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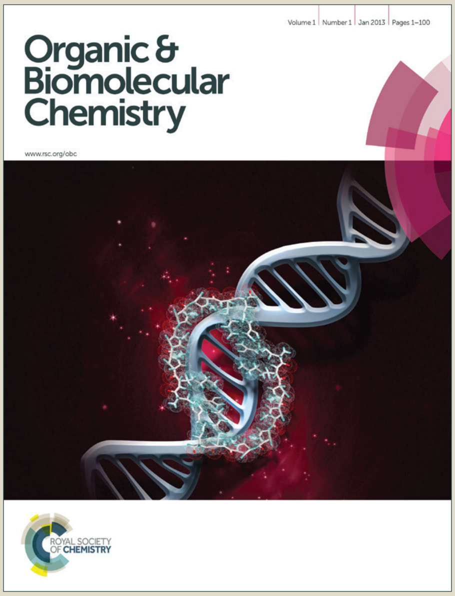

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On the origin of the anomeric effect. Probing the impacts of the stereoelectronic interactions and staric exchange components on the structural and configurational behaviors of 2,3- and 2,5-dihalo-1,4-oxathianes

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Abstract

To gain further insight on the origin of the *anomeric effect* [stabilization energies associated with the electron delocalization (*SE*), electrostatic model associated with the dipole-dipole interactions (*EM*) and Pauli exchange-type repulsions (*PETR*)], the correlations between the *SE*, *EM*, *PETR*, bond-orders, donor and acceptor orbital energies and occupancies, structural parameters and configurational behavior of 2,3-difluoro- (**1**), 2,3-dichloro- (**2**), 2,3-dibromo-1,4-oxathiane (**3**) and 2,5-difluoro- (**4**), 2,5-dichloro- (**5**), 2,5-dibromo-1,4-oxathiane (**6**) were investigated by means of the complete basis set (CBS-4), hybrid density functional theory method (B3LYP/6-311+G**) and natural bond orbital (NBO) interpretations. The differences in the total energies among four possible configurations of compounds **1-6** do not correlate with the differences in their corresponding *SE*, *EM* or *PETR* values but can be controlled by their cooperative or uncooperative impacts. The results obtained showed that the *SE* has a determinant impact on the structural properties of compounds **1-6** but fails to account solely for the variations of the energy differences between the configurations in compounds **1-6**. The *SE* and *PETR* components are in favor of the (*ax,ax*) forms (the most stable configuration) ongoing from compound **1** to compound **3** but the *EM* has opposite impact; therefore, these factors have counterintuitive impacts on the configurational properties of compounds **1-3**. Since there are no significant dipole moment values for the (*ax,ax*) and (*eq,eq*) forms of compounds **4-6**, the energy differences between these forms can result from the conflict between the *SE* and *PETR* components. Therefore, the conclusions published previously in the literature about the origin of the *anomeric effect* should be reexamined.

Keywords: anomeric effects, NBO, 2,3-dihalo-1,4-oxathianes, 2,5-dihalo-1,4-oxathianes

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Introduction

The most dominant conformation-controlling factor in the structures of the chemical compounds including carbohydrates is known as the *anomeric effect*.[1-20] It should be noted that the *anomeric effect* is defined as the preference of an electronegative substituent to be axially rather than equatorially oriented in opposition to the steric effect which normally leads to a preference for the equatorial conformation.

Although the origin of the anomeric effect has remained an open question,[21] overall, it is understood to be the result of multiple steric (i.e. Pauli exchange) and stereoelectronic interactions (associated with the dipole-dipole interactions and donor-acceptor electron delocalization). Nevertheless, some researchers believe that there is no general consensus about its actual origin.[21]

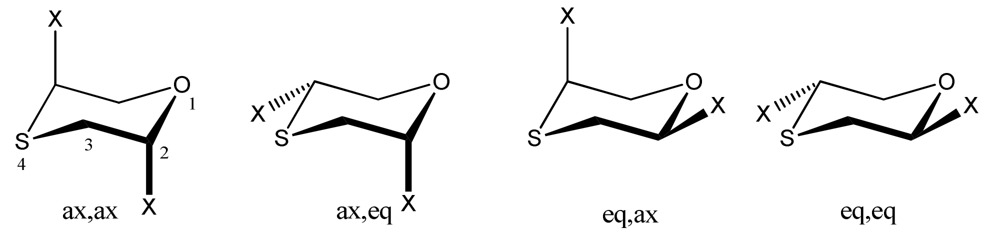
In 2010, Mo performed the extended block-localized wavefunction (*BLW*) method to investigate the origin of the anomeric effect.[22] He concluded that the electrostatic interaction associated with the dipole-dipole interactions is responsible for the *anomeric effect*.

In 2007 and 2011, Liu and coworkers pointed out that the electron delocalization and electrostatic interactions alone is not adequately convincing to explain the general validity of the *anomeric effect*.[23,24]

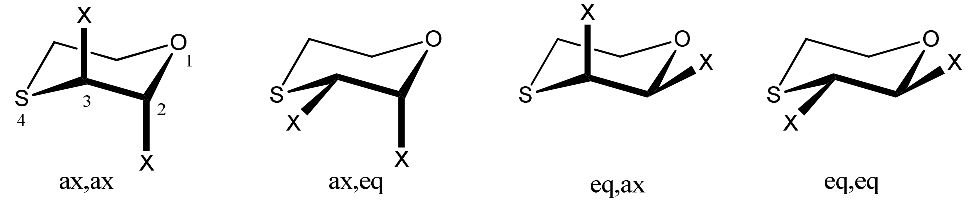
In 2013, Bauerfeldt pointed out that the differences in the total energies among the most stable rotamers of each anomer correlate very well with the differences in the exchange components, revealing that the anomeric effect has no electrostatic origin.[25]

To gain further insight on the origin of the *anomeric effect*, we have investigated the correlations between the differences in the total energies, steric exchanges [total steric exchange energies, *TSEE*, which is considered to represent Pauli exchange-type repulsions between filled orbitals (or the quasi-classical "Lennard-Jones repulsion") between hard-shell sphere atoms],[26-30] electrostatic model associated with the dipole-dipole interactions and structural parameters among the axial-axial (*ax,ax*), axial-equatorial (*ax,eq*), equatorial-axial (*eq,ax*) and equatorial-equatorial (*eq,eq*) forms of compounds **1-6**.

Since the preferred geometry of a molecule can be viewed as the result of the maximization of the interaction between the best donor and the best acceptor bond,[31,32] the stereoelectronic interactions are expected to play an important role in the conformational properties of heterocyclic compounds. In this context, there is a stereoelectronic preference for conformations in which the best donor lone pair is antiperiplanar to the best acceptor bond.



1: X=F, **2**: X=Cl, **3**: X=Br



4: X=F, **5**: X=Cl, **6**: X=Br

Scheme 1: Schematic representation of conformations of compounds **1-6**.

Praly and Lemieux have pointed out that the *anomeric-effect* in six membered saturated heterocyclic compounds can be considered as the difference between the sum of the *endo-anomeric-effect* and *exo-anomeric-effect* in the equatorial and axial conformations.[33] Also, they have pointed out that the equatorial conformation is exclusively stabilized by *exo-anomeric-effect* interactions because there is no *endo-anomeric-effect* in this conformation.

According to the statement mentioned above, the differences between the stabilization energies (*SE*) associated with the electron delocalizations for the axial-axial (*ax,ax*), axial-equatorial (*ax,eq*), equatorial-axial (*eq,qx*) and equatorial-equatorial (*eq,eq*) forms of compounds **1-6** can be estimated as follow:

$$\Delta(SE_{\mathrm{ax,eq}}\text{-}SE_{\mathrm{ax,ax}}) = \Sigma(exo\text{-}SE_{\mathrm{ax,eq}} + endo\text{-}SE_{\mathrm{ax,eq}}) - \Sigma(exo\text{-}SE_{\mathrm{ax,ax}} + endo\text{-}SE_{\mathrm{ax,ax}}) \quad \text{Eq. (1)}$$

$$\Delta(SE_{\mathrm{eq,ax}}\text{-}SE_{\mathrm{ax,ax}}) = \Sigma(exo\text{-}SE_{\mathrm{eq,ax}} + endo\text{-}SE_{\mathrm{eq,ax}}) - \Sigma(exo\text{-}SE_{\mathrm{ax,ax}} + endo\text{-}SE_{\mathrm{ax,ax}}) \quad \text{Eq. (2)}$$

$$\Delta(SE_{\mathrm{eq,eq}}\text{-}SE_{\mathrm{ax,ax}}) = \Sigma(exo\text{-}SE_{\mathrm{eq,eq}} + endo\text{-}SE_{\mathrm{eq,eq}}) - \Sigma(exo\text{-}SE_{\mathrm{ax,ax}} + endo\text{-}SE_{\mathrm{ax,ax}}) \quad \text{Eq. (3)}$$

$$\Delta(SE_{\mathrm{eq,eq}}\text{-}SE_{\mathrm{eq,ax}}) = \Sigma(exo\text{-}SE_{\mathrm{eq,eq}} + endo\text{-}SE_{\mathrm{eq,eq}}) - \Sigma(exo\text{-}SE_{\mathrm{eq,ax}} + endo\text{-}SE_{\mathrm{eq,ax}}) \quad \text{Eq. (4)}$$

$$\Delta(SE_{\mathrm{eq,eq}}\text{-}SE_{\mathrm{ax,eq}}) = \Sigma(exo\text{-}SE_{\mathrm{eq,eq}} + endo\text{-}SE_{\mathrm{eq,eq}}) - \Sigma(exo\text{-}SE_{\mathrm{ax,eq}} + endo\text{-}SE_{\mathrm{ax,eq}}) \quad \text{Eq. (5)}$$

