ORIGINAL PAPER

Conformational behaviors of trans-2,3- and trans-2,5-dihalo-1,4-diselenanes. A complete basis set, hybrid-density functional theory study and natural bond orbital interpretations

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Abstract Complete basis set CBS-4, hybrid-density functional theory (hybrid-DFT: B3LYP/6-311+G**) based methods and natural bond orbital (NBO) interpretations have been used to examine the contributions of the hyperconjugative, electrostatic, and steric effects on the conformational behaviors of *trans*-2,3-dihalo-1,4-diselenane [halo=F (**1**), Cl (**2**), Br (**3**)] and *trans*-2,5-dihalo-1,4-diselenane [halo = F (**4**), Cl (**5**), Br (**6**)]. Both levels of theory showed that the axial conformation stability, compared to its corresponding equatorial conformation, decreases from compounds **1→3** and **4→6**. Based on the results obtained from the NBO analysis, there are significant *anomeric effects* for compounds **1-6**. The *anomeric effect* associated with the electron delocalization is in favor of the axial conformation and increases from compounds **1→3** and **4→6**. On the other hand, dipole moment differences between the axial and equatorial conformations [$\Delta(\mu_{eq} - \mu_{ax})$] decrease from compounds **1→3**. Although $\Delta(\mu_{eq}-\mu_{ax})$ parameter decreases from compound **1** to compound **3**, the dipole moment values of the axial conformations are smaller than those of their corresponding equatorial conformations. Therefore, the *anomeric effect* associated with the electron delocalizations (for halogen-C-Se segments) and the *electrostatic model* associated with the dipole-dipole interactions fail to account for the increase of the equatorial conformations stability on going from compound **1** to compound **3**. Since there is no dipole moment for the axial and equatorial conformations of compounds **4-6**, consequently, the conformational preferences in compounds **1-6** is in general dictated by the steric hindrance factor associated with the 1,3-syn-axial repulsions. Importantly, the CBS-4 results show that the entropy difference (ΔS) between the equatorial axial conformations increases from compounds **1→3** and **4→6**. This fact can be explained by the *anomeric effect* associated with the electron delocalization which affects the C_2-Se bond orders and increase the rigidity of the corresponding rings. The Gibbs free energy difference values between the axial and equatorial conformations (i.e. ΔG_{ax-ax} and ΔG_{eq-eq}) of compounds **1** and **4**, **2** and **5** and also **3** and **6** have been calculated. The correlations between the *anomeric effect*, *electrostatic model*, ΔG_{eq-ax}, ΔG_{ax-ax}, ΔG_{eq-eq}, bond orders, dipole-dipole interactions, structural parameters and conformational behaviors of compounds **1-6** have been investigated.

Dedicated to the memory of Professor James E. Boggs

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Introduction

Numerous effects have been proposed to rationalize the observed preferred conformation of organic compounds. These have included the anomeric effect, hyperconjugation, dipole-dipole interactions, resonance, steric repulsions, and others. Often several of these are invoked for one compound or series of compounds.

One of the best approaches is a quantitative or semi-quantitative treatment of the pseudo-Jahn-Teller effect involving non-Born-Oppenheimer interactions with excited vibronic

states, which has been shown to be the fundamental cause of molecular asymmetries responsible for the observed structures [1]. This has the advantage of being reliably predictive for experimentally unknown molecules, whereas the other methods are not. However, it is computationally extremely expensive and its use is confined to molecules with a very small number of atoms. It seems to us that there is value in extending and applying the descriptive effects to aid in the chemical understanding of observed structures of somewhat larger molecules, and that is what we do in this paper for two series of dihalo-diselananes.

Heterocycles are of immense importance biologically and industrially [2]. For more than a century, heterocycles have constituted one of the largest areas of research in organic chemistry. Among the approximately 20 million chemical compounds, more than two-thirds are fully or partially aromatic and approximately half are heterocyclic.

The knowledge about conformational properties of heterocyclic compounds is of very general interest since saturated heterocyclic compounds comprise a large segment of organic and inorganic chemistry and are quite widespread in nature, e.g., in alkaloids, carbohydrates, and plant growth regulators, among other compounds. The heterocyclic compounds containing sulfur and nitrogen have maintained the interest of researchers [3]; however, heterocycles with other heteroatoms such as oxygen [4], phosphorus [5], and selenium [6] also are important.

