100.7^{a}	96.9^{a}	96.1^{a}	97.4^{a}	93.6^{a}	93.2^{a}	118.4^{a}	113.9^{a}	111.4^{a}	101.2^{a}	97.2^{a}	96.0^{a}	97.7^{a}	94.0^{a}	93.6^{a}
	117.7^{b}	113.8^{b}	112.1^{b}	100.6^{b}	97.0^{b}	96.2^{b}	97.3^{b}	93.8^{b}	93.4^{b}	118.8^{b}	114.5^{b}	112.2^{b}	101.0^{b}	97.3^{b}	96.2^{b}	97.6^{b}	94.1^{b}	93.8^{b}
	116.9^{c}	113.2^{c}	111.4^{c}	99.8^{c}	96.3^{c}	95.6^{c}	96.2^{c}	92.6^{c}	92.7^{c}	118.1^{c}	113.9^{c}	111.4^{c}	100.0^{c}	96.4^{c}	95.6^{c}	96.1^{c}	93.0^{c}	93.2^{c}
	115.5^{d}	111.9^{d}	110.3^{d}	99.3^{d}	95.9^{d}	95.6^{d}	95.6^{d}	92.2^{d}	92.6^{d}	117.1^{d}	112.7^{d}	110.4^{d}	100.0^{d}	95.9^{d}	95.4^{d}	96.2^{d}	92.5^{d}	92.7^{d}
$\theta_{1\text{-}2\text{-}C\equiv N}$	112.5	110.9	110.9	112.5	110.8	107.3	111.7	110.2	106.8	-	-	-	-	-	-	-	-	-
	112.4^{a}	110.7^{a}	107.5^{a}	112.7^{a}	110.7^{a}	107.5^{a}	112.0^{a}	110.2^{a}	107.3^{a}	-	-	-	-	-	-	-	-	-
	112.2^{b}	110.5^{b}	107.5^{b}	112.7^{b}	110.8^{b}	107.7^{b}	112.1^{b}	110.3^{b}	107.4^{b}	-	-	-	-	-	-	-	-	-
	112.3^{c}	110.5^{c}	107.3^{c}	112.1^{c}	110.1^{c}	107.1^{c}	111.3^{c}	109.4^{c}	106.9^{c}	-	-	-	-	-	-	-	-	-
	112.3	110.5^{d}	106.8^{d}	112.5^{d}	110.3^{d}	107.2^{d}	111.6^{d}	109.5^{d}	106.8^{d}	-	-	-	-	-	-	-	-	-
$\theta_{1\text{-}2\text{-}N\equiv C}$	-	-	-	-	-	-	-	-	-	111.5	110.6	106.7	112.5	111.6	106.9	112.0	111.3	106.9
	-	-	-	-	-	-	-	-	-	111.4^{a}	110.3^{a}	106.9^{a}	112.4^{a}	111.4^{a}	107.0^{a}	112.1^{a}	111.1^{a}	107.0^{a}
	-	-	-	-	-	-	-	-	-	111.2^{b}	110.2^{b}	106.9^{b}	112.3^{b}	111.3^{b}	107.0^{b}	112.0^{b}	111.1^{b}	107.1^{b}
	-	-	-	-	-	-	-	-	-	111.2^{c}	110.2^{c}	106.7^{c}	111.9^{c}	110.9^{c}	106.7^{c}	111.6^{c}	110.5^{c}	106.9^{c}

	-	-	-	-	-	-	-	-	-	111.3^{d}	109.9^{d}	106.0^{d}	112.4^{d}	110.9^{d}	106.6^{d}	111.8^{d}	110.8^{d}	106.6^{d}
$\Delta[\theta_{6\text{-}1\text{-}2(ax,eq)}-\theta_{6\text{-}1\text{-}2(ax,ax)}]$		-3.9			-3.7			-3.6			-4.3			-3.8			-3.4	
		-4.0^{a}			-3.8^{a}			-3.8^{a}			-4.5^{a}			-4.0^{a}			-3.7^{a}	
		-3.9^{b}			-3.6^{b}			-3.5^{b}			-4.3^{b}			-3.7^{b}			-3.5^{b}	
		-3.7^{c}			-3.5^{c}			-3.6^{c}			-4.2^{c}			-3.6^{c}			-3.1^{c}	
		-3.6^{d}			-3.4^{d}			-3.4^{d}			-4.4^{d}			-4.1^{d}			-3.7^{d}	
$\Delta[\theta_{6\text{-}1\text{-}2(ax,eq)}-\theta_{6\text{-}1\text{-}2(eq,eq)}]$		2.0			1.0			۰,۵			2.5			1.3			0.3	
		1.8^{a}			0.8^{a}			0.4^{a}			2.5^{a}			1.2^{a}			0.4^{a}	
		1.7^{b}			0.8^{b}			0.4^{b}			2.3^{b}			1.1^{b}			0.3^{b}	
		1.8^{c}			0.7^{c}			-0.1^{c}			2.5^{c}			0.8^{c}			-0.2^{c}	
		1.6^{d}			0.3^{d}			-0.4^{d}			2.3^{d}			0.5^{d}			-0.2^{d}	

Table 3. B3LYP/6-311+G**, LC-ωPBE6-311+G**$^{(a)}$, LC-BLYP/6-311+G**$^{(b)}$, M06-2X/6-311+G**$^{(c)}$ and MP2/6-311+G**$^{(d)}$ calculated Torsion angles (degree)for the conformations of compounds **1-6.**

	1			**2**			**3**			**4**			**5**			**6**		
Geometry	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
Torsion Angles (°)																		
$\phi_{1\text{-}2\text{-}3\text{-}4}$	51.3	53.6	53.6	57.6	60.5	61.6	58.4	61.6	62.1	50.1	52.6	56.2	56.9	59.8	61.6	58.0	60.7	61.7
	52.2^{a}	54.7^{a}	56.9^{a}	58.6^{a}	61.5^{a}	62.5^{a}	59.5^{a}	62.6^{a}	63.2^{a}	51.0^{a}	53.6^{a}	57.1^{a}	58.0^{a}	60.7^{a}	62.6^{a}	59.0^{a}	61.7^{a}	63.0^{a}
	51.9^{b}	54.3^{b}	56.5^{b}	58.6^{b}	61.4^{b}	62.2^{b}	59.4^{b}	62.4^{b}	62.9^{b}	50.9^{b}	53.3^{b}	56.6^{b}	58.0^{b}	60.6^{b}	62.3^{b}	59.0^{b}	61.6^{b}	62.6^{b}
	52.7^{c}	55.0^{c}	57.1^{c}	59.4^{c}	62.0^{c}	62.9^{c}	60.5^{c}	63.4^{c}	63.5^{c}	51.6^{c}	54.0^{c}	57.3^{c}	59.1^{c}	61.5^{c}	63.0^{c}	60.5^{c}	62.7^{c}	63.2^{c}
	53.9^{d}	56.3^{d}	58.0^{d}	60.3^{d}	62.9^{d}	63.2^{d}	61.4^{d}	64.1^{d}	63.8	52.3^{d}	55.3^{d}	58.0^{d}	59.2^{d}	62.3^{d}	63.4^{d}	60.4^{d}	63.5^{d}	63.7^{d}
$\phi_{2\text{-}3\text{-}4\text{-}5}$	-54.7	-52.0	-52.0	-62.2	-59.4	-59.9	-65.8	-62.8	-63.6	-54.9	-51.7	-52.1	-62.5	-59.6	-60.3	-66.0	-63.1	-64.6
	-55.7^{a}	-52.9^{a}	-52.9^{a}	-62.5^{a}	-59.2^{a}	-59.9^{a}	-65.3^{a}	-62.0^{a}	-62.8^{a}	-56.0^{a}	-52.6^{a}	-52.8^{a}	-62.6^{a}	-59.3^{a}	-60.1^{a}	-65.5^{a}	-62.2^{a}	-63.6^{a}
	-55.7^{b}	-52.9^{b}	-52.9^{b}	-62.3^{b}	-59.2^{b}	-59.8^{b}	-65.2^{b}	-62.0^{b}	-62.8^{b}	-55.9^{b}	-52.6^{b}	-52.8^{b}	-62.5^{b}	-59.3^{b}	-60.0^{b}	-65.3^{b}	-62.2^{b}	-63.6^{b}
	-56.2^{c}	-53.3^{c}	-53.2^{c}	-62.8^{c}	-59.5^{c}	-60.5^{c}	-65.5^{c}	-62.1^{c}	-63.4^{c}	-56.4^{c}	-53.1^{c}	-53.1^{c}	-62.6^{c}	-59.5^{c}	-60.7^{c}	-65.4^{c}	-62.5^{c}	-64.3^{c}
	-55.9^{d}	-53.5^{d}	-54.0^{d}	-62.3^{d}	-59.5^{d}	-60.5^{d}	-65.3^{d}	-62.0^{d}	-63.6^{d}	-56.7^{d}	-53.3^{d}	-53.6^{d}	-63.3^{d}	-59.4^{d}	-60.7^{d}	-66.1^{d}	-62.9^{d}	-64.2^{d}