2,3-dichloro-, -chlorobromo and –dibromo-1,4-dithiane and also 2,5-dichloro-1,4-dithiane synthesized in 1964 by Kalff.[24] Since the cell units of 2,3-dichloro-1,4-dithiane contains only two molecules and its absorption coefficient is the lowest, this compound was chosen for X-ray structure determination by Kalff and Romres.[34] The X-ray structure investigation demonstrated the existence of only the axial-axial form for this compound (see scheme 1). Also the results showed that S_1-C_2 bond length is shorter than the S_1-C_6 bond length in the axial-axial form of 2,3-dichloro-1,4-dithiane.[35] The shorter S_1-C_2 bond length compared to the S_1-C_6 bond length in the axial-axial form of 2,3-dichloro-1,4-dithiane is attributed to the presence of the $LPS_1 \rightarrow \sigma_{C2\text{-}Cl}$ (*endo-SE*) electron delocalization.[35]

Recently, we reported the impacts of the *anomeric effect*, dipole-dipole interactions and steric repulsions on the conformational properties of *trans*-2,3- and -2,5-dihalo-1,4-dithiane, *trans*-2,3- and -2,5-dihalo-1,4-diselenane.[14,15] It is worth noting that there is no published experimental or theoretical data concerning the magnitude and the impacts of the stabilization energies associated with the electron delocalizations (*SE*), electrostatic model associated with the dipole-dipole interactions (*EM*) and steric repulsions (i.e. Pauli exchange energies, *PEE*) on the configurational preferences in 2,3-dihalo-1,4-oxathiane [halo = F (**1**), Cl (**2**), Br (**3**)] and 2,5-dihalo-1,4- oxathiane [halo = F (**4**), Cl (**5**), Br (**6**)]. In the present work, we investigate the impacts of the above-mentioned factors on the structural and configurational properties of compounds **1-6** by means of the complete basis set composite method CBS-4, hybrid-DFT based methods and natural bond orbital (NBO) interpretations.[36-47] Because of the differences between the halogen-C-O, halogen-C-S and halogen-C-Se segments, we expected that different results would be obtained for O- and S-containing heterocyles (i.e. thioxanes) compared to their dioxane and dithiane analogs. This expectation is confirmed by the results of this work.

Computational details

Hybrid DFT and composite complete basis set (CBS) calculations were carried out using the B3LYP/6-311+G** and CBS-4 levels of theory with the GAUSSIAN 98 package of programs for the (*ax,ax*), (*ax,eq*), (*eq,ax*) and (*eq,eq*) forms of compounds **1-6**.[48] It should be noted that the CBS models are compound methods that extrapolate to the CBS limit by using the N-1 asymptotic convergence of MP2 pair energies calculated from pair natural orbital expansions.[40-47] CBS-4 is a six-step method. It starts with UHF/3-21G* geometry and frequency calculations, followed by UHF, CBS2, MP4(SDQ) and empirical corrections.[42] The energy minimizations were carried out only for the (*ax,*ax), (*ax,eq*), (*eq,ax*) and (*eq,eq*) forms of compounds **1-6**.

An NBO analysis was then performed for the (*ax,ax*), (*ax,eq*), (*eq,ax*) and (*eq,eq*) forms of compounds **1-6** by the NBO 5.G program contained in the PC-GAMESS interface.[47,49,50] The bonding and antibonding orbital occupancies in the (*ax,ax*), (*ax,eq*), (*eq,ax*) and (*eq,eq*) forms of compounds **1-6**, and also the stabilization energies associated with *endo-anomeric-effects* and *exo--anomeric-effects* and also the natural steric analysis were examined using the NBO analysis. The stabilization (or resonance) energies of donor (*i*)→acceptor (*j*) interactions are proportional directly to the magnitudes of the orbital overlap integrals and inversely to the energy differences between the donor and acceptor orbitals:[14-20,31,32]

$$\textit{Stabilization or resonance energy}\ \alpha\ (S_{ij}^2/\Delta\varepsilon_{ij})$$

Accordingly, the stabilization energy (E_2) associated with $i \rightarrow j$ delocalization, is explicitly estimated by the following equation:

$$E_2 = q_i \frac{F^2(i,j)}{\varepsilon_j - \varepsilon_i} \qquad \text{Eq. (7)}$$

where q_i is the i^th^ donor orbital occupancy, ε_i, ε_j are diagonal elements (orbital energies) and *F*(i,j) off-diagonal elements, respectively, associated with the NBO Fock matrix. Therefore, there is a direct relationship between *F*(i,j) off-diagonal elements and the orbital overlap (S).

The stabilization energies (E_2) associated with $LP_{ax}O_1 \rightarrow \sigma^*_{C2\text{-}X}$, $LP_{eq}O_1 \rightarrow \sigma^*_{C2\text{-}X}$, $LP_{ax}S_4 \rightarrow \sigma^*_{C3\text{-}X}$, $LP_{eq}S_4 \rightarrow \sigma^*_{C3\text{-}X}$ (*endo-SE*), $LP_3X_{C2} \rightarrow \sigma^*_{C2\text{-}O1}$, $LP_1X_{C3} \rightarrow \sigma^*_{C3\text{-}S4}$, $LP_2X_{C3} \rightarrow \sigma^*_{C3\text{-}S4}$, $LP_3X_{C3} \rightarrow \sigma^*_{C3\text{-}S4}$ (*axo-SE*), $\sigma_{C2\text{-}X} \rightarrow \sigma^*_{C3\text{-}X}$ and $\sigma_{C3\text{-}X} \rightarrow \sigma^*_{C2\text{-}X}$ (*trans-effects*) electron delocalizations (see Figure 1), dipole-dipole interactions and steric repulsions (i.e. *TSEE*) and their influences on the conformational properties of compounds **1-6** were quantitatively investigated by the NBO analysis.[47] It is worth noting that that the NBO interpretation is a sufficient approach to investigate quantitatively the impacts of the stereoelectronic interactions on the reactivity and dynamic behaviors of chemical compounds.[51]

Results and Discussion

1-*Configurational preference*

Table 1 shows the Gibbs free energy, enthalpy and entropy differences (i.e. Δ*G*, Δ*H* and Δ*S*) for the (*ax,ax*), (*ax,eq*), (*eq,ax*) and (*eq,eq*) forms of compounds **1-6**, as calculated at the

CBS-4 and B3LYP/6-311+G** levels of theory. Both methods showed that the (*ax,ax*) configurations are the most stable forms of compounds **1-6** and their corresponding (*eq,eq*) configurations are the least stable forms. The energy difference between the most and least stable forms decreases from compound **1** to compound **2** but increase from compound **2** to compound **3** as calculated at the levels of both methods. Similar to trend observed for compounds **1-3**, the energy difference between the most and least stable forms decreases from compound **4** to compound **5** but increase from compound **5** to compound **6** as calculated at the B3LYP/6-311+G** level of theory but there is no significant differences between them at the CBS-4 level. This trend is similar to that we obtained previously for dithiane analogs.[14] It should be noted that the energy differences between the *ax,ax* and *eq,eq* forms of 2,5-dihalo-1,4-thioxanes (**4-6**) and 2,5-dihalo-1,4-dithianes[14] are in the opposite trend compared to 2,5-dihalo-1,4-diselenanes.[15] Note that the configurations of the molecules with the greater stabilization energies associated with the electron delocalizations (*SE*), the smaller dipole moments and steric repulsions are supposed to be more stable than the other forms which possess the smaller *SE* and larger dipole moments and steric repulsions. Obviously, the factors mentioned above have no similar impacts on the configurational properties of the molecules. Effectively, the results of this work revealed that the *SE*, *EM* or *PETR* components have counterintuitive impacts on the configurational properties of compounds **1-6**.

The (*eq,ax*) form stability, compared to its (*ax,ax*) configuration, increases from compound **1** to compound **3**. There are no significant differences between the stabilities of the (*eq,ax*) forms compared to their (*ax,ax*) configurations in compounds **4** and **5** but increase slightly from compound **5** to compound **6**. The (*ax,eq*) form stability, compared to its (*ax,ax*) configuration, decreases from compound **1** to compound **2** but increases from compound **2** to compound **3**. Contrary to the trend observed for compounds **1-3**, the (*ax,eq*) form stability compared to its (*ax,ax*) configuration decreases from compound **4** to compound **6**.