Organoselenium compounds are essential micronutrients whose absence from the diet causes cardiac muscle and skeletal dysfunction. Organoselenium compounds are required for cellular defense against oxidative damage and for the correct functioning of the immune system. They may also play a role in prevention of premature aging and cancer. Selenaheterocyclic compounds have unique redox properties and possess therapeutic potentials against various diseases as antioxidants, enzyme inhibitors, anti-inflammatory and anti-infective agents, and immune modulators [7].

The maximization of an interaction between the best donor lone pair and the best acceptor bond results in the preferred geometry of many molecules [8], therefore, the stereoelectronic interactions are expected to play an important role in the conformational properties of heterocyclic compounds [9, 10]. The most dominant conformation-controlling factor in carbohydrate compounds is known as the *anomeric effect* [10–28]. The *anomeric effect* describes the tendency of polar substituents to prefer the axial orientation in a six-membered saturated ring instead of the less hindered equatorial orientation that would be expected from steric considerations.

Several explanations have been proposed for the validity of the *anomeric effect* [10–28]. The simplest justification is through the repulsive interaction between the ring dipole (generated by the lone pair (LP) of the endocyclic heteroatom)

and the nearly parallel polar bonds in the equatorial conformation, see Scheme 1).

An alternative explanation is the hyperconjugation interaction between the lone pair (LP) of the endocyclic heteroatom in a six membered heterocycle and the antibonding orbital (σ^*) for the exocyclic C-X bond in the axial position (see Scheme 2).

There is a stereoelectronic preference for conformations in which the best donor lone pair is antiperiplanar to the best acceptor bond. Praly and Lemieux have stressed that the *anomeric effect* (AE) associated with the electron delocalization in six membered saturated heterocyclic compounds must be considered as the difference between the sum of the *endo-anomeric effect* (AE) and *exo-anomeric effect* (AE) in the equatorial conformer and the same sum for the axial conformer [27]:

$$anomeric\ effect\ =\ \sum\left(endo{-}AE_{\mathrm{eq}} + exo{-}AE_{\mathrm{eq}}\right) \quad (1)$$

$$-\sum\left(endo{-}AE_{\mathrm{ax}} + exo{-}AE_{\mathrm{ax}}\right).$$

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 [28]. The results showed that the conflict between the increase of anomeric effect and the decrease of difference between the dipole moments of the equatorial and axial conformations, $\Delta(\mu_{\mathrm{eq}} - \mu_{\mathrm{ax}})$, explains the variation of the calculated $\Delta G_{\mathrm{eq\text{-}ax}}$ for *trans*-2,3-dihalo-1,4-dithiane [28]. In the present work, we investigate the impacts of the *anomeric effect*, dipole-dipole interactions, and steric repulsions on the conformational preferences in *trans*-2,3-dihalo-1,4-diselenane [halo = F (**1**), Cl (**2**), Br (**3**)] and *trans*-2,5-dihalo-1,4-diselenane [halo = F (**4**), Cl (**5**), Br (**6**)] by means of the complete basis set composite method CBS-4, hybrid-DFT based methods, and natural bond orbital (NBO) interpretations (see Scheme 3) [29–35]. Because of the differences between the halogen-C-S and halogen-C-Se segments, we expected that different results would be obtained for Se-containing heterocyles. This expectation is confirmed by the results of this work.

Computational details

Hybrid DFT calculations were carried out using the B3LYP method with the 6-311+G** basis set with the PC GAMESS
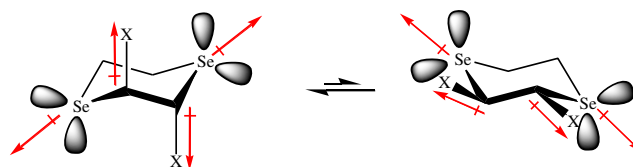
Scheme 1 Schematic representation of dipole-dipole interactions

Scheme 2 Schematic representation of the *endo-* and *exo-anomeric effects* in terms of the negative hyperconjugation effect (as a no bond-double bond model)

endo-anomeric effects

exo-anomeric effects