$\phi_{3-4-5-6}$	54.7	52.7	52.7	62.2	59.5	59.9	65.8	62.8	63.6	54.9	53.1	52.1	62.5	60.2	60.3	66.0	63.6	64.6
	55.7^a	53.5^a	52.9^a	62.5^a	59.4^a	59.9^a	65.3^a	62.1^a	62.8^a	56.0^a	53.9^a	52.8^a	62.6^a	60.0^a	60.1^a	65.5^a	62.8^a	63.6^a
	55.7^b	53.5^b	53.0^b	62.3^b	59.4^b	59.8^b	65.2^b	62.0^b	62.8^b	55.9^b	53.9^b	52.8^b	62.5^b	59.9^b	60.0^b	65.3^b	62.7^b	63.6^b
	56.2^c	53.8^c	53.2^c	62.8^c	59.7^c	60.5^c	65.5^c	62.1^c	63.4^c	56.4^c	54.3^c	53.1^c	62.6^c	60.1^c	60.7^c	65.4^c	62.9^c	64.3^c
	55.9^d	53.7^d	53.6^d	٦٢,٣^d	59.3^d	60.5^d	65.3^d	61.8^d	63.6^d	56.7^d	54.1^d	53.6^d	63.3^d	59.9^d	60.7^d	66.1^d	63.3^d	64.2^d
$\phi_{4-5-6-1}$	-51.3	-55.5	-55.5	-57.6	-61.1	-61.6	-58.4	-62.1	-62.1	-50.1	-55.5	-56.2	-56.9	-61.1	-61.6	-58.0	-62.0	-61.7
	-52.2^a	-56.3^a	61.6^a	-58.6^a	-62.1^a	-62.5^a	-59.5^a	-63.1^a	-63.2^a	-51.0^a	-56.4^a	-57.1^a	-58.0^a	-62.2^a	-62.6^a	-59.0^a	-63.2^a	-63.0^a
	-51.9^b	-55.8^b	-56.5^b	-58.6^b	-61.8^b	-62.2^b	-59.4^b	-62.8^b	-62.9^b	-50.9^b	-55.9^b	-56.6^b	-58.0^b	-61.9^b	-62.3^b	-59.0^b	-62.9^b	-62.6^b
	-52.7^c	-56.4^c	-57.1^c	-59.4^c	-62.6^c	-62.9^c	-60.5^c	-63.8^c	-63.5^c	-51.6^c	-56.4^c	-57.3^c	-59.1^c	-62.7^c	-63.0^c	-60.5^c	-63.8^c	-63.2^c
	-53.9^d	-56.9^d	-58.0^d	-60.2^d	-62.7^d	-63.2^d	-61.4^d	-64.0^d	-63.8^d	-52.3^d	-56.7^d	-58.0^d	-59.2^d	-63.0^d	-63.4^d	-60.4^d	-64.4^d	-63.7^d
$\phi_{5-6-1-2}$	49.4	58.7	58.7	47.5	54.9	55.6	45.1	52.7	52.5	46.8	58.0	61.7	46.1	54.1	55.4	44.4	51.9	51.3
	50.0^a	59.3^a	61.6^a	48.9^a	56.4^a	56.8^a	47.2^a	54.8^a	54.5^a	47.3^a	58.6^a	62.4^a	47.7^a	55.8^a	56.9^a	46.3^a	54.1^a	53.8^a
	49.8^b	58.9^b	61.1^b	49.0^b	56.1^b	56.4^b	47.3^b	54.4^b	54.0^b	47.5^b	58.4^b	61.8^b	47.8^b	55.5^b	56.3^b	46.4^b	53.7^b	53.2^b
	50.6^c	59.2^c	61.8^c	49.9^c	56.8^c	56.8^c	48.4^c	55.5^c	54.6^c	48.2^c	58.5^c	62.6^c	49.3^c	56.5^c	56.8^c	48.6^c	54.8^c	53.7^c
	52.4^d	60.0^d	62.2^d	51.4^d	57.5^d	57.3^d	49.9^d	56.2^d	54.8^d	48.3^d	58.8^d	62.4^d	48.7^d	56.9^d	57.2^d	47.7^d	55.3^d	54.1^d
$\phi_{6-1-2-3}$	-49.4	-57.4	-60.4	-47.5	-54.3	-55.6	-45.1	-52.1	-52.5	-46.8	-56.2	-61.7	-46.1	-53.1	-55.4	-44.4	-50.7	-51.3
	-50.0^a	-58.2^a	-61.6^a	-48.9^a	-55.9^a	-56.8^a	-47.2^a	-54.2^a	-54.5^a	-47.3^a	-56.9^a	-62.4^a	-47.7^a	-54.7^a	-56.9^a	-46.3^a	-53.0^a	-53.8^a
	-49.8^b	-57.9^b	-61.1^b	-49.0^b	-55.6^b	-56.4^b	-47.3^b	-53.9^b	-54.0^b	-47.5^b	-56.8^b	-61.8^b	-47.8^b	-54.5^b	-56.3^b	-46.4^b	-52.7^b	-53.2^b
	-50.6^c	-58.2^c	-61.8^c	-49.9^c	-56.3^c	-56.8^c	-48.4^c	-55.0^c	-54.6^c	-48.2^c	-57.1^c	-62.6^c	-49.3^c	-55.6^c	-56.8^c	-48.6^c	-53.9^c	-53.7^c
	-52.4^d	-59.5^d	-62.2^d	-51.4^d	-57.4^d	-57.3^d	-49.9^d	-56.1^d	-54.8^d	-48.3^d	-58.0^d	-62.4^d	-48.7^d	-56.4^d	-57.2^d	-47.7^d	-54.5^d	-54.1^d
$\Delta[\phi_{6-1-2-3(ax,eq)}-\phi_{6-1-2-3(ax,ax)}]$		-8.0			-6.8			-7.0			-9.4			-7.0			-6.3	
		-8.2^a			-7.0^a			-7.0^a			-9.6^a			-7.0^a			-6.7^a	
		-8.1^b			-6.6^b			-6.6^b			-9.3^b			-6.7^b			-6.3^b	
		-7.6^c			-6.4^c			-6.6^c			-8.9^c			-6.3^c			-5.3^c	
		-7.1^d			-6.0^d			-6.2^d			-9.7^d			-7.7^d			-6.8^d	
$\Delta[\phi_{6-1-2-3(ax,eq)}-\phi_{6-1-2-3(eq,eq)}]$		3.0			1.3			0.4			5.5			2.3			0.6	
		3.4^a			0.9^a			0.3^a			5.5^a			2.2^a			0.8^a	
		3.2^b			0.8^b			0.1^b			5.0^b			1.8^b			0.5^b	
		3.6^c			0.5^c			-0.4^c			5.5^c			1.2^c			-0.2^c	
		2.7^d			-0.1^d			-1.3^d			4.4^d			0.8^d			-0.4^d	

Table 4. LC-wPBE/6-311+G**, LC-BLYP/6-311+G**(a), MP2/6-311+G**(b), B3LYP/6-311+G**(c) and M06-2X/6-311+G**(d), calculated zero-point energies (ZPE), corrected electronic energies (Eo), thermodynamic functions (H, G in hartree, S in cal mol^{-1}K^{-1}) and parameters [ΔZPE, ΔEo, ΔH, ΔG (in kcal mol^{-1})] and ΔS (in cal mol^{-1}K^{-1})] at 25ºC and 1 atm pressure for the conformations of compounds **1-6**.