2-*Stabilization energies associated with the electron delocalizations*

The stabilization energies associated with the electron delocalizations have significant impacts on the energy differences between the different configuratons of the molecules; we conducted NBO analyses to estimate quantitatively the magnitude of the plausible donor-acceptor hyperconjugative interactions. The NBO analysis shows that there are effective electron delocalization in the *ax,ax*, *ax,eq*, *eq,ax* and *eq,eq* configurations of compounds **1-6**. The NBO-B3LYP/6-311+G** analysis of donor-acceptor interactions showed that the stabilization energies associated with $LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$ delocalizations (*endo-SE*) for the *ax,ax* configurations increase from compound **1** to compound **3** and from compound **4** to compound **6** (see Table 2). It should be noted that the stabilization energies associated with $LP_{ax}S_4 \rightarrow \sigma^*_{C3-X}$ electron delocalizations in the (*ax,ax*) configurations of compounds **1-6** are less than the corresponding values for the $LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$ electron delocalizations. The stabilization energies associated with the electron delocalizations can be controlled by two factors (i.e F_{ij} and $\Delta\varepsilon_{ij}$). The results obtained showed that the F_{ij} values for the $LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$ electron delocalizations are greater than the corresponding values for the $LP_{ax}S_4 \rightarrow \sigma^*_{C3-X}$ electron delocalizations. This fact can also be explained by the profiles of the orbital amplitudes (or electron densities) for the mixing of the doubly occupied orbitals of $LP_{ax}O_1$ and $LP_{ax}S_4$ with the adjacent unoccupied orbitals of σ_{C2-X} and σ_{C3-X} bonds (i.e. σ^*_{C2-X} and $+\sigma^*_{C3-X}$ antibonding orbitals). Due to the electronegativity of oxygen, $LP_{ax}O_1$ has much lower orbital energy than $LP_{ax}S_4$ and the energy difference between the donor $LP_{ax}O_1$ bonding and the acceptor σ^*_{C2-X} antibonding orbitals are greater than the energy difference between $LP_{ax}S_4$ with σ^*_{C3-X} (see Table 2). Based on this fact, $LP_{ax}S_4$ could be a better electron donor to the σ^*_{C-X} antibonding orbitals than $LP_{ax}O_1$ but the results obtained do not confirm this expectation. As seen in Figure 2, the overlap of the main lobe of the O_1 non-bonding orbital ($LP_{ax}O_1$) with the anti-bonding orbital of C_2-F bond (σ^*_{C2-X}) is greater than the corresponding value for the overlap of $LP_{ax}S_4$ with σ^*_{C3-X}. This fact can be justified by the greater off-diagonal element (F_{ij}) values of the $LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$ electron delocalizations compared to the $LP_{ax}S_4 \rightarrow \sigma^*_{C3-X}$ electron delocalizations.

Based on equations 1-5, $\Delta(SE_{ax,eq}\text{-}SE_{ax,ax})$, $\Delta(SE_{eq,ax}\text{-}SE_{ax,ax})$, $\Delta(SE_{eq,eq}\text{-}SE_{ax,ax})$, $\Delta(SE_{eq,eq}\text{-}SE_{eq,ax})$ and $\Delta(SE_{eq,eq}\text{-}SE_{ax,eq})$ associated with $LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$, $LP_{eq}O_1 \rightarrow \sigma^*_{C2-X}$, $LP_{ax}S_4 \rightarrow \sigma^*_{C3-X}$, $LP_{eq}S_4 \rightarrow \sigma^*_{C3-X}$ (*endo-SE*), $LP_3X_{C2} \rightarrow \sigma^*_{C2-O1}$, $LP_1X_{C3} \rightarrow \sigma^*_{C3-S4}$, $LP_2X_{C3} \rightarrow \sigma^*_{C3-S4}$, $LP_3X_{C3} \rightarrow \sigma^*_{C3-S4}$ (*axo-SE*), $\sigma_{C2-X} \rightarrow \sigma^*_{C3-X}$ and $\sigma_{C3-X} \rightarrow \sigma^*_{C2-X}$ (*trans-effects*) electron delocalizations increase (without considering their negative signs) from compound **1** to compound **3** and also from compound **4** to compound **6**. Since the calculated $\Delta G_{eq,eq\text{-}ax,ax}$ decreases from compound **1** to compound **2** and increases from compound **2** to compound **3** and also decreases from compound **4** to compound **6**, the rationalization of the conformational preference solely in terms of the stabilization energies associated with the electron delocalization (*SE*) (or hyperconjugative effect) fails to account for compounds **1-6**.

3-*Orbital occupancies*

Based on the results obtained by the NBO analysis, the $LP_{ax}O_1$ nonbonding orbital occupancies in the (*ax,ax*) configurations decrease from compound **1** to compound **3** and from compound **4** to compound **6** (see Table 2). Also, the $\sigma^*_{C2\text{-}X}$ anti-bonding orbital occupancies increase from the (*ax,ax*) configurations of compound **1** to compound **3** and from compound **4** to compound **6**. These trends can be justified by the increase of the $LP_{ax}O_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalization (*endo-SE*) from the (*ax,ax*) configuration of compound **1** to compound **3** and compound **4** to compound **6**. It has to be noted that the increase of the *trans-effect* associated with the $\sigma_{C2\text{-}X} \rightarrow \sigma^*_{C3\text{-}X}$ and $\sigma_{C3\text{-}X} \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalizations may also increase the $\sigma^*_{C2\text{-}X}$ and $\sigma^*_{C3\text{-}X}$ antibonding orbital occupancies.

4-*Orbital energies and off-diagonal elements*

Since the overlap of the donor-acceptor orbitals in their antiperiplanar position is greater than their *syn* or *gauche* arrangement (see Figure 2), therefore, the stereoelectronic orbital interactions are anticipated to be more effective for the *anti* rather than the *syn* or *gauche* arrangement between the donor and acceptor orbitals.

NBO results showed that the energy differences between donor (E_{LPaxO1}) and acceptor [$E\sigma^*_{(C2\text{-}X)}$] orbitals [i.e. $\Delta(E\sigma^*_{(C2\text{-}X)} - E_{LPaxO1})$] decrease from the (*ax,ax*) configurations of compound **1**to compound **3** and also from compound **4** to compound **6**. It can be concluded that the strong acceptor antibonding orbital of compound **3** (compared to those in compounds **1** and **2**) and compound **6** (compared to those in compounds **4** and **5**) may give rise to strong *endo-SE* (see Tables 2, 3). It should be noted that the *orbital overlap* (S) [off-diagonal elements (F_{ij})] values for the $LP_{ax}O_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalization (*endo-SE*) decrease from the *ax,ax* configurations of compound **1** to compound **2** but increase from compound **2** to compound **3**. Also, the F_{ij} value for the $LP_{ax}O_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalization (endo-*SE*) decreases from the *ax,ax* configurations compound **4** to compound **5** but does not change from compound **5** to compound **6**. Accordingly, compared to the role of the F_{ij}, $\Delta(E_{acceptor} - E_{donor})$ parameter has determinant impact on the increase of the *endo*-*SE* associated with $LP_{ax}O_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalization from compound **1**to compound **3** and also from compound **4** to compound **6**.

5-*Dipole moments*

Generally, it has been accepted that there is a preference for the conformation with the smallest resultant dipole moment.[52] In the gas phase or in the nonpolar media, the conformations with the larger dipole moment may have the larger electrostatic energy. Therefore, we may expect that the conformation with the larger dipole moment may has greater overall energy.[52] The calculated dipole moments for the (*ax,ax*), (*ax,eq*), (*eq,ax*) and (*eq,eq*) forms of compounds **1-6** are given in Tables 2 and 3. B3LYP/6-311+G** results showed that the dipole moments for the (*ax,ax*) configurations of compounds **1-3** are smaller than those in their (*ax,eq*), (*eq,ax*) and (*eq,eq*) configurations.

Since we consider the energy difference between the different configurations as the main descriptor, it is useful if we consider the differences between the other descriptors and compare their impacts on the structural and energetic properties of the different configurations of the molecules. In this regard, using the dipole moments obtained, a "Δ" parameter is found as $\Delta(\mu_{eq,eq}\text{-}\mu_{ax,ax})$. There is an opposite trend for the variations of $\Delta(\mu_{eq,eq}\text{-}\mu_{ax,ax})$ and $\Delta(SE_{eq,eq}\text{-}SE_{ax,ax})$ parameters. Based on the results obtained, $\Delta(SE_{eq,eq}\text{-}SE_{ax,ax})$ increase from compound **1** to compound **3** but $\Delta(\mu_{eq,eq}\text{-}\mu_{ax,ax})$ decrease. The decrease of the calculated $\Delta G_{eq,eq\text{-}ax,ax}$ from compound **1** to compound **2** and its increase from compound **2** to compound **3** may be resulted from the conflicts between $\Delta(\mu_{eq,eq}\text{-}\mu_{ax,ax})$ and $\Delta(SE_{eq,eq}\text{-}SE_{ax,ax})$ parameters. This trend is similar to that we previously obtained for the dithiane analogs.[17]

Contrary to compounds **1-3**, there are no significant differences between the dipole moment values of the (*ax,ax*) and (*eq,eq*) configurations [i.e. $\Delta(\mu_{eq,eq}\text{-}\mu_{ax,ax})$] of compounds **4-6**. Since there are remarkable differences between the energies of the (*ax,ax*) and (*eq,eq*) configurations of compounds **4-6**, therefore, the electrostatic model associated with the dipole-dipole interaction does play a role here. This fact clearly demonstrates that the energy differences between the (*ax,ax*) and (*eq,eq*) configurations of compounds **4-6** are not attributed to their corresponding dipole-dipole interactions. It is timely to revise the conclusion published previously in the literature concerning the origin of the *anomeric effect*[21-25] by the statements of the present work.

Although there are no significant differences between the energies of the (*ax,ax*) and (*eq,eq*) configurations of compounds **4-6**, there are remarkable differences for (*ax,eq*) and (*eq,ax*) configurations. Based on the results obtained, the electrostatic model associated with the dipole-dipole interactions has an effective contribution on the overall energies of the (*ax,eq*) and (*eq,ax*) configurations of compounds **4-6**. For instance, $\Delta(\mu_{eq,ax}-\mu_{eq,eq})$ parameter decrease from compound **4** to compound **6** but the energy differences between the (*eq,ax*) and (*eq,eq*) forms decrease from compound **4** to compound **5** but increase from compound **5** to compound **6**. This fact obviously demonstrate that the energy differences between the (*eq,ax*) and (*eq,eq*) forms of compounds **4-6** can be resulted from the conflict between the impacts of the *SE* and *EM*.

6-*Bond orders*

The structural parameters of the different configurations of a molecule can be affected by the electron delocalization *via* affecting their corresponding bond orders. Based on the results obtained, the calculated bond orders [i.e. Wiberg Bond Index (*WBI*)] for O_1-C_2 bonds of the (*ax,ax*) configurations of compound **1-3** and compounds **4-6** are greater than those for their corresponding (*eq,ax*) and (*eq,eq*) configurations (see Tables 2, 3). In this regard, the differences between the *WBI* of O_1-C_2 bonds in the (*eq,eq*) and (*ax,ax*) conformations, $\Delta[WBI(O_1\text{-}C_{2ax,ax})\text{-}WBIO_1\text{-}C_{2eq,eq})]$, increase from compound **1** to compound **3** and also compound **4** to compound **6**. The variations of $\Delta[WBI(O_1\text{-}C_{2ax,ax})\text{-}WBIO_1\text{-}C_{2eq,eq})]$ parameters are in accordance with the increase of the calculated *endo-SE* associated with $LP_{ax}O_1\rightarrow\sigma^*_{C2\text{-}X}$ electron delocalization from compound **1** to compound **3** and from compound **4** to compound **6** (see Tables 2, 3).

7-*Total steric exchange energies* (*TSEE*)

Natural steric analysis expresses steric exchange repulsion as the energy difference due to orbital orthogonalization, in accordance with a well-established physical picture of steric repulsions.[44,45] The steric exchange energy (or Pauli exchange-type repulsion, *PETR*) includes effects from all occupied orbitals and therefore typically contains contributions from covalent (intrabond) groups.

NBO analysis was used to calculate the steric repulsion contributions in the (*ax,ax*), (*ax,eq*), (*eq,ax*) and (*eq,eq*) configurations of compounds **1-6**. Total steric exchange energy differences between the (*eq,eq*) and (*ax,ax*) forms [*i.e.* $\Delta(TSEE_{\text{eq-eq}}\text{-}TSEE_{\text{ax-ax}})$] increase from compound **1** to compound **3**. This fact demonstrate that the steric repulsions in the (*ax,ax*) forms decrease from compound **1** to compound **3** compared to their corresponding (*eq,eq*) configurations. In this regard, $\Delta(TSEE_{\text{eq-eq}}\text{-}TSEE_{\text{ax-ax}})$ parameters increase dramatically from compound **4** to compound **5** but decrease slightly from compound **5** to compound **6**. Based on the results obtained, the *SE* and Pauli exchange energies are in favor of the (*ax,ax*) forms ongoing from compound **1** to compound **3** but the *EM* have opposite impacts. Contrary to the trend observed for compounds **1-3**, the energy differences between the (*ax,ax*) and (*eq,eq*) forms of compounds **4-6** can be resulted from the conflict between the *SE* and *PETR* (see Tables 1-3).

8-*Structural parameters*

Representative structural parameters (bond lengths, bond angles and torsion angles) for the axial and equatorial conformations of compounds **1-6**, as calculated at the B3LYP/6-311+G** level of theory, are shown in Tables 4 and 5. Although we do not expect to obtain exactly the experimental values because of the differences in definition of bond length values in the theoretical techniques, it is possible to carry out theoretical calculations to obtain many properties and structures with an accuracy that is competitive with experiments.

It is worth noting that in the (*ax,ax*) forms of compounds of compounds **1-6**, the $\sigma_{\text{O1-C2}}$ bond lengths are significantly shortened compared to those in their corresponding (*eq,eq*) conformations. The shorter $\sigma_{\text{O1-C2}}$ bond lengths in the (*ax,ax*) conformations of compounds **1-6**, compared to those in their (*eq,eq*) conformations can be resulted from the $\text{LP}_{\text{ax}}\text{O}_1\rightarrow\sigma^*_{\text{C2-X}}$ electron delocalization (*endo-SE*). The variation of the $\sigma_{\text{O1-C2}}$ bond length in the (*ax,ax*) forms of compounds **1-6** is in accordance with the variation of resonance energies associated with the $\text{LP}_{\text{ax}}\text{O}_1\rightarrow\sigma^*_{\text{C2-X}}$ electron delocalization (see Tables 2-5). The increase of the $\text{LP}_{\text{ax}}\text{O}_1\rightarrow\sigma^*_{\text{C2-X}}$ electronic delocalizations can increase the bond orders of the $\sigma_{\text{O1-C2}}$ bonds, therefore, this fact justify the contracted $\sigma_{\text{O1-C2}}$ bond lengths in the (*ax,ax*) conformations of compounds **1-6**.

Using the structural parameters obtained, a "Δ" parameter could be found as $\Delta(r_{\text{1-2eq,eq}}\text{-}r_{\text{1-2ax,ax}})$. $\Delta(r_{\text{1-2eq,eq}}\text{-}r_{\text{1-2ax,ax}})$ parameter increases from compound **1** to compound **3** and also from compound **4** to compound **6** (see tables 4 and 5). There is a direct correlation between the *SE* (especially *endo-SE* associated with $LP_{ax}O_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalization) and $\Delta(r_{1\text{-}2eq,eq}\text{-}r_{1\text{-}2ax,ax})$ parameters (see Tables 2-5). These results indicate that with the increase of $\Delta(r_{1\text{-}2eq,eq}\text{-}r_{1\text{-}2ax,ax})$ parameter, the corresponding $\Delta(SE_{eq,eq}\text{-}SE_{ax,ax})$ values increase from compound **1** to compound **3** and from compound **4** to compound **6**.

Another evidence which shows the unnegotiable impacts of the *SE* associated with the electron delocalization on the structural parameters is the decrease of the $\phi_{6\text{-}1\text{-}2\text{-}3}$ torsion angle ongoing from the (*ax,ax*) forms of compound **1** to compound **3** and from compound **4** to compound **6**. This fact can be rationalized by the variations of the *endo-SE* associated with $LP_{ax}O_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalizations. Interestingly, $\Delta[\phi_{6\text{-}1\text{-}2\text{-}3eq,eq}\text{-}\phi_{6\text{-}1\text{-}2\text{-}3ax,ax}]$ parameter increase from the *ax,ax* forms of compound **1** to compound **3** and from compound **4** to compound **6** which can be resulted from the increase of their corresponding O_1-C_2 bond orders. There are published data in the literature in which the researchers claim that the electrostatic model associated with the dipole-dipole interactions has greater impact on the structural and energetic properties of chemical compounds than the hyperconjugation effect; however, the results of this work provides remarkable evidence that the conclusion published in the literature[21-25] concerning the interpretation of the *anomeric effect* in terms of the electrostatic model can be revised by the statements of the present work.

Conclusions

The CBS-4, B3LYP/6-311+G** calculations reported above and NBO analysis provided a reasonable picture from energetic, structural, bonding and stereoelectronic points of view for compounds **1-6**. Effectively, the CBS-4, B3LYP/6-311+G** and NBO results showed that the the stabilization energy associated with the electron delocalization (*SE*) fails solely to account for the variations of the energy differences between the different forms in compounds **1-6** but still shows unnegotiable impacts on the structural features (bond lengths, bond angles, torsion angles and bond orders) of these compounds. Importantly, there is no significant correlation between the electrostatic model associated with the dipole-dipole interactions (*EM*) and the structural and energetic features of compounds **1-6**. Consequently, the conclusion published previously in the literature should be reexamined. Since, there are no remarkable dipole moment values for the (*ax,ax*) and (*eq,eq*) forms of compounds **4-6**, the energy differences between the (*ax,ax*) and (*eq,eq*) forms of compounds **4-6** can be resulted from the conflict between the *SE* and *PETR*. Most importantly, the results of this work revealed that the *SE*, *EM* and *PETR* are not solely responsible for the calculated *anomeric effect* in compounds **1-6** but it can be resulted from their cooperative or uncooperative (confrontational) impacts.