	H	S	G	ZPE	E_o	ΔH	ΔS	ΔG	ΔZPE	ΔE_o
1*ax-ax*	-455.893668	91.653	-455.937215	0.146291	-455.903356	2.51	0.00	2.55	0.23	2.51
	-454.974863$^{(a)}$	91.141$^{(a)}$	-455.018167$^{(a)}$	0.147514$^{(a)}$	-454.984432$^{(a)}$	2.64$^{(a)}$	0.00$^{(a)}$	2.67$^{(a)}$	0.21$^{(a)}$	2.64$^{(a)}$
	-454.942319$^{(b)}$	92.378$^{(b)}$	-454.986211$^{(b)}$	0.143600$^{(b)}$	-454.952197$^{(b)}$	1.93$^{(b)}$	0.00$^{(b)}$	2.03$^{(b)}$	0.19$^{(b)}$	1.94$^{(b)}$
	-456.209418$^{(c)}$	92.617$^{(c)}$	-456.253423$^{(c)}$	0.142757$^{(c)}$	-456.219316$^{(c)}$	2.69$^{(c)}$	0.00$^{(c)}$	2.70$^{(c)}$	0.19$^{(c)}$	2.69$^{(c)}$
	-456.028559$^{(d)}$	91.327$^{(d)}$	-456.071952$^{(d)}$	0.145120$^{(d)}$	-456.038242$^{(d)}$	1.96$^{(d)}$	0.00$^{(d)}$	2.11$^{(d)}$	0.23$^{(d)}$	1.99$^{(d)}$
1ax-*eq*	-455.897661	91.808	-455.941283	0.146172	-455.907357	0.00	0.15	0.00	0.23	0.00
	-454.979076$^{(a)}$	91.240$^{(a)}$	-455.022428$^{(a)}$	0.147443$^{(a)}$	-454.988644$^{(a)}$	0.00$^{(a)}$	0.10$^{(a)}$	0.00$^{(a)}$	0.16$^{(a)}$	0.00$^{(a)}$
	-454.945397$^{(b)}$	92.706$^{(b)}$	-454.989445$^{(b)}$	0.143578$^{(b)}$	-454.955293$^{(b)}$	0.00$^{(b)}$	0.33$^{(b)}$	0.00$^{(b)}$	0.18$^{(b)}$	0.00$^{(b)}$
	-456.213713$^{(c)}$	92.638$^{(c)}$	-456.257728$^{(c)}$	0.142701$^{(c)}$	-456.223599$^{(c)}$	0.00$^{(c)}$	0.02$^{(c)}$	0.00$^{(c)}$	0.16$^{(c)}$	0.00$^{(c)}$
	-456.031686$^{(d)}$	91.827$^{(d)}$	-456.075316$^{(d)}$	0.144753$^{(d)}$	-456.041412$^{(d)}$	0.00$^{(d)}$	0.50$^{(d)}$	0.00$^{(d)}$	0.00$^{(d)}$	0.00$^{(d)}$
1eq-*eq*	-455.895143	92.056	-455.938882	0.145919	-455.904880	1.58	0.40	1.51	0.00	1.55
	-454.976784$^{(a)}$	91.487$^{(a)}$	-455.020252$^{(a)}$	0.147185$^{(a)}$	-454.986394$^{(a)}$	1.44$^{(a)}$	0.35$^{(a)}$	1.36$^{(a)}$	0.00$^{(a)}$	1.41$^{(a)}$
	-454.942594$^{(b)}$	92.955$^{(b)}$	-454.986760$^{(b)}$	0.143289$^{(b)}$	-454.952532$^{(b)}$	1.76$^{(b)}$	0.58$^{(b)}$	1.68$^{(b)}$	0.00$^{(b)}$	1.73$^{(b)}$
	-456.212040$^{(c)}$	92.780$^{(c)}$	-456.256123$^{(c)}$	0.142449$^{(c)}$	-456.221955$^{(c)}$	1.05$^{(c)}$	0.16$^{(c)}$	1.01$^{(c)}$	0.00$^{(c)}$	1.03$^{(c)}$
	-456.028240$^{(d)}$	91.874$^{(d)}$	-456.071893$^{(d)}$	0.144578$^{(d)}$	-456.037978$^{(d)}$	2.16$^{(d)}$	0.00$^{(d)}$	2.15$^{(d)}$	0.11$^{(d)}$	2.15$^{(d)}$
2*ax-ax*	-778.793599	94.643	-778.838567	0.143198	-778.803806	1.58	0.00	1.67	0.11	1.60
	-777.829320$^{(a)}$	94.109$^{(a)}$	-777.874034$^{(a)}$	0.144355$^{(a)}$	-777.839405$^{(a)}$	1.67$^{(a)}$	0.00$^{(a)}$	1.75$^{(a)}$	0.11$^{(a)}$	1.69$^{(a)}$
	-777.554772$^{(b)}$	95.404$^{(b)}$	-777.600101$^{(b)}$	0.140366$^{(b)}$	-777.565196$^{(b)}$	1.12$^{(b)}$	0.00$^{(b)}$	1.26$^{(b)}$	0.07$^{(b)}$	1.14$^{(b)}$
	-779.197972$^{(c)}$	95.873$^{(c)}$	-779.243524$^{(c)}$	0.139607$^{(c)}$	-779.208441$^{(c)}$	1.78$^{(c)}$	0.00$^{(c)}$	1.88$^{(c)}$	0.07$^{(c)}$	1.81$^{(c)}$
	-779.012101$^{(d)}$	94.689$^{(d)}$	-779.057091$^{(d)}$	0.141332$^{(d)}$	-779.022382$^{(d)}$	1.16$^{(d)}$	0.00$^{(d)}$	1.29$^{(d)}$	0.00$^{(d)}$	1.18$^{(d)}$
2ax-*eq*	-778.796116	94.961	-778.841236	0.143148	-778.806351	0.00	0.32	0.00	0.07	0.00
	-777.831990$^{(a)}$	94.373$^{(a)}$	-777.876829$^{(a)}$	0.144314$^{(a)}$	-777.842096$^{(a)}$	0.00$^{(a)}$	0.26$^{(a)}$	0.00$^{(a)}$	0.08$^{(a)}$	0.00$^{(a)}$
	-777.556564$^{(b)}$	95.877$^{(b)}$	-777.602118$^{(b)}$	0.140437$^{(b)}$	-777.567017$^{(b)}$	0.00$^{(b)}$	0.47$^{(b)}$	0.00$^{(b)}$	0.12$^{(b)}$	0.00$^{(b)}$
	-779.200817$^{(c)}$	96.183$^{(c)}$	-779.246517$^{(c)}$	0.139519$^{(c)}$	-779.211321$^{(c)}$	0.00$^{(c)}$	0.31$^{(c)}$	0.00$^{(c)}$	0.02$^{(c)}$	0.00$^{(c)}$
	-779.013955$^{(d)}$	95.102$^{(d)}$	-779.059141$^{(d)}$	0.141498$^{(d)}$	-779.024263$^{(d)}$	0.00$^{(d)}$	0.41$^{(d)}$	0.00$^{(d)}$	0.10$^{(d)}$	0.00$^{(d)}$
2eq-*eq*	-778.793071	95.388	-778.838393	0.143028	-778.803375	1.91	0.74	1.78	0.00	1.87
	-777.829057$^{(a)}$	94.805$^{(a)}$	-777.874102$^{(a)}$	0.144180$^{(a)}$	-777.839234$^{(a)}$	1.84$^{(a)}$	0.70$^{(a)}$	1.71$^{(a)}$	0.00$^{(a)}$	1.80$^{(a)}$
	-777.553073$^{(b)}$	96.434$^{(b)}$	-777.598892$^{(b)}$	0.140248$^{(b)}$	-777.563607$^{(b)}$	2.19$^{(b)}$	1.03$^{(b)}$	2.02$^{(b)}$	0.00$^{(b)}$	2.14$^{(b)}$
	-779.198731$^{(c)}$	96.319$^{(c)}$	-779.244496$^{(c)}$	0.139487$^{(c)}$	-779.209267$^{(c)}$	1.31$^{(c)}$	0.45$^{(c)}$	1.27$^{(c)}$	0.00$^{(c)}$	1.29$^{(c)}$
	-779.010300$^{(d)}$	95.549$^{(d)}$	-779.055698$^{(d)}$	0.141391$^{(d)}$	-779.020669$^{(d)}$	2.29$^{(d)}$	0.86$^{(d)}$	2.16$^{(d)}$	0.04$^{(d)}$	2.25$^{(d)}$
3*ax-ax*	-2781.895619	97.695	-2781.942037	0.142014	-2781.906190	1.68	0.00	1.83	0.15	1.71
	-2781.020344$^{(a)}$	97.281$^{(a)}$	-2781.066565$^{(a)}$	0.143140$^{(a)}$	-2781.030803$^{(a)}$	1.74$^{(a)}$	0.00$^{(a)}$	1.83$^{(a)}$	0.13$^{(a)}$	1.75$^{(a)}$
	-2779.805918$^{(b)}$	98.633$^{(b)}$	-2779.852782$^{(b)}$	0.139020$^{(b)}$	-2779.816737$^{(b)}$	1.09$^{(b)}$	0.00$^{(b)}$	1.24$^{(b)}$	0.12$^{(b)}$	1.11$^{(b)}$
	-2782.533108$^{(c)}$	99.068$^{(c)}$	-2782.580179$^{(c)}$	0.138476$^{(c)}$	-2782.543958$^{(c)}$	1.88$^{(c)}$	0.00$^{(c)}$	2.01$^{(c)}$	0.18$^{(c)}$	1.92$^{(c)}$
	-2782.379405$^{(d)}$	97.523$^{(d)}$	-2782.425742$^{(d)}$	0.140699$^{(d)}$	-2782.389995$^{(d)}$	1.46$^{(d)}$	0.00$^{(d)}$	1.67$^{(d)}$	0.37$^{(d)}$	0.24$^{(d)}$
3ax-*eq*	-2781.898294	98.190	-2781.944947	0.141902	-2781.908911	0.00	0.49	0.00	0.08	0.00

	-2781.023113(a)	97.580(a)	-2781.069476(a)	0.143081(a)	-2781.033598(a)	0.00(a)	0.30(a)	0.00(a)	0.09(a)	0.00(a)
	-2779.807659(b)	99.125(b)	-2779.854757(b)	0.139035(b)	-2779.818510(b)	0.00(b)	0.49 (b)	0.00(b)	0.13(b)	0.00(b)
	-2782.536109(c)	99.514(c)	-2782.583391(c)	0.138320(c)	-2782.547010(c)	0.00(c)	0.45 (c)	0.00(c)	0.08(c)	0.00(c)
	-2782.381740 (d)	98.219 (d)	-2782.428407(d)	0.140320 (d)	-2782.392413 (d)	0.00 (d)	0.70 (d)	0.00 (d)	0.13 (d)	0.00 (d)
3eq-*eq*	-2781.895786	98.752	-2781.942706	0.141769	-2781.906488	1.57	1.06	1.41	0.00	1.52
	-2781.020681(a)	98.104(a)	-2781.067293(a)	0.142934(a)	-2781.031249(a)	1.53(a)	0.82 (a)	1.37(a)	0.00(a)	1.47(a)
	-2779.804466(b)	99.869(b)	-2779.851917(b)	0.138821(b)	-2779.815416(b)	2.00(b)	1.24(b)	1.78(b)	0.00(b)	1.94(b)
	-2782.534591(c)	100.002(c)	-2782.582105(c)	0.138188(c)	-2782.545572(c)	0.95(c)	0.93 (c)	0.81(c)	0.00(c)	0.90(c)
	-2782.378606 (d)	99.096 (d)	-2782.425690(d)	0.140104 (d)	-2782.389391 (d)	1.97 (d)	1.57 (d)	1.70 (d)	0.00 (d)	1.90 (d)
4ax-ax	-455.837788	92.525	-455.881750	0.145529	-455.847725	1.57	0.00	1.67	0.34	1.60
	-454.924172(a)	91.889(a)	-454.967831(a)	0.146739(a)	-454.933977(a)	1.56(a)	0.00 (a)	1.66(a)	0.31(a)	1.59(a)
	-454.874415(b)	93.472(b)	-454.918827(b)	0.143610(b)	-454.884534(b)	1.41(b)	0.00 (b)	1.48(b)	0.29(b)	1.42(b)
	-456.153069(c)	93.859(c)	-456.197665(c)	0.141963(c)	-456.163268(c)	1.92(c)	0.00 (c)	1.95(c)	0.28(c)	1.92(c)
	-455.978318 (d)	91.963 (d)	-456.022012 (d)	0.144641 (d)	-455.988191 (d)	1.21 (d)	0.00 (d)	1.41 (d)	0.55 (d)	1.27 (d)
4ax-*eq*	-455.840293	92.841	-455.884405	0.145362	-455.850269	0.00	0.32	0.00	0.23	0.00
	-454.926665(a)	92.213(a)	-454.970478(a)	0.146598(a)	-454.936507(a)	0.00(a)	0.32 (a)	0.00(a)	0.31(a)	0.00(a)
	-454.876662(b)	93.699(b)	-454.921181(b)	0.143584(b)	-454.886799(b)	0.00(b)	0.23(b)	0.00(b)	0.27(b)	0.00(b)
	-456.156127(c)	93.961(c)	-456.200771(c)	0.141877(c)	-456.166336(c)	0.00(c)	0.10 (c)	0.00(c)	0.23(c)	0.00(c)
	-455.980254(d)	92.604 (d)	-456.024253 (d)	0.144146 (d)	-455.990209 (d)	0.00 (d)	0.64 (d)	0.00 (d)	0.23 (d)	0.00 (d)
4eq-*eq*	-455.836405	93.193	-455.880684	0.144993	-455.846447	2.44	0.35	2.33	0.00	2.40
	-454.922834(a)	92.543(a)	-454.966804(a)	0.146244(a)	-454.932738(a)	2.40(a)	0.65 (a)	2.30(a)	0.00(a)	2.36(a)
	-454.872030(b)	94.199(b)	-454.916787(b)	0.143150(b)	-454.882252(b)	2.91(b)	0.73(b)	2.76(b)	0.00(b)	2.85(b)
	-456.153137(c)	94.169(c)	-456.197880(c)	0.141516(c)	-456.163392(c)	1.88(c)	0.31 (c)	1.81(c)	0.00(c)	1.85(c)
	-455.975465 (d)	92.659 (d)	-456.019491 (d)	0.143771 (d)	-455.985445 (d)	3.00 (d)	0.70(d)	2.99 (d)	0.00 (d)	2.99 (d)
5*ax-ax*	-778.727618	95.307	-778.772901	0.142323	-778.738061	0.61	0.00	0.79	0.17	0.65
	-777.768539(a)	94.755(a)	-777.813560(a)	0.143436(a)	-777.778859(a)	0.67(a)	0.00 (a)	0.82(a)	0.16(a)	0.70(a)
	-777.476787(b)	96.204(b)	-777.522496(b)	0.140223(b)	-777.487426(b)	0.32(b)	0.00 (b)	0.48(b)	0.13(b)	0.35(b)
	-779.132300(c)	96.874(c)	-779.178328(c)	0.138653(c)	-779.143057(c)	1.02(c)	0.00 (c)	1.16(c)	0.10(c)	1.06(c)
	-778.952004 (d)	95.415 (d)	-778.997339 (d)	0.140605 (d)	-778.962508 (d)	0.40 (d)	0.00 (d)	0.62 (d)	0.12 (d)	0.46 (d)
5ax-*eq*	-778.728587	95.915	-778.774159	0.142200	-778.739101	0.00	0.61	0.00	0.10	0.00
	-777.769600(a)	95.265(a)	-777.814863(a)	0.143349(a)	-777.779978(a)	0.00(a)	0.51 (a)	0.00(a)	0.11(a)	0.00(a)
	-777.477304(b)	96.717(b)	-777.523257(b)	0.140264(b)	-777.487986(b)	0.00(b)	0.51 (b)	0.00(b)	0.13(b)	0.00(b)
	-779.133900(c)	97.351(c)	-779.180200(c)	0.138548(c)	-779.144700(c)	0.00(c)	0.48 (c)	0.00(c)	0.04(c)	0.00(c)
	-778.952644 (d)	96.145 (d)	-778.998326 (d)	0.140417 (d)	-778.963235 (d)	0.00 (d)	0.73(d)	0.00 (d)	0.00 (d)	0.00 (d)
5eq-*eq*	-778.724735	96.366	-778.770522	0.142047	-778.735329	2.42	1.06	2.28	0.00	2.37
	-777.765906(a)	95.742(a)	-777.811396(a)	0.143174(a)	-777.776368(a)	2.32(a)	0.48(a)	2.18(a)	0.00(a)	2.26(a)
	-777.472545(b)	97.538(b)	-777.518889(b)	0.140010(b)	-777.483350(b)	2.99(b)	1.33 (b)	2.74(b)	0.00(b)	2.91(b)
	-779.131200(c)	97.548(c)	-779.1775(c)	0.138487(c)	-779.142100(c)	1.71(c)	0.67 (c)	1.65(c)	0.00(c)	1.68(c)
	-778.948279 (d)	96.540 (d)	-778.994148 (d)	0.14045 (d)	-778.958922 (d)	2.74(d)	1.12 (d)	2.62 (d)	0.02 (d)	2.71 (d)
6*ax-ax*	-2781.827579	98.565	-2781.874411	0.141065	-2781.838412	0.83	0.00	0.99	0.19	0.87
	-2780.957515(a)	97.937(a)	-2781.004048(a)	0.142193(a)	-2780.968218(a)	0.86(a)	0.00 (a)	1.02(a)	0.19(a)	0.90(a)
	-2779.725861(b)	99.410(b)	-2779.773094(b)	0.138826(b)	-2779.736903(b)	0.39(b)	0.00 (b)	0.50(b)	0.20(b)	0.40(b)

	-2782.465490$^{(c)}$	100.223$^{(c)}$	-2782.513109$^{(c)}$	0.137433$^{(c)}$	-2782.476653$^{(c)}$	1.25$^{(c)}$	0.00$^{(c)}$	1.37$^{(c)}$	0.18$^{(c)}$	1.27$^{(c)}$
	-2782.317896$^{(d)}$	98.800$^{(d)}$	-2782.364839$^{(d)}$	0.139276$^{(d)}$	-2782.328808$^{(d)}$	0.37$^{(d)}$	0.00$^{(d)}$	0.47$^{(d)}$	0.06$^{(d)}$	0.38$^{(d)}$
6ax-*eq*	-2781.828902	99.104	-2781.875990	0.140948	-2781.839797	0.00	0.54	0.00	0.12	0.00
	-2780.958894$^{(a)}$	98.465$^{(a)}$	-2781.005678$^{(a)}$	0.142092$^{(a)}$	-2780.969655$^{(a)}$	0.00$^{(a)}$	0.53$^{(a)}$	0.00$^{(a)}$	0.12$^{(a)}$	0.00$^{(a)}$
	-2779.726489$^{(b)}$	99.777$^{(b)}$	-2779.773896$^{(b)}$	0.138831$^{(b)}$	-2779.737548$^{(b)}$	0.00$^{(b)}$	0.37$^{(b)}$	0.00$^{(b)}$	0.20$^{(b)}$	0.00$^{(b)}$
	-2782.467477$^{(c)}$	100.627$^{(c)}$	-2782.515288$^{(c)}$	0.137346$^{(c)}$	-2782.478682$^{(c)}$	0.00$^{(c)}$	0.40$^{(c)}$	0.00$^{(c)}$	0.12$^{(c)}$	0.00$^{(c)}$
	-2782.318489$^{(d)}$	99.122$^{(d)}$	-2782.365585$^{(d)}$	0.139461$^{(d)}$	-2782.32941$^{(d)}$	0.00$^{(d)}$	0.32$^{(d)}$	0.00$^{(d)}$	0.18$^{(d)}$	0.00$^{(d)}$
6eq-*eq*	-2781.825942	99.723	-2781.873324	0.140755	-2781.836938	1.86	1.16	1.67	0.00	1.79
	-2780.956046$^{(a)}$	99.031$^{(a)}$	-2781.003099$^{(a)}$	0.141897$^{(a)}$	-2780.966902$^{(a)}$	1.79$^{(a)}$	0.57$^{(a)}$	1.62$^{(a)}$	0.00$^{(a)}$	1.73$^{(a)}$
	-2779.722446$^{(b)}$	100.983$^{(b)}$	-2779.770426$^{(b)}$	0.138502$^{(b)}$	-2779.733677$^{(b)}$	2.54$^{(b)}$	1.57$^{(b)}$	2.18$^{(b)}$	0.00$^{(b)}$	2.43$^{(b)}$
	-2782.465643$^{(c)}$	101.144$^{(c)}$	-2782.513700$^{(c)}$	0.137147$^{(c)}$	-2782.476942$^{(c)}$	1.15$^{(c)}$	0.92$^{(c)}$	1.00$^{(c)}$	0.00$^{(c)}$	1.09$^{(c)}$
	-2782.315078$^{(d)}$	100.022$^{(d)}$	-2782.362602$^{(d)}$	0.139175$^{(d)}$	-2782.326132$^{(d)}$	2.14$^{(d)}$	1.22$^{(d)}$	1.87$^{(d)}$	0.00$^{(d)}$	2.06$^{(d)}$

Table 5. NBO-LC-wPBE/6-311+G** calculated stabilization energies (*E*2, in kcal mol^{-1}) associated with the *HC-endo-AE* and *HC-exo-AE* for the axial –axial,axial-equatorial and equatorial-equatorial conformations of compounds **1-3**.

	1			**2**			**3**		
HC-endo-AE	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
$LP_{eq}M_1 \rightarrow \sigma^*_{C2-CN(ax)}$	-	0.54	-	-	-	-	-	-	-
$LP_{ax}M_1 \rightarrow \sigma^*_{C2-CN(ax)}$	9.84	9.53	-	7.57	7.35	-	4.16	3.85	-
$LP_{eq}M_1 \rightarrow \sigma^*_{C6-CN(ax)}$	-	-	-	-	-	-	-	-	-
$LP_{ax}M_1 \rightarrow \sigma^*_{C6-CN(ax)}$	9.85	-	-	7.71	-	-	4.14	-	-
$LP_{eq}M_1 \rightarrow \sigma^*_{C6-CN(eq)}$	-	2.31	2.32	-	-	-	-	-	-
$LP_{ax}M_1 \rightarrow \sigma^*_{C6-CN(eq)}$	-	-	-	-	-	-	-	-	-
$LP_{eq}M_1 \rightarrow \sigma^*_{C2-CN(eq)}$	-	-	2.32	-	-	-	-	-	-
$LP_{ax}M_1 \rightarrow \sigma^*_{C2-CN(eq)}$	-	-	-	-	-	-	-	-	-
$LP_{ax}M_1 \rightarrow \pi^*_{C\equiv N(ax)(2)}$	1.61	1.70	-	2.23	2.41	-	2.89	2.94	-
$LP_{ax}M_1 \rightarrow \pi^*_{C\equiv N(ax)(6)}$	1.61	-	-	2.24	-	-	2.91	-	-
$LP_{eq}M_1 \rightarrow \pi^*_{C\equiv N(eq)(2)}$	-	-	-	-	-	-	-	-	-
$LP_{eq}M_1 \rightarrow \pi^*_{C\equiv N(eq)(6)}$	-	0.51	-	-	-		-	-	-
$\sigma_{M1-C2} \rightarrow \pi^*_{C\equiv N(ax)(2)}$	1.89	2.05	-	6.19	6.31	-	11.32	11.53	-
$\sigma_{M1-C6} \rightarrow \pi^*_{C\equiv N(ax)(6)}$	1.89	-	-	6.20	-	-	11.22	-	-
$\sigma_{M1-C2} \rightarrow \sigma^*_{C\equiv N(ax)(2)}$	2.20	2.20	-	2.94	3.16	-	2.64	2.85	-
$\sigma_{M1-C6} \rightarrow \sigma^*_{C\equiv N(ax)(6)}$	2.20	-	-	3.07	-	-	2.64	-	-
$\sigma_{M1-C6} \rightarrow \pi^*_{C\equiv N(eq)(6)}$	-	2.60	2.61	-	8.40	8.24	-	13.27	9.99
$\sigma_{M1-C2} \rightarrow \pi^*_{C\equiv N(eq)(2)}$	-	-	2.62	-	-	8.28	-	-	9.99
$\sigma_{M1-C6} \rightarrow \sigma^*_{C\equiv N(eq)(6)}$	-	2.38	2.39	-	3.50	3.58	-	3.08	2.90
$\sigma_{M1-C2} \rightarrow \sigma^*_{C\equiv N(eq)(2)}$	-	-	2.38	-	-	3.58	-	-	2.90
$\sigma_{C3-Hax} \rightarrow \sigma^*_{C2-C\equiv N(ax)}$	3.82	3.89	-	4.12	4.24	-	4.88	5.01	-
$\sigma_{C5-Hax} \rightarrow \sigma^*_{C6-C\equiv N(ax)}$	3.79	-	-	4.09	-	-	4.87	-	-