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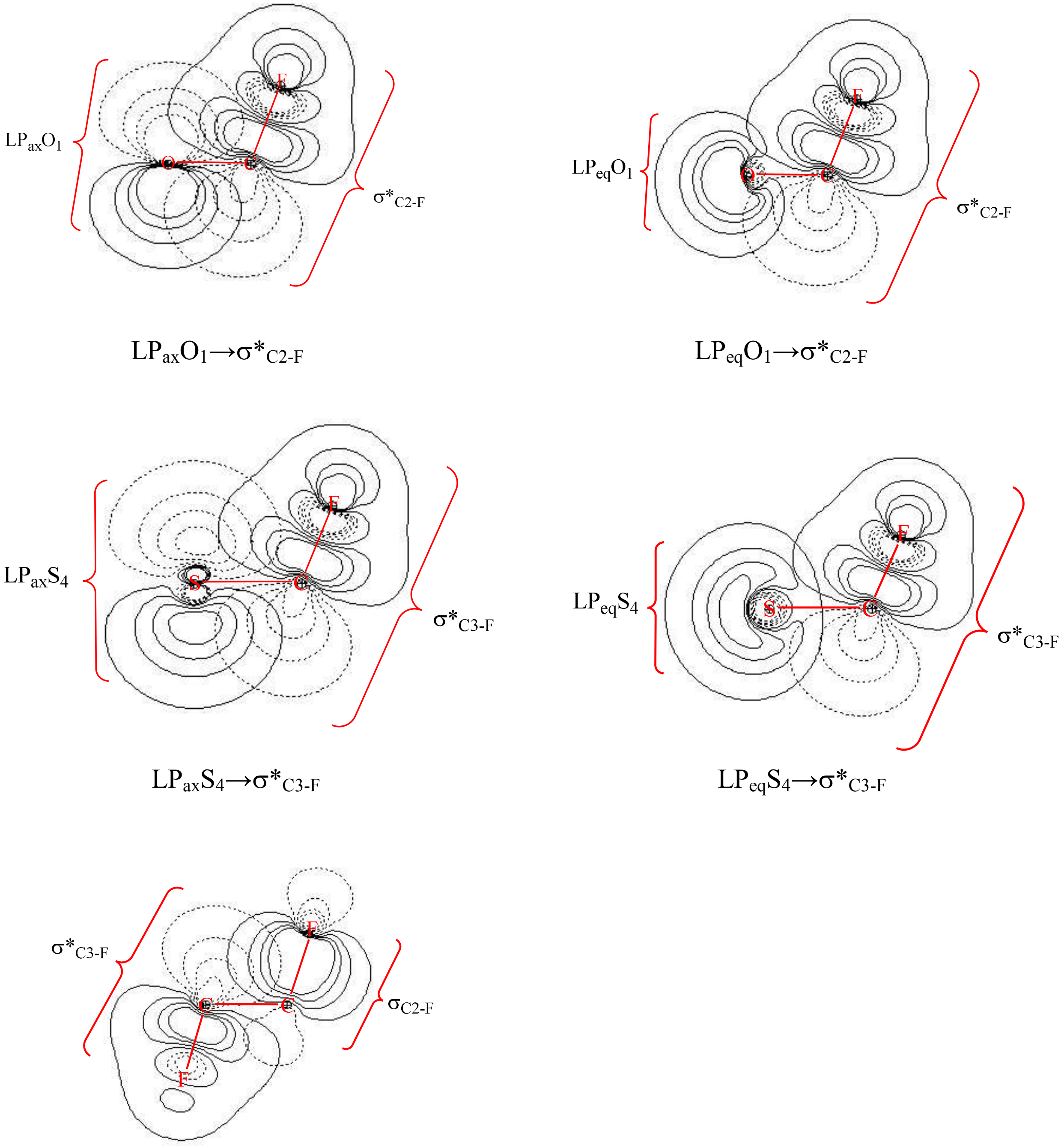

$LP_{ax}O_1 \rightarrow \sigma^*_{C2-F}$ $LP_{eq}O_1 \rightarrow \sigma^*_{C2-F}$

$LP_{ax}S_4 \rightarrow \sigma^*_{C3-F}$ $LP_{eq}S_4 \rightarrow \sigma^*_{C3-F}$

$\sigma_{C2-F} \rightarrow \sigma^*_{C3-F}$

Figure 2. The calculated profiles of the orbital amplitudes (electron densities) for $LP_{ax}O_1 \rightarrow \sigma^*_{C2-F}$, $LP_{eq}O_1 \rightarrow \sigma^*_{C2-F}$, $LP_{ax}S_4 \rightarrow \sigma^*_{C3-F}$, $LP_{eq}S_4 \rightarrow \sigma^*_{C3-F}$ and $\sigma_{C2-F} \rightarrow \sigma^*_{C3-F}$ electron delocalizations.

Table 1. B3LYP/6-311+G** and CBS-4 calculated thermodynamic parameters [Δ*H*, Δ*G* (in kcal mol^{-1}) and Δ*S* (in cal mol^{-1}K^{-1})] at 25 ºC and 1 atm pressure for the *ax,ax, ax,eq, eq,ax* and *eq,eq* conformations of compounds **1-6**.

	B3LYP/6-311+G**			CBS-4		
	Δ*H*[a]	Δ*S*[a]	Δ*G*[a]	Δ*H*[a]	Δ*S*[a]	Δ*G*[a]
Geometry						
1-*ax,ax*	0.00	0.000	0.00	0.00	0.000	0.00
1-*ax,eq*	4.09	-0.212	4.16	3.95	-0.590	4.12
1-*eq,ax*	3.19	-0.270	3.27	2.86	-0.248	2.93
1-*eq,eq*	4.72	0.240	4.64	4.21	0.314	4.12
2-*ax,ax*	0.00	0.000	0.00	0.00	0.000	0.00
2-*ax,eq*	3.56	-0.300	3.65	2.70	-0.095	2.73
2-*eq,ax*	3.57	-0.167	3.62	2.25	-0.141	2.29
2-*eq,eq*	4.25	0.544	4.09	3.30	0.849	3.04
3-*ax,ax*	0.00	0.000	0.00	0.00	0.000	0.00
3-*ax,eq*	4.60	-0.366	4.71	3.47	0.008	3.47
3-*eq,ax*	4.82	-0.385	4.94	3.21	0.042	3.20
3-*eq,eq*	5.44	0.324	5.34	4.23	1.122	3.89
4-*ax,ax*	0.00	0.000	0.00	0.00	0.000	0.00
4-*ax,eq*	3.26	0.304	3.17	3.18	-0.208	3.24
4-*eq,ax*	1.59	-0.035	1.60	1.30	0.261	1.22
4-*eq,eq*	4.56	0.296	4.47	3.86	0.168	3.81
5-*ax,ax*	0.00	0.00	0.00	0.00	0.000	0.00
5-*ax,eq*	1.70	0.199	1.64	1.57	-0.497	1.42
5-*eq,ax*	1.67	0.275	1.58	1.15	-0.486	1.00
5-*eq,eq*	2.63	0.557	2.47	2.10	-1.009	1.80
6-*ax,ax*	0.00	0.000	0.00	0.00	0.000	0.00
6-*ax,eq*	1.67	0.404	1.55	1.32	-0.644	1.13
6-*eq,ax*	1.99	0.269	1.91	1.84	-0.762	1.61
6-*eq,eq*	2.70	0.657	2.51	2.20	-1.394	1.78

[a] Relative to the most stable form

Table 2. NBO-B3LYP/6-311+G** calculated stabilization energies (*SE*, in kcal mol^{-1}) associated with the electron delocalizations, anomeric effect, off-diagonal elements (F_{ij}, in a.u.), orbital energy (ε, in a.u.), orbital energy differences ($\Delta\varepsilon$, in a.u.), orbital occupancies (e), bond orders (Wiberg bond indexes, *WBI*), dipole moments (μ, in debye) and total steric exchange energies (*TSEE*) for the *ax,ax*, *ax,eq*, *eq,ax* and *eq,eq* forms of compounds **1-3**.