$\sigma_{C3\text{-}Hax}\rightarrow\sigma^*_{C2\text{-}Hax}$	-	-	3.62	-	-	3.69	-	-	3.43
HC-exo-AE									
$\pi_{C\equiv N(ax)(2)}\rightarrow\sigma^*_{M1\text{-}C2}$	6.27	6.11	-	3.85	3.54	-	4.44	3.93	-
$\pi_{C\equiv N(ax)(6)}\rightarrow\sigma^*_{M1\text{-}C6}$	6.23	-	-	3.85	-	-	4.44	-	-
$\pi_{C\equiv N(eq)(6)}\rightarrow\sigma^*_{M1\text{-}C6}$	-	6.34	6.34	-	3.96	3.78	-	4.28	3.83
$\pi_{C\equiv N(eq)(2)}\rightarrow\sigma^*_{M1\text{-}C2}$	-	-	6.34	-	-	3.78	-	-	3.83
$\sigma_{C\equiv N(ax)(2)}\rightarrow\sigma^*_{M1\text{-}C2}$	-	-	-	-	-	-	-	-	-
$\sigma_{C\equiv N(ax)(6)}\rightarrow\sigma^*_{M1\text{-}C6}$	-	-	-	-	-	-	-	-	-
$\sigma_{C\equiv N(eq)(6)}\rightarrow\sigma^*_{M1\text{-}C6}$	-	-	-	-	-	-	-	-	-
$\sigma_{C\equiv N(eq)(2)}\rightarrow\sigma^*_{M1\text{-}C2}$	-	-	-	-	-	-	-	-	-
$\sigma_{C2\text{-}C\equiv N(ax)}\rightarrow\sigma^*_{C3\text{-}Hax}$	1.95	1.93	-	1.95	1.95	-	1.85	1.80	-
$\sigma_{C6\text{-}C\equiv N(ax)}\rightarrow\sigma^*_{C5\text{-}Hax}$	1.95	-	-	1.94	-	-	1.85	-	-
$\sigma_{C2\text{-}Hax}\rightarrow\sigma^*_{C3\text{-}Hax}$	-	-	3.23	-	-	3.65	-	-	2.82
$\sigma_{C6\text{-}Hax}\rightarrow\sigma^*_{C5\text{-}Hax}$	-	3.32	3.23	-	3.69	3.65	-	3.51	2.82
Σ(*HCAE*)	55.13	45.41	37.4	57.95	48.51	42.23	64.25	56.05	42.51
$\Sigma(HCAE)_{ax,ax} - \Sigma(HCAE)_{ax,eq}$		9.72			9.44			8.2	
$\Sigma(HCAE_{eq,eq} - \Sigma(HCAE)_{ax,eq}$		-8.01			-6.28			-13.54	

Table 6. NBO-LC-wPBE/6-311+G** calculated stabilization energies (*E*2, in kcal mol^{-1}) associated with the *HC-endo-AE* and *HC-exo-AE* for the axial–axial,axial-equatorial and equatorial-equatorial conformations of compounds **4-6**.

	4			5			6		
HC-endo-AE	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
$LP_{eq}M_1\rightarrow\sigma^*_{C2\text{-}NC(ax)}$	-	-	-	-	0.57	-	-	-	-
$LP_{ax}M_1\rightarrow\sigma^*_{C2\text{-}NC(ax)}$	16.17	16.33	-	13.38	13.17	-	7.79	7.22	-
$LP_{eq}M_1\rightarrow\sigma^*_{C6\text{-}NC(ax)}$	-	-	-	-	-	-	-	-	-
$LP_{ax}M_1\rightarrow\sigma^*_{C6\text{-}NC(ax)}$	16.23	-	-	13.41	-	-	7.78	-	-
$LP_{eq}M_1\rightarrow\sigma^*_{C6\text{-}NC(eq)}$	-	4.20	4.23	-	0.61	0.90	-	-	-
$LP_{ax}M_1\rightarrow\sigma^*_{C6\text{-}NC(eq)}$	-	-	-	-	-	-	-	-	-
$LPeqM1\rightarrow\sigma^*_{C2\text{-}NC(eq)}$	-	-	4.23	-	-	0.90	-	-	-
$LPaxM1\rightarrow\sigma^*_{C2\text{-}NC(eq)}$	-	-	-	-	-	-	-	-	-
$LP_{ax}M_1\rightarrow\pi^*_{N=C(ax)(2)}$	0.72	0.76	-	0.95	0.99	-	1.16	1.17	-
$LP_{ax}M_1\rightarrow\pi^*_{N=C(ax)(6)}$	0.72	-	-	0.94	-		1.18	-	
$LP_{eq}M_1\rightarrow\pi^*_{N=C(eq)(2)}$	-	-	-	-	-	-	-	-	-
$LP_{eq}M_1\rightarrow\pi^*_{N=C(eq)(6)}$	-	-	-	-			-		
$\sigma_{M1\text{-}C2}\rightarrow\pi^*_{N=C(ax)(2)}$	1.05	1.15	-	3.63	3.64	-	6.33	6.61	-
$\sigma_{M1\text{-}C6}\rightarrow\pi^*_{N=C(ax)(6)}$	1.04	-	-	3.61	-	-	6.29	-	-
$\sigma_{M1\text{-}C2}\rightarrow\sigma^*_{N=C(ax)(2)}$	1.54	1.53	-	2.39	2.33	-	2.34	2.43	-
$\sigma_{M1\text{-}C6}\rightarrow\sigma^*_{N=C(ax)(6)}$	1.55	-	-	2.39	-	-	2.38	-	-

$\sigma_{M1-C2} \rightarrow \pi^*_{N=C(eq)(2)}$	-	-	1.37	-	-	4.45	-	-	5.38
$\sigma_{M1-C6} \rightarrow \pi^*_{N=C(eq)(6)}$	-	1.37	1.36	-	4.34	4.43	-	6.97	5.38
$\sigma_{M1-C2} \rightarrow \sigma^*_{N=C(eq)(2)}$	-	-	1.58	-	-	2.62	-	-	2.31
$\sigma_{M1-C6} \rightarrow \sigma^*_{N=C(eq)(6)}$	-	1.60	1.59	-	2.44	2.63	-	2.39	2.31
$\sigma_{C3-Hax} \rightarrow \sigma^*_{C2-N=C(ax)}$	5.62	5.78	-	6.04	6.26	-	7.10	7.30	-
$\sigma_{C5-Hax} \rightarrow \sigma^*_{C6-N=C(ax)}$	5.58	-	-	6.01	-	-	7.09	-	-
$\sigma_{C3-Hax} \rightarrow \sigma^*_{C2-Hax}$	-	-	3.50	-	-	3.62	-	-	3.33
HC-exo-AE									
$\sigma_{C2-Hax} \rightarrow \sigma^*_{C3-Hax}$	-	-	-	-	-	3.59	-	-	2.79
$\sigma_{C6-Hax} \rightarrow \sigma^*_{C5-Hax}$	-	3.22	-	-	3.41	3.60	-	3.43	2.79
$\pi_{N=C(ax)(2)} \rightarrow \sigma^*_{M1-C2}$	8.91	8.55	-	5.80	5.22	-	6.66	6.01	-
$\pi_{N=C(ax)(6)} \rightarrow \sigma^*_{M1-C6}$	8.86	-	-	5.76	-	-	6.65	-	-
$\pi_{N=C(eq)(6)} \rightarrow \sigma^*_{M1-C6}$	-	8.93	8.85	-	5.12	5.28	-	6.00	5.27
$\pi_{N=C(eq)(2)} \rightarrow \sigma^*_{M1-C2}$	-	-	8.86	-	-	5.29	-	-	5.27
$\sigma_{C2-N=C(ax)} \rightarrow \sigma^*_{C3-Hax}$	1.24	1.24	-	1.27	1.28	-	1.21	1.18	-
$\sigma_{C6-N=C(ax)} \rightarrow \sigma^*_{C5-Hax}$	1.24	-	-	1.27	-	-	1.21	-	-
$\Sigma(HCAE)$	70.47	54.66	35.57	66.85	49.38	37.31	65.17	50.71	34.83
$\Sigma(HCAE)_{ax,ax} - \Sigma(HCAE)_{ax,eq}$		15.81			17.47			14.46	
$\Sigma(HCAE_{eq,eq} - \Sigma(HCAE)_{ax,eq}$		-19.09			-12.07			-15.88	

Total Steric Exchange Energies (TSEE):

The calculation of NBO-LC-wPBE/6-311+G** exposed that axial-axial conformations of compounds **1-6** possess smallest TSEE values compared to their axial-equatorial and equatorial-equatorial conformations (Table **10**). Based on the results obtained, the calculated total steric exchange energy differences between the axial-equatorial and axial–axial forms [*i.e.* Δ[$TSEE_{ax,eq}$⁻ $TSEE_{ax,ax}$]] decrease from compound **1** to compound **3** and also from compound **4** to compound **5**,but increase from compound **5** to compound **6**. The Δ[$TSEE_{ax,eq}$⁻ $TSEE_{eq,eq}$] parameters increase from compound **1** to compound **2** and decrease from compound **2** to compound **3**, decrese from compound **4** to compound **5** and from compound **5** to compound **6**. Accordingly, the variations of Δ[$TSEE_{ax,eq}$⁻ $TSEE_{eq,eq}$] correlate very well with the differences energy between the equatorial- equatorial and the axial-equatorial conformations of compounds **1-6**, and variations of Δ[$TSEE_{ax,eq}$⁻ $TSEE_{ax,ax}$] parameters except that compound **2** to compound **3**, with the differences energy between the axial-axial and axial-equatorial conformations of compounds **1-2** and **4-6** are in line.

Table 7. LC-wPBE/6-311+G** calculated total SCF energies, energies of deletions associated with the deletion of LPM1→π*N=C and LPM1→σ*C2-N=C electron delocalizations and their corresponding energy changes (in a.u.) in the axial and equatorial conformations of compounds **1-3**.

Deletion of $LP_{M1}\rightarrow\pi^*_{C\equiv N}$ electron delocalizations

	1			**2**			**3**		
Geometries	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
Total SCF energies	-456.049647	-456.053529	-456.050799	-778.947004	-778.949499	-778.946402	-2782.048204	-2782.050812	-380.683981
Energies of deletion	-456.041378	-456.051670	-456.047651	-778.938840	-778.944998	-778.944790	-2782.040372	-2782.046598	-380.683239
Energy Changes(EC)	0.008269(5.189)[a]	0.001859(1.167)[a]	0.003148(1.975)[a]	0.008164(5.123)[a]	0.004500(2.824)[a]	0.001613 (1.012)[a]	0.007832(4.915)[a]	0.004215(2.645)[a]	0.000742(0.466)[a]
$\Delta(EC_{ax,eq}-EC_{ax,ax})$		-4.022[a]			-2.299[a]			-2.270[a]	
$\Delta(EC_{ax,eq}-EC_{eq,eq})$		-0.808[a]			1.812[a]			2.179[a]	

Deletion of $LP_{M1}\rightarrow\sigma^*_{C\equiv N}$ electron delocalizations

	1			**2**			**3**		
Geometries	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
Total SCF energies	-456.049647	-456.053529	-456.050799	-778.947004	-778.949499	-778.946402	-2782.048204	-2782.050812	-380.683981
Energies of deletion	-456.000548	-456.026047	-456.037268	-778.925181	-778.940381	-778.944727	-2782.031211	-2782.043619	-380.683968
Energy Changes(EC)	0.049099(41.74)[a]	0.027482(17.245)[a]	0.013532(8.491)[a]	0.021823(13.694)[a]	0.009117(5.721)$_{a}$	0.001676(1.051)[a]	0.016994(10.664)[a]	0.007193(4.514)[a]	0.000013(0.008)[a]
$\Delta(EC_{ax,eq}-EC_{ax,ax})$		-24.495[a]			-7.973[a]			-6.150[a]	
$\Delta(EC_{ax,eq}-EC_{eq,eq})$		8.754[a]			4.670[a]			4.506[a]	

[a] Values in kcal mol^{-1}

Table 8. LC-wPBE/6-311+G** calculated total SCF energies, energies of deletions associated with the deletion of LPM1→π^*N=C and LPM1→σ^*C_2-N=C electron delocalizations and their corresponding energy changes (in a.u.) in the axial and equatorial conformations of compounds **4-6**.

Deletion of $LP_{M1}\rightarrow\pi^*_{N\equiv C}$ electron delocalizations

	4			**5**			**6**		
Geometries	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
Total SCF energies	-455.993254	-455.995630	-455.991440	-778.880384	-778.881300	-778.877375	-2781.979477	-2781.980745	-2781.977693
Energies of deletion	-455.987492	-455.992384	-455.990345	-778.876052	-778.881300	-778.876978	-2781.975523	-2781.978743	-2781.977436
Energy Changes(EC)	0.005763(3.620)[a]	0.003246(2.040)[a]	0.001095(0.687)[a]	0.004332(2.720)[a]	0.000000(0.000)[a]	0.000397(0.249)[a]	0.003954(2.480)[a]	0.002001(1.260)[a]	0.000256(0.161)[a]
$\Delta(EC_{ax,eq}-EC_{ax,ax})$		-1.580[a]			-2.720[a]			-1.220[a]	
$\Delta(EC_{ax,eq}-EC_{eq,eq})$		1.350[a]			-0.249[a]			1.100[a]	

Deletion of $LP_{M1}\rightarrow\sigma^*_{N\equiv C}$ electron delocalizations

	4			**5**			**6**		
Geometries	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
Total SCF energies	-455.993254	-455.995630	-455.991440	-778.880384	-778.881300	-778.877375	-2781.979477	-2781.980745	-2781.977693
Energies of deletion	-455.926732	-455.954758	-455.970056	-778.849518	-778.881301	-778.874066	-2781.955237	-2781.969984	-2781.975876
Energy Changes(EC)	0.066522(41.740)[a]	0.040872(25.650)[a]	0.021383(13.420)[a]	0.030866(19.370)[a]	-0.000001(0.000)[a]	0.003309(2.080)[a]	0.024240(15.210)[a]	0.010761(6.750)[a]	0.001817(1.140)[a]
$\Delta(EC_{ax,eq}-EC_{ax,ax})$		-16.900[a]			-19.370[a]			-8.460[a]	
$\Delta(EC_{ax,eq}-EC_{eq,eq})$		12.230[a]			-2.080[a]			5.610[a]	

[a] Values in kcal mol^{-1}

Bond orders:

The HCAE affects the structural parameters of the different configurations of a molecule via affecting their corresponding bond orders. Based on the results obtained, the calculated bond orders [*i.e.* Wiberg Bond Index (WBI)] for M_1–C_2 bonds of the axial-equatorial conformations of compounds **1-3** and compounds **4-6** are greater than the M_1–C_6 bonds of the axial-equatorial conformations of the mention compounds (Table **11**). Along of dominant impacts of their HCAE associated with the $LP_{ax}M_1 \rightarrow \sigma^*_{C2-CN(ax)}$ and $LP_{ax}M_1 \rightarrow \sigma^*_{C2-NC(ax)}$ electron delocalizations the bond orders of M1–C2 bonds in the axial-equatorial conformations of compound **1-6** are greater than their other conformations.

Table 9. NBO-LC-wPBE/6-311+G** calculated dipole moments (μ, in debye) for the axial–axial,axial-equatorial and equatorial-equatorial conformations of compounds **1**-**6**.

	1			**2**			**3**		
	ax,ax	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
μ	6.92	5.31	6.78	7.24	5.03	6.16	7.33	5.17	5.37
$\Delta(\mu_{eq,eq}-\mu_{ax,eq})$		1.47			1.13			0.20	
$\Delta(\mu_{ax,ax}-\mu_{ax,eq})$		1.60			2.21			2.15	
	4			**5**			**6**		
	ax,ax	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
μ	6.88	5.28	6.71	7.01	4.91	6.01	6.95	5.03	5.47
$\Delta(\mu_{eq,eq}-\mu_{ax,eq})$		1.43			1.10			0.44	
$\Delta(\mu_{ax,ax}-\mu_{ax,eq})$		1.59			2.09			1.91	

Table 10. NBO-LC-wPBE/6-311+G** calculated total steric exchange energies (TSEE, in kcal mol^{-1}) for the axial –axial,axial-equatorial and equatorial-equatorial conformations of compounds **1**-**6**.

	1			**2**			**3**		
	ax,ax	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
TSEE	349.48	405.83	410.77	397.79	404.58	410.13	401.25	404.20	405.07
$\Delta[TSEE_{ax,eq}-TSEE_{ax,ax}]$		56.35			6.79			2.95	
$\Delta[TSEE_{ax,eq}-TSEE_{eq,eq}]$		-4.94			-5.55			-0.87	
	4			**5**			**6**		
	ax,ax	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,eq*
TSEE	423.04	426.88	431.27	424.97	426.00	426. 39	422.66	423.79	424.15
$\Delta[TSEE_{ax,eq}-TSEE_{ax,ax}]$		-3.84			1.03			1.13	
$\Delta[TSEE_{ax,eq}-TSEE_{eq,eq}]$		-4.39			-0.39			-0.36	

Table 11. NBO-LC-wPBE/6-311+G** calculated bond orders (Wiberg bond indexes, *WBI* for the axial–axial, axial-equatorial and equatorial-equatorial conformations of compounds **1**-**6**.

	1	**2**	**3**

WBI	ax,ax	ax,eq	eq,eq	ax,ax	ax,eq	eq,eq	ax,ax	ax,eq	eq,eq
C_2-M_1	0.9103	0.9148	0.9032	0.9778	0.9755	0.9706	0.9257	0.9269	0.9352
M_1-C_6	0.9107	0.8993	0.9033	0.9780	0.9707	0.9707	0.9258	0.9228	0.9352
$\Delta[WBI(C_2\text{-}M_1)_{ax,eq}\text{-}WBI(C_2\text{-}M_1)_{ax,ax}]$		0.0045			-0.0023			-0.0088	
$\Delta[WBI(C_2\text{-}M_1)_{ax,eq}\text{-}WBI(C_2\text{-}M_1)_{eq.eq}]$		0.0116			0.0049			-0.0183	

		4			**5**			**6**	
WBI	ax,ax	ax,eq	eq,eq	ax,ax	ax,eq	eq,eq	ax,ax	ax,eq	eq,eq
C_2-M_1	0.9213	0.8992	0.9050	1.0048	1.0044	0.9787	0.9501	0.9418	0.9426
M_1-C_6	0.9218	0.8982	0.9050	1.0050	0.9792	0.9787	0.9502	0.9345	0.9426
$\Delta[WBI(C_2\text{-}M_1)_{ax,eq}\text{-}WBI(C_2\text{-}M_1)_{ax,ax}]$		-0.0231			-0.0004			-0.0083	
$\Delta[WBI(C_2\text{-}M_1)_{ax,eq}\text{-}WBI(C_2\text{-}M_1)_{eq.eq}]$		-0.0068			0.0257			-0.0008	

Application of the maximum hardness principle for the conformational properties of compounds 1–3 and 4–6:

The conformational properties of compounds **1-3** and **4-6** may be interpreted by means of the Principle of maximum hardness. Global hardness (η) in chemical species are related to the energy gaps between their frontier molecular orbitals (i.e. the HOMO–LUMO gap):

$$\eta = 0.5(\varepsilon_{LUMP} - \varepsilon_{HOMO}) \quad (1)$$

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. HOMO and LUMO help to describe the chemical reactivity and kinetic stability of the molecule. The energy of HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Based on the maximum hardness principle, the hardest conformation of a molecule could be its most stable from. LC-WPBE/6-311+G** results showed that the axial-axial conformations of compounds **1-3** and **4-6** are hardest conformation compared to their corresponding other forms (Table **12**). Accordingly the maximum hardness principle could not be justified the axial-equtorial conformation preferences between conformations of compound **1-6**.