	1				**2**				**3**			
Geometry	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*
endo-SE												
$LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$	18.98	16.49	0.82	1.15	21.83	17.96	0.99	1.01	25.57	20.27	1.13	1.08
$LP_{eq}O_1 \rightarrow \sigma^*_{C2-X}$	0.63	0.86	5.36	5.24	0.80	1.20	2.08	2.14	0.79	1.28	1.65	1.74
$LP_{ax}S_4 \rightarrow \sigma^*_{C3-X}$	13.42	-	11.75	-	13.21	-	10.39	-	16.16	-	11.70	-
$LP_{eq}S_4 \rightarrow \sigma^*_{C3-X}$	-	0.72	-	0.92	1.00	-	1.22	-	1.24	-	1.58	-
exo-SE												
$LP_3X_{C2} \rightarrow \sigma^*_{C2-O1}$	10.36	11.25	10.83	10.77	6.30	7.37	7.56	7.18	4.04	5.38	5.62	5.23
$LP_3X_{C3} \rightarrow \sigma^*_{C3-S4}$	8.85	8.67	9.85	8.39	4.54	5.40	6.52	4.60	2.02	3.64	4.67	2.96
$LP_1X_{C3} \rightarrow \sigma^*_{C3-S4}$	-	-	-	-	0.52	-	0.52	-	0.53	0.50	0.53	-
$LP_2X_{C3} \rightarrow \sigma^*_{C3-S4}$	-	-	-	-	1.30	-	-	0.55	1.96	0.64	-	0.54
trans-effect												
$\sigma_{C2-X} \rightarrow \sigma^*_{C3-X}$	1.55	-	-	-	3.72	-	-	-	5.23	-	-	-
$\sigma_{C3-X} \rightarrow \sigma^*_{C2-X}$	1.39	-	-	-	3.62	-	-	-	5.19	-	-	-
Σ	55.18	37.92	38.61	26.47	56.84	31.93	29.28	15.48	62.73	31.71	26.88	11.55
$\Delta(SE_{ax,eq}-SE_{ax,ax})$	-17.26				-24.91				-31.02			
$\Delta(SE_{eq,ax}-SE_{ax,ax})$	-16.57				-27.56				-35.85			
$\Delta(SE_{eq,eq}-SE_{ax,ax})$	-28.71				-41.36				-51.18			
$\Delta(SE_{eq,eq}-SE_{eq,ax})$	-12.14				-13.80				-15.33			
$\Delta(SE_{eq,eq}-SE_{ax,eq})$	-11.45				-16.45				-20.16			
F_{ij} (a.u.)												
$LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$	0.090	0.085	0.019	0.023	0.083	0.077	0.018	0.019	0.084	0.077	0.018	0.018
$LP_{eq}O_1 \rightarrow \sigma^*_{C2-X}$	0.020	0.023	0.059	0.058	0.020	0.025	0.034	0.034	0.019	0.025	0.029	0.029
$LP_{ax}S_4 \rightarrow \sigma^*_{C3-X}$	0.068	-	0.066	-	0.058	-	0.053	-	0.058	-	0.052	-
$LP_{eq}S_4 \rightarrow \sigma^*_{C3-X}$	-	0.022	-	0.025	0.024	-	0.027	-	0.026	-	0.030	-
$LP_3X_{C2} \rightarrow \sigma^*_{C2-O1}$	0.078	0.080	0.078	0.078	0.056	0.060	0.060	0.058	0.044	0.050	0.051	0.049
$LP_1X_{C3} \rightarrow \sigma^*_{C3-S4}$	-	-	-	-	0.021	-	0.021	-	0.022	0.021	0.022	-

Table 2 continued…

$LP_2X_{C3}\rightarrow\sigma^*_{C3\text{-}S4}$	-	-	-	-	0.022	-	-	0.014	0.027	0.015	-	0.014
$LP_3X_{C3}\rightarrow\sigma^*_{C3\text{-}S4}$	0.063	0.062	0.066	0.060	0.041	0.044	0.048	0.040	0.027	0.035	0.040	0.031
ε												
$LP_{ax}O_1$	-0.336	-0.340	-0.332	-0.341	-0.351	-0.349	-0.332	-0.338	-0.359	-0.354	-0.332	-0.338
$LP_{ax}S_4$	-0.257	-0.254	-0.262	-0.261	-0.264	-0.256	-0.265	-0.261	-0.270	-0.256	-0.267	-0.262
LP_3X_{C2}	-0.417	-0.415	-0.417	-0.418	-0.322	-0.318	-0.321	-0.320	-0.296	-0.292	-0.297	-0.295
LP_3X_{C3}	-0.423	-0.431	-0.424	-0.429	-0.329	-0.335	-0.330	-0.331	-0.300	-0.310	-0.306	-0.306
$\sigma^*_{C2\text{-}X}$	0.186	0.198	0.217	0.215	0.044	0.061	0.084	0.083	-0.012	0.007	0.029	0.027
$\sigma^*_{C3\text{-}X}$	0.174	0.195	0.193	0.194	0.048	0.086	0.074	0.077	-0.010	0.027	0.017	0.025
$\sigma^*_{C2\text{-}O1}$	0.313	0.301	0.291	0.284	0.303	0.287	0.280	0.272	0.309	0.290	0.283	0.273
$\sigma^*_{C3\text{-}S4}$	0.139	0.119	0.127	0.112	0.132	0.117	0.118	0.107	0.138	0.120	0.120	0.109
$\Delta\varepsilon$												
$\Delta[\varepsilon(\sigma^*_{C2\text{-}X}) - \varepsilon(LP_{ax}O_1)]$	0.522	0.538	0.548	0.557	0.394	0.410	0.416	0.421	0.346	0.361	0.350	0.365
$\Delta[\varepsilon(\sigma^*_{C3\text{-}X}) - \varepsilon(LP_{ax}S_4)]$	0.431	0.449	0.456	0.455	0.312	0.341	0.339	0.339	0.259	0.283	0.285	0.286
$\Delta[\varepsilon(\sigma^*_{C2\text{-}O1}) - \varepsilon(LP_3X_{C2})]$	0.730	0.716	0.708	0.703	0.625	0.605	0.601	0.591	0.605	0.582	0.579	0.568
$\Delta[\varepsilon(\sigma^*_{C3\text{-}S4}) - \varepsilon(LP_3X_{C3})]$	0.569	0.550	0.551	0.541	0.461	0.452	0.448	0.438	0.438	0.430	0.426	0.415
e												
$LP_{ax}O_1$	1.884	1.895	1.918	1.919	1.869	1.883	1.916	1.914	1.853	1.870	1.915	1.911
$LP_{eq}O_1$	1.959	1.960	1.951	1.952	1.954	1.953	1.958	1.957	1.953	1.952	1.957	1.957
$LP_{ax}S_4$	1.888	1.932	1.897	1.931	1.881	1.925	1.892	1.922	1.862	1.923	1.880	1.918
$LP_{eq}S_4$	1.985	1.983	1.985	1.983	1.981	1.986	1.980	1.985	1.979	1.985	1.978	1.985
$\sigma^*_{C2\text{-}X}$	0.083	0.076	0.057	0.055	0.117	0.098	0.062	0.059	0.149	0.118	0.071	0.068
$\sigma^*_{C3\text{-}X}$	0.079	0.036	0.069	0.034	0.099	0.034	0.077	0.033	0.131	0.037	0.094	0.037
μ	1.705	3.463	3.661	3.807	2.087	3.426	3.548	3.566	2.400	3.378	3.524	3.414
$\Delta(\mu_{eq,eq} - \mu_{eq,ax})$	0.146				0.018				-0.110			
$\Delta(\mu_{eq,eq} - \mu_{ax,ax})$	2.102				1.479				1.014			
$\Delta(\mu_{eq,ax} - \mu_{ax,ax})$	1.956				1.461				1.124			
WBI												

Table 2 continued...

O_1-C_2	0.994	0.972	0.939	0.931	0.999	0.967	0.939	0.928	1.013	0.974	0.943	0.930
S_4-C_3	1.062	0.987	1.036	0.979	1.046	0.987	1.006	0.968	1.067	0.996	1.014	0.972
C_2-X	0.806	0.8272	0.849	0.849	0.920	0.961	0.998	0.997	0.873	0.930	0.974	0.972
C_3-X	0.812	0.855	0.837	0.854	0.938	1.019	0.982	1.013	0.889	0.998	0.950	0.992
$\Delta[WBI_{O1\text{-}C2}(ax,ax) - WBI_{O1\text{-}C2}(eq,eq)]$	0.064				0.071				0.083			
$\Delta[WBI_{S4\text{-}C3}(ax,ax) - WBI_{S4\text{-}C3}(eq,eq)]$	0.082				0.078				0.095			
$\Delta[WBI_{C2\text{-}X}(eq,eq) - WBI_{C2\text{-}X}(ax,ax)]$	0.043				0.078				0.099			
$\Delta[WBI_{C3\text{-}X}(eq,eq) - WBI_{C3\text{-}X}(ax,ax)]$	0.041				0.073				0.103			
TSEE	300.71	297.01	306.81	300.48	327.51	331.25	332.83	333.46	325.47	333.64	337.88	333.42
$\Delta[TSEE_{eq,eq}\text{-}TSEE_{ax,ax})$	-0.23				5.95				7.95			
$\Delta[TSEE_{eq,ax}\text{-}TSEE_{ax,ax})$	6.1				5.32				12.41			
$\Delta[TSEE_{ax,eq}\text{-}TSEE_{ax,ax})$	-3.7				3.74				8.17			

Table 3. NBO-B3LYP/6-311+G** calculated stabilization energies (*SE*, in kcal mol^{-1}) associated with the electron delocalizations, anomeric effect (*AE*, in kcal mol^{-1}), off-diagonal elements (F_{ij}, in a.u.), orbital energy (ε, in a.u.), orbital energy differences ($\Delta\varepsilon$, in a.u.), orbital occupancies (e), bond orders (Wiberg bond indexes, *WBI*), dipole moments (μ, in debye) and total steric exchange energies (*TSEE*) for the *ax,ax*, *ax,eq*, *eq,ax* and *eq,eq* forms of compounds **4-6**.