Atoms in molecules analyses (AIM):

The AIM analysis for the optimized structures (Figure 1) has been performed to obtain the topological properties of the bonds, such as the electron density at the bond critical point (BCP), ρ, and its Laplacian, $\nabla^2\rho$.The ρ(r) is indicated the strength of a bond and $\nabla^2\rho(r)$ is used to describe the characteristic of the bond [49]. The $\nabla^2\rho < 0$ values represent shared interactions, characteristic of covalent bonds and $\nabla^2\rho > 0$ are indicative of closed-shell interactions typically found in ionic bonds and hydrogen bonds as well as in van der Waals' interactions. The ellipticity, ε, is a measure of the anisotropy of the electron density curvature at the BCP. It is zero for a single C-C bond, because the electron density distribution at this BCP is symmetric.

The calculated AIM descriptors at M_1-C_2 and M_1-C_6 bond for the axial-equatorial conformations of compounds **1-6** at B3LYP method are given in Table **13**.Plural show the Laplacian values of the electron density at **1-6** are negative, indicating that the charge density has been concentrated in the internuclear region and all mention bonds are covalent . The obtained values of ρ(r), for the M_1-C_2 and M_1-C_6 bond in the axial-equatorial conformations of compounds **1-6**, showed that the charge density at the critical point decrease from M_1-C_2 to M_1-C_6 bond, accordingly the strength of M_1-C_2 bonds are greather than M_1-C_6 bonds in the axial- equatorial conformations of compounds **1-6**. This confirms the results of NBO analysis associated by the hyper-conjugative interactions ($LP_{ax}M_1 \rightarrow \sigma^*_{C2\text{-}CN}$) and ($LP_{ax}M_1 \rightarrow \sigma^*_{C2\text{-}NC(ax)}$) that are responsible for decrease the M_1-C_2 bond lengths compared to M_1-C_6 bond lengths in the axial-equatorial conformations of compounds **1-6** and the calculated bond orders for M_1–C_2 bonds of the axial-equatorial conformations of compounds **1-6** that are greater than the M_1–C_6 bonds in the axial-equatorial conformations of the mention compounds.

Computational Methods:

The physical nature of the wavefunction is not very intuitive, but its square is physically meaningful probability of finding simultaneously all N_{elec} electrons in volume elements $dx_1, dx_2, \ldots, dx_{N_{elec}}$ [50]:

$$|\Psi(x_1,x_2,\ldots,x_{N_{elec}})|^2\, dx_1\, dx_2 \ldots dx_{N_{elec}} \tag{1}$$

Electron density or probability density $\rho(\mathbf{r})$ is the probability of finding any of N_{elec} electrons with any spin in volume element $d\boldsymbol{r}_1$ defined by the following multiple integral [51]:

$$\rho(\mathbf{r}) = N_{elec} \int \ldots \int |\Psi(x_1,x_2,\ldots,x_{N_{elec}})|^2\, dx_1\, dx_2 \ldots dx_{N_{elec}} \tag{2}$$

The *ab initio* and semiempirical methods discussed above are based on a wavefunction that depends on $4N_{elec}$ coordinates arising from three spatial coordinates and spin of each electron out of N_{elec} electrons in the system. On the other hand, density functional theory (DFT) is based on the electron density, which is a function of only three spatial coordinates, no matter how many electrons the system has [52].

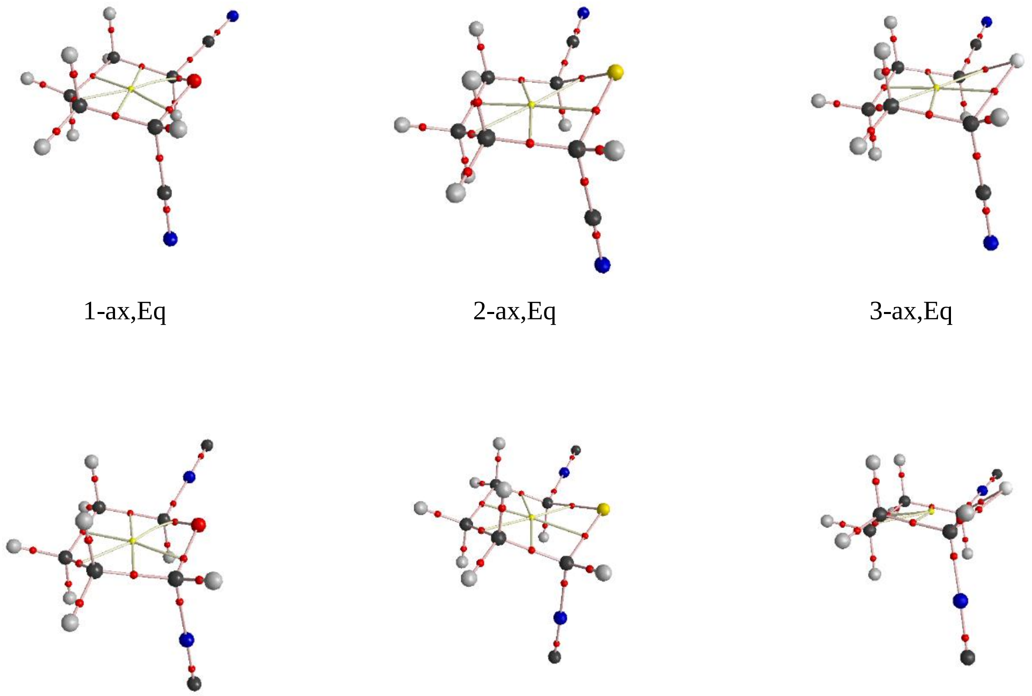
The structural parameters optimizations and the thermodynamic functions calculation in this work were carried out using the LC-WPBE, LC-BLYP, B3LYP, M06-2X and MP2 methods by means the 6-311+G** basis set, natural bond orbital (NBO) interpretation and atoms in molecules theory (AIM) with the GAMESS US package of programs. It has been found that The axial-axial conformations of compounds **1–6** are the most stable compounds here.

Table 12. LC-ωPBE/6-311+G** calculated energies (in hartree) of HOMO (ε HOMO), LUMO (ε LUMO), ε LUMO-ε HOMO and global hardness (η) for the axial and equatorial conformations of compounds **1-6**.

	ε HOMO	ε LUMO	ε LUMO-ε HOMO	I	A	η	$\Delta\eta$
1*ax-ax*	-0.42883	0.04075	0.46958	0.42883	-0.04075	0.23479	0.00519
1ax-*eq*	-0.42290	0.04267	0.46557	0.42290	-0.04267	0.23278	0.00000
1eq-*eq*	-0.41997	0.03923	0.45920	0.41997	-0.03923	0.22960	0.00316
2*ax-ax*	-0.38231	0.04048	0.42279	0.38231	-0.04048	0.21139	0.00222
2ax-*eq*	-0.38034	0.04188	0.42222	0.38034	-0.04188	0.21111	0.00000
2eq-*eq*	-0.37958	0.03876	0.41834	0.37958	-0.03876	0.20917	0.00194
3*ax-ax*	-0.36545	0.03527	0.40072	0.36545	-0.03527	0.20045	-0.00009
3ax-*eq*	-0.36468	0.03318	0.39786	0.36468	-0.03318	0.19893	0.00000
3eq-*eq*	-0.36462	0.03629	0.40091	0.36462	-0.03629	0.20036	-0.00152
4ax-ax	-0.42751	0.04063	0.46814	0.42751	-0.04063	0.23407	0.00556
4ax-*eq*	-0.42155	0.04350	0.46505	0.42155	-0.04350	0.23252	0.00000
4eq-*eq*	-0.41598	0.04103	0.45701	0.41598	-0.04103	0.22850	0.00402
5*ax-ax*	-0.38352	0.04049	0.42401	0.38352	-0.04049	0.21200	0.00478
5ax-*eq*	-0.37876	0.04167	0.42043	0.37876	-0.04167	0.21021	0.00000
5eq-*eq*	-0.37549	0.03895	0.41444	0.37549	-0.03895	0.20722	0.00299
6*ax-ax*	-0.36504	0.03713	0.40217	0.36504	-0.03713	0.20108	0.00259
6ax-*eq*	-0.36212	0.03434	0.39646	0.36212	-0.03434	0.19823	0.00000
6eq-*eq*	-0.36013	0.03685	0.39698	0.36013	-0.03685	0.19849	-0.00026

Table 13. AIM analyses at B3LYP/6-311+G** level for the compounds **1-6**. The quantities given are the electron density (ρ, a.u.), its Laplacian ($\nabla^2\rho$, a.u.), the bond ellipticity (ε,a.u.) at the bond critical point (BCP)

	1	**2**	**3**	**4**	**5**	**6**
	ax-eq	ax-eq	ax-eq	ax-eq	ax-eq	ax-eq
M1-C2 bond						
ρ	0.256	0.167	0.131	0.265	0.171	0.134
$\nabla^2\rho$	-0.542	-0.226	-0.070	-0.583	-0.239	-0.073
ε	0.049	0.085	0.103	0.120	0.080	0.095
M1-C6 bond						
ρ	0.252	0.165	0.130	0.263	0.167	0.132
$\nabla^2\rho$	-0.538	-0.217	-0.073	-0.658	-0.226	-0.078
ε	0.086	0.114	0.129	0.157	0.135	0.148



1-ax,Eq 2-ax,Eq 3-ax,Eq

4-ax,Eq 5-ax,Eq 6-ax,Eq

Figure 1: The AIM analysis for the optimized structures of compounds **1-6**.