	4				**5**				**6**			
Geometry	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*
endo-SE												
$LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$	17.68	17.11	1.12	0.88	20.20	19.28	0.69	0.84	23.19	22.11	0.70	0.97
$LP_{eq}O_1 \rightarrow \sigma^*_{C2-X}$	0.63	0.65	5.19	5.22	0.74	0.92	2.27	2.10	0.75	0.99	1.90	1.66
$LP_{ax}S_4 \rightarrow \sigma^*_{C5-X}$	12.86	-	12.67	-	12.64	-	11.92	-	15.08	-	13.88	-
$LP_{eq}S_4 \rightarrow \sigma^*_{C5-X}$	-	0.82	-	0.81	1.04	-	1.08	-	1.31	-	1.42	-
exo-SE												
$LP_3X_{C2} \rightarrow \sigma^*_{C2-O1}$	10.33	10.64	10.80	10.87	6.74	7.00	7.30	7.36	4.92	5.14	5.40	5.44
$LP_3X_{C5} \rightarrow \sigma^*_{C5-S4}$	8.91	8.47	9.10	8.62	6.05	4.94	6.27	5.13	4.37	3.25	4.59	-
$LP_1X_{C5} \rightarrow \sigma^*_{C5-S4}$	-	-	-	-	-	-	-	-	-	-	0.51	-
$LP_2X_{C5} \rightarrow \sigma^*_{C5-S4}$	-	-	-	-	-	0.52	-	-	-	0.65	-	0.53
Σ	50.41	37.69	38.88	26.4	47.41	32.66	29.53	15.43	49.62	32.14	28.4	8.6
$\Delta(SE_{ax,eq}-SE_{ax,ax})$	-12.72				-14.75				-17.48			
$\Delta(SE_{eq,ax}-SE_{ax,ax})$	-11.53				-17.88				-21.22			
$\Delta(SE_{eq,eq}-SE_{ax,ax})$	-24.01				-31.98				-41.02			
$\Delta(SE_{eq,eq}-SE_{eq,ax})$	-12.48				-14.1				-19.8			
$\Delta(SE_{eq,eq}-SE_{ax,eq})$	-11.29				-17.23				-23.54			
F_{ij}												
$LP_{ax}O_1 \rightarrow \sigma^*_{C2-X}$	0.087	0.086	0.022	0.020	0.081	0.079	0.015	0.017	0.081	0.080	0.014	0.017
$LP_{eq}O_1 \rightarrow \sigma^*_{C2-X}$	0.020	0.020	0.058	0.058	0.019	0.022	0.035	0.034	0.019	0.022	0.031	0.029
$LP_{ax}S_4 \rightarrow \sigma^*_{C5-X}$	0.067	-	0.067	-	0.057	-	0.056	-	0.057	-	0.056	-
$LP_{eq}S_4 \rightarrow \sigma^*_{C5-X}$	-	0.024	-	0.024	0.025	-	0.026	-	0.027	-	0.028	-
$LP_3X_{C2} \rightarrow \sigma^*_{C2-O1}$	0.077	0.078	0.078	0.078	0.058	0.058	0.059	0.059	0.048	0.049	0.050	0.050
$LP_1X_{C5} \rightarrow \sigma^*_{C5-S4}$	-	-	-	-	-	-	-	-	-	-	0.021	-
$LP_2X_{C5} \rightarrow \sigma^*_{C5-S4}$	-	-	-	-	-	0.014	-	-	-	0.015	-	0.014
$LP_3X_{C5} \rightarrow \sigma^*_{C5-S4}$	0.063	0.061	0.064	0.061	0.048	0.042	0.048	0.043	0.040	0.033	0.041	-

Table 3 continued…

ε												
$LP_{ax}O_1$	-0.336	-0.342	-0.336	-0.339	-0.352	-0.353	-0.334	-0.339	-0.359	-0.358	-0.335	-0.340
$LP_{ax}S_4$	-0.256	-0.255	-0.263	-0.261	-0.266	-0.257	-0.268	-0.263	-0.272	-0.258	-0.271	-0.264
LP_3X_{C2}	-0.413	-0.415	-0.417	-0.420	-0.322	-0.322	-0.323	-0.325	-0.297	-0.297	-0.299	-0.230
LP_3X_{C5}	-0.429	-0.430	-0.431	-0.435	-0.342	-0.337	-0.342	-0.34-	-0.322	-0.313	-0.321	-0.315
$\sigma^*_{C2\text{-}X}$	0.188	0.189	0.213	0.211	0.050	0.053	0.081	0.080	-0.002#	0.001	0.027	0.024
$\sigma^*_{C5\text{-}X}$	0.183	0.191	0.183	0.188	0.055	0.075	0.058	0.073	0.001	0.023	0.005	0.021
$\sigma^*_{C2\text{-}O1}$	0.304	0.295	0.284	0.276	0.293	0.287	0.270	0.266	0.298	0.293	0.273	0.270
$\sigma^*_{C5\text{-}S4}$	0.135	0.118	0.129	0.111	0.129	0.115	0.125	0.110	0.134	0.117	0.129	0.114
$\Delta\varepsilon$												
$\Delta[\varepsilon(\sigma^*_{C2\text{-}X}) - \varepsilon(LP_{ax}O_1)]$	0.524	0.531	0.549	0.550	0.402	0.406	0.415	0.418	0.357	0.359	0.361	0.364
$\Delta[\varepsilon(\sigma^*_{C5\text{-}X}) - \varepsilon(LP_{ax}S_4)]$	0.439	0.446	0.446	0.450	0.321	0.332	0.392	0.337	0.273	0.280	0.276	0.285
$\Delta[\varepsilon(\sigma^*_{C2\text{-}O1}) - \varepsilon(LP_3X_{C2})]$	0.717	0.711	0.700	0.696	0.615	0.609	0.593	0.591	0.595	0.590	0.572	0.570
$\Delta[\varepsilon(\sigma^*_{C5\text{-}S4}) - \varepsilon(LP_3X_{C5})]$	0.564	0.548	0.560	0.546	0.471	0.452	0.466	0.450	0.456	0.430	0.451	0.429
e												
$LP_{ax}O_1$	1.892	1.895	1.918	1.921	1.876	1.878	1.918	1.916	1.861	1.864	1.917	1.914
$LP_{eq}O_1$	1.958	1.960	1.951	1.953	1.955	1.954	1.957	1.958	1.954	1.953	1.956	1.957
$LP_{ax}S_4$	1.896	1.932	1.896	1.931	1.886	1.926	1.887	1.923	1.870	1.924	1.872	1.919
$LP_{eq}S_4$	1.984	1.983	1.984	1.984	1.981	1.985	1.980	1.985	1.979	1.985	1.978	1.985
$\sigma^*_{C2\text{-}X}$	0.082	0.079	0.057	0.055	0.107	0.104	0.059	0.059	0.129	0.125	0.068	0.069
$\sigma^*_{C5\text{-}X}$	0.081	0.035	0.078	0.033	0.107	0.033	0.087	0.033	0.114	0.036	0.105	0.037
μ	0.242	2.655	2.822	0.308	0.234	2.566	2.767	0.337	0.344	2.545	2.730	0.415
$\Delta(\mu_{eq,ax}-\mu_{eq,eq})$		2.514				2.430				2.315		
$\Delta(\mu_{eq,eq}-\mu_{ax,ax})$		0.066				0.103				0.071		
$\Delta(\mu_{eq,ax}-\mu_{ax,ax})$		2.580				2.533				2.386		
WBI												
O_1-C_2	0.971	0.965	0.9229	0.918	0.977	0.971	0.923	0.920	0.991	0.984	0.929	0.929
S_4-C_3	1.0023	1.002	0.9950	0.999	1.0061	0.997	0.986	0.980	1.006	0.993	0.980	0.967
C_2-X	0.808	0.815	0.8411	0.843	0.936	0.944	0.990	0.990	0.907	0.915	0.969	0.968

Table 3 continued…

C_3-X	0.816	0.846	0.821	0.848	0.954	1.008	0.963	1.008	0.922	0.990	0.933	0.989
$\Delta[WBI_{O1\text{-}C2}(ax,ax) - WBI_{O1\text{-}C2}(eq,eq)]$	0.054				0.058				0.062			
$\Delta[WBI_{S4\text{-}C5}(ax,ax) - WBI_{S4\text{-}C5}(eq,eq)]$	0.004				0.026				0.038			
$\Delta[WBI_{C2\text{-}X}(eq,eq) - WBI_{C2\text{-}X}(ax,ax)]$	0.035				0.054				0.060			
$\Delta[WBI_{C5\text{-}X}(eq,eq) - WBI_{C5\text{-}X}(ax,ax)]$	0.032				0.054				0.067			
TSEE												
$TSEE_{ax,ax}$	305.50	297.74	306.14	297.71	321.61	325.34	331.75	331.35	319.76	326.36	326.62	328.62
$\Delta TSEE$												
$\Delta[TSEE_{eq,eq} - TSEE_{ax,ax}]$	-7.79				9.74				8.86			
$\Delta[TSEE_{eq,ax} - TSEE_{ax,ax}]$	0.64				10.14				6.86			
$\Delta[TSEE_{ax,eq} - TSEE_{ax,ax}]$	-7.76				3.73				6.60			