Conclusion

The conformational preference and the influences of various parameters have investigated in compounds **1-6** using LC-WPBE and NBO analyses. LC-BLYP, B3LYP, M06-2X and MP2 methods are also employed to support the results of investigating different parameters . According to the computational results the axial- equatorial conformations of compounds **1-6** are most stable compared to their corresponding other conformations. The hyper-conjugative interactions between the non-bonded lone pairs of the six-membered rings [LPM, M = O, S, Se] and the σ^*_{C2-CN} and σ^*_{C2-NC} anti-bonding orbitals ($LP_{ax}M_1 \rightarrow \sigma^*_{C2-CN}$) and ($LP_{ax}M_1 \rightarrow \sigma^*_{C2-NC(ax)}$) are responsible for decrease the σ_{M1-C2} bond lengths compared the σ_{M1-C6} bond lengths and increase σ_{C2-CN} and σ_{C2-NC} bond lengths in the axial-equatorial conformations compared the σ_{C6-CN} and σ_{C6-NC} bond lengths in axial-equatorial conformations of compounds **1-6**. Results of NBO analysis show that the hyper-conjugative anomeric effect (HCAE) have not determinant impacts on the conformation preferences in compounds **1-6**. The obtained results showed that the dipole moments (μ) of the axial-equatorial conformations of compounds **1-6** have the smallest value compared their other forms. The axial-axial conformations of compounds **1-6** possess smallest TSEE values compared to their axial-equatorial and equatorial-equatorial conformations. The Maximum hardness principle could not be justified the axial-equatorial conformation preferences between conformations of compound **1-6**. The variations of $\Sigma(HCAE_{eq,eq}$ $-\Sigma(HCAE)_{ax,eq}$, $\Delta(\mu_{eq,eq}-\mu_{ax,eq})$, $\Delta[TSEE_{eq,eq}-TSEE_{ax,eq}]$, parameters correlate very well with the differences energies between the equatorial-equatorial and axial-equatorial conformations of compounds **4-5**. The AIM calculations confirm the results of NBO analysis.

Experimental Section

Conformational preference:

The calculated Gibbs free energy, enthalpy, entropy, electronic energy, zero point energy and their differences (*i.e.* ΔG, ΔH, ΔS, ΔE_0 and ΔZPE) for the axial-axial, axial-equatorial and equatorial-equatorial conformations of compounds **1-3** and **4-6**, as calculated at the LC-wPBE/6-311+G**, the LC-BLYP/6-311+G** and B3LYP/6-311+G**, B3LYP/6-311+G** and M06-2X/6311+G** are given in Table 4. The results of calculations showed that the axial-equatorial conformations of compounds **1-3** and **4-6** are most stable compared to corresponding axial-axial and equatorial-equatorial conformations. The energy difference between the axial-axial and axial-equatorial conformations decreases from compound **1** to compound **2** but increases from compound **2** to compound **3**, decreases from compound **4** to compound **5** but increases from compound **5** to compound **6**. This energy difference between the equatorial-equatorial and axial-equatorial conformations increases from compound **1** to compound **2** but decreases from compound **2** to compound **3**, decreases from compound **4** to compound **5** and from compound **5** to compound **6**.

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References

[1] Hohenberg, P.; Kohn, W. *Phys. Rev. B.*, **1964**, *136*, 864.

[2] Kohn,W.; Sham, L. *J. Phys. Rev.*, **1965**, *140*, 1133.

[3] Rez-Balado, C.; Marko, I.; *Tetrahedron Lett.* **2005**, *46*, 4887.

[4] Neto, A.; Santos, F. P.; Paula, A. S.; Tormena, C. F.; Rittner, R. *Chem. Phys. Lett.*, **2008**, *454*, 129.

[5] Kozmon, S.; Tvaroska. I.; *Collect. Czech. Chem. Commun*., **2006**, *71*, 1453.

[6] Langenhan, J. M.; McLaughlin, R. P.; Loskot, S. A.; Rozal, L. M.; Clay, M. S.; Alaimo, P. J. *J .Carbohydr. Chem*., **2016** , *35*, 106.

[7] Szücova, L.; Spichal, L. *Bioorg. Med. Chem*., **2009**, *17* ,1938.

[8] Kohn, W. *J. Comput. Chem*., **1999**, 20.

[9] Schreckenbach, G. *J. Comput. Chem*., **1999**, 20 ,70.

[10] Slater, J. C. The self-consistent field for molecular solids, Quantum Theory of Molecular Solids, 4, McGraw-Hill, New York, **1974**.

[11] Vosko, H.; Wilk. L.; Nusair. M. *Can J. Phys*., **1980**, *58* , 1200.

[12] Becke, A. D. *Phys. Rev. A*., **1988**, *38*, 3098.

[13] Becke, A. D. *J. Chem. Phys*., **1993**, *98*, 5648.

[14] Becke, A. D. *J. Chem. Phys*., **1993**, *98*, 1372.

[15] Becke, A. D. *J. Chem. Phys*., **1996**, *104*, 1040.

[16] Becke, A. D. *J. Chem. Phys*., **1997**, *107*, 8554.

[17] Lee, C.; Yang. W.; Parr. R.G. *Phys. Rev. B*., **1988**, *41*, 785.

[18] Parr, R.G.; Yang, W. Density-functional Theory of Atoms and Molecules, Oxford University Press, Oxford, **1989**.

[19] Perdew, J.D.; Wang, Y. *Phys. Rev. B*., **1986**, *33*, 8800.

[20] Jensen, F. Introduction to Computational Chemistry, Wiley, New York, **1999**.

[21] Perrin, C. L.; Armstrong, K. B.; Fabian, M. A. *J. Am. Chem. Soc*., **1994**, *116*, 715–722.

[22] Salzner, U.; Schleyer, P. V. R. *J. Am. Chem. Soc*., **1993**, *115*, 10231–10236.

[23] Vila, A.; Mosquera, R. A. *J. Comput. Chem*., **2007**, *28*, 1516–1530.

[24] Mo, Y. *Nat. Chem*., **2010**, *2*, 666–671.

[25] Huang, Y.; Zhong, A. G.; Yang, Q.; Liu, S. *J. Chem. Phys*., **2011**, *134*, 1031–1039.

[26] Bauerfeldt, G. F.; Cardozo, T. M.; Pereira, M. S.; Silva, C. S. da.*Org. Biomol. Chem*., **2013**, *11*, 299–308.

[27] Freitas, M. P. *Org. Biomol. Chem*., **2013**, *11*, 2885.

[28] Pozharskii, A. F.; Soldatenkov, A. T.; Katritzky, A. R. Heterocycles in Life and Society; Wiley: Chichester, UK, **1997**.

[29] Bottoni, A.; Frenna, V.; Lanza, C. Z.; Macaluso, G.; Spinelli, D. *J. Phys. Chem. A*., **2004**, *108*, 1731–1740.

[30] Kirby, A. J. The Anomeric and Related Stereoelectronic Effects at Oxygen, Springer-Verlag, Berlin-Heidelberg, **1983**.

[31] Kirby, A. J. *Acc. Chem. Res*. **1984**, *17*, 305–311.

[32] Kirby, A. J. *Pure Appl. Chem*., **1987**, *59*, 1605–1612.

[33] Eliel, E. L.; Wilen. S. H.; Mander, L. N. Stereochemistry of Organic Compounds, John Wiley, New York, **1994**.

[34] Chandrasekhar, S. **2005**, 37–66.

[35] Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. *J. Chem. Phys*., **2004**, *120*, 8425.

[36] Vydrov, O. A. ; Scuseria, G. E. *J. Chem. Phys*., **2006**, *125*, 234109.

[37] Zhao, Y.; Truhlar, D. G.; *Theor. Chem. Acc*., **2008**, *120*, 215.

[38] Becke, A. D. *Phys. Rev. A*., **1988**, *38*, 3098.

[39] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*: *Condens. Matter Mater. Phys*., **1988**, *37*, 785.

[40] Becke, A. D. *J. Chem. Phys*., **1993**, *98*, 1372.

[41] Moller, C. ; Plesset, M. S. *Phys. Rev*., **1934**, *46*, 618.

[42]Cremer, D. In Encyclopedia of Computational Chemistry, ed. P.v. R. Schleyer, Wiley, New York, **1998**.

[43] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem.Phys*., **1980**, *72*, 650.

[44] McLean, A. D.; Chandler, G. S. *J. Chem. Phys*., **1980**, *72*, 5639.

[45] Blaudeau, J. P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *J. Chem. Phys*., **1997**, *107*, 5016.

[46] Curtiss, L. A.; McGrath, M. P.; Blandeau, J. P.; Davis, N. E.; Binning Jr, R. C. ; Radom. L. *J. Chem. Phys*., **1995**, *103*, 6104.

[47] Weinhold, F.; Schleyer, P. v. R.; Allinger, N. L.; Clark, T.; Gasteiger, J.; Kollman, P. A.; Schaefer, H. F.; Schreiner, P. R. Natural Bond Orbital Methods. in Encyclopedia of Computational Chemistry, Wiley, Chichester, U. K, **1998**.

[48] Bader, R. F. W. Atoms in Molecules. A Quantum Theory, Clarendon Press, Oxford, UK, **1990**.

[49] Biegler Konig, F. W., Schonbohm. J., Bayles. D. *J. Comput. Chem*., **2001**, *22*, 545- 559.

[50] Koch, W.; Holthausen, M. C. A Chemist's Guide to Density Functional Theory. Second ed.; WILEY-VCH Verlag GmbH: Weinheim., **2001**, 3-18.

[51] Koch, W.; Holthausen, M. C.; A Chemist's Guide to Density Functional Theory. Second ed.; WILEY-VCH Verlag GmbH: Weinheim., **2001**, 19-28.

[52] Jensen, F. Introduction to Computational Chemistry. John Wiley & Sons Ltd: Baffins Lane, Chichester, West Sussex PO19 1UD, England., **1999**, 177-19