Table 4. B3LYP/6-311+G** calculated structural parameters for the *ax,ax*, *ax,eq*, *eq,ax* and *eq,eq* forms of compounds **1-3.**

	1				**2**				**3**			
Geometry	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*
Bond lengths (Å)												
$r_{1\text{-}2}$	1.373	1.384	1.391	1.396	1.370	1.386	1.393	1.402	1.363	1.382	1.391	1.401
$r_{2\text{-}3}$	1.537	1.532	1.532	1.526	1.537	1.536	1.535	1.531	1.530	1.533	1.531	1.527
$r_{3\text{-}4}$	1.805	1.836	1.819	1.845	1.804	1.830	1.824	1.844	1.794	1.825	1.821	1.841
$r_{4\text{-}5}$	1.839	1.841	1.840	1.838	1.835	1.840	1.836	1.836	1.834	1.842	1.836	1.838
$r_{5\text{-}6}$	1.517	1.518	1.522	1.521	1.518	1.519	1.522	1.519	1.518	1.519	1.522	1.519
$r_{6\text{-}1}$	1.441	1.443	1.429	1.430	1.439	1.440	1.433	1.432	1.439	1.440	1.435	1.434
$r_{2\text{-}X}$	1.403	1.390	1.374	1.375	1.865	1.837	1.804	1.805	2.061	2.021	1.977	1.980
$r_{3\text{-}X}$	1.402	1.382	1.388	1.383	1.846	1.795	1.817	1.799	2.037	1.960	1.992	1.966
$\Delta[r_{1\text{-}2}(\text{eq,eq}) - r_{1\text{-}2}(\text{ax,ax})]$	0.023				0.032				0.038			
Bond angles (°)												
$\theta_{1\text{-}2\text{-}3}$	116.0	112.5	113.5	111.3	115.9	111.3	113.7	110.7	116.7	111.4	113.9	110.8
$\theta_{2\text{-}3\text{-}4}$	114.8	113.4	110. 6	110.8	114.5	113.8	108.9	110.2	115.3	114.3	108.7	110. 2
$\theta_{3\text{-}4\text{-}5}$	97.8	95.0	97.7	97.2	97.3	94.9	97.5	97.9	97.5	94.9	97.7	98.4
$\theta_{4\text{-}5\text{-}6}$	111.0	111.5	111.6	111.4	111.2	111.5	111.6	110.8	111.2	111.5	111.7	110.9
$\theta_{5\text{-}6\text{-}1}$	112.1	112.2	111. 8	111.2	112.3	112.5	111.8	110.9	112.3	112. 6	111.8	111. 0
$\theta_{6\text{-}1\text{-}2}$	116.8	116.0	114.0	114.6	117.9	117.3	113.7	114.8	118.2	117.5	113.5	115.0
$\theta_{X\text{-}2\text{-}1}$	110.6	110.8	106.0	105.7	112.0	112. 0	107.4	105.8	111.8	111.7	107.5	105.2
$\Delta[\theta_{X\text{-}2\text{-}1}(\text{ax,ax})-\theta_{X\text{-}2\text{-}1}(\text{eq,eq})]$	4.9				6.2				6.6			
Torsion angles (°)												
$\phi_{1\text{-}2\text{-}3\text{-}4}$	-50.0	-59.4	-61.4	-62.2	-50.7	-59.6	-63.7	-62.0	-48.6	-59.2	-64.0	-62.0
$\phi_{2\text{-}3\text{-}4\text{-}5}$	44.0	51.3	49.2	50.2	46.0	52.5	51.1	50.5	44.5	52.2	51.0	50.1
$\phi_{3\text{-}4\text{-}5\text{-}6}$	-50.5	-52.6	-50.0	-50.0	-51. 9	-52.6	-51.4	-50.3	-51.3	-52. 3	-51.1	-49.6
$\phi_{4\text{-}5\text{-}6\text{-}1}$	62.5	62.1	60.0	60.5	61.7	60.8	59.8	60.7	61.5	60.5	59. 3	59.8
$\phi_{5\text{-}6\text{-}1\text{-}2}$	-64.2	-64.6	-66.5	-68.7	-61.8	-63.6	-65.4	-69.7	-61.1	-63.3	-65.1	-69.5
$\phi_{6\text{-}1\text{-}2\text{-}3}$	56.7	62.1	67.7	69.6	55.2	61.3	68.5	70.2	53.4	60.7	68.9	70.6
$\Delta[\phi_{6\text{-}1\text{-}2\text{-}3}(\text{eq,eq})-\phi_{6\text{-}1\text{-}2\text{-}3}(\text{ax,ax})]$	12.9				15.0				17.2			

Table 5. B3LYP/6-311+G** calculated structural parameters for the *ax,ax*, *ax,eq*, *eq,ax* and *eq,eq* forms of compounds **4-6.**

Geometry	**4**				**5**				**6**			
	ax,ax	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*	*ax,ax*	*ax,eq*	*eq,ax*	*eq,eq*
Bond lengths (Å)												
$r_{1\text{-}2}$	1.384	1.387	1.380	1.403	1.382	1.385	1.404	1.406	1.376	1.379	1.401	1.403
$r_{2\text{-}3}$	1.521	1.522	1.517	1.519	1.523	1.524	1.518	1.518	1.522	1.522	1.516	1.515
$r_{3\text{-}4}$	1.834	1.837	1.840	1.837	1.829	1.834	1.840	1.842	1.828	1.834	1.842	1.847
$r_{4\text{-}5}$	1.814	1.840	1.816	1.844	1.812	1.835	1.815	1.838	1.803	1.830	1.807	1.833
$r_{5\text{-}6}$	1.519	1.520	1.525	1.525	1.524	1.523	1.529	1.526	1.523	1.522	1.528	1.525
$r_{6\text{-}1}$	1.431	1.435	1.420	1.422	1.428	1.435	1.421	1.427	1.428	1.437	1.423	1.431
$r_{2\text{-}X}$	1.403	1.399	1.380	1.379	1.859	1.852	1.810	1.810	2.044	2.037	1.982	1.984
$r_{5\text{-}X}$	1.402	1.388	1.399	1.387	1.839	1.804	1.833	1.804	2.019	1.968	2.011	1.970
$\Delta[r_{1\text{-}2}(\text{eq,eq}) - r_{1\text{-}2}(\text{ax,ax})]$	0.019				0.024				0.027			
Bond angles (°)												
$\theta_{1\text{-}2\text{-}3}$	114.6	114.4	112.0	112.1	114.3	114.0	112.1	112.0	114.8	114.5	112.3	112.3
$\theta_{2\text{-}3\text{-}4}$	113.6	113.9	110.1	110.6	114.1	114.2	109.9	110.1	114.2	114.4	109.5	109.5
$\theta_{3\text{-}4\text{-}5}$	97.8	95.5	98.7	96. 5	97.3	95.5	98.2	96. 7	97.4	95.5	98.3	96.7
$\theta_{4\text{-}5\text{-}6}$	112.9	111.4	113.2	111.8	111.9	111.3	112.0	111.5	112.3	111.6	112.4	111.8
$\theta_{5\text{-}6\text{-}1}$	114.3	111.5	113.5	111.1	114.3	111.4	113.6	110.6	114.5	111.3	113.6	110.2
$\theta_{6\text{-}1\text{-}2}$	116.9	116.3	114.2	114.0	117.7	117.5	113.9	113.8	118.0	117.8	113. 9	113.7
$\theta_{X\text{-}2\text{-}1}$	109. 9	110.0	105.4	105.3	111.6	111. 8	106.5	106.4	111.6	111.9	106.5	106.4
$\Delta[\theta_{X\text{-}2\text{-}1}(\text{ax,ax})-\theta_{X\text{-}2\text{-}1}(\text{eq,eq})]$	4.6				5.1				5.2			
Torsion angles (°)												
$\phi_{1\text{-}2\text{-}3\text{-}4}$	55.3	55.2	63.6	63.1	54.5	54.6	63.9	63.3	53. 6	53.7	64.2	63.7
$\phi_{2\text{-}3\text{-}4\text{-}5}$	-46.4	-48.5	-48.6	-50.7	-48.1	-49.2	-50.6	-51.2	-47.4	-48.6	-50.7	-51.2
$\phi_{3\text{-}4\text{-}5\text{-}6}$	47.2	52.8	44.9	50.5	49.3	53.5	47.5	51.41	48.9	53.4	47.5	51.6
$\phi_{4\text{-}5\text{-}6\text{-}1}$	-56.7	-63.6	-54.3	-60.9	-58.2	-63.3	-56.6	-61.6	-57.6	-63.1	-56.2	-61.5
$\phi_{5\text{-}6\text{-}1\text{-}2}$	60.6	64.6	64.5	67.7	60.2	63.6	64.8	68.2	59.1	62.9	64.1	68.0
$\phi_{6\text{-}1\text{-}2\text{-}3}$	-59.6	-59.9	-70.2	-69.5	-57.3	-58.5	-69.1	-70.1	-56.3	-57.6	-69.1	-70.7
$\Delta[\phi_{6\text{-}1\text{-}2\text{-}3}(\text{eq,eq})-\phi_{6\text{-}1\text{-}2\text{-}3}(\text{ax,ax})]$	9.9				12.7				14.4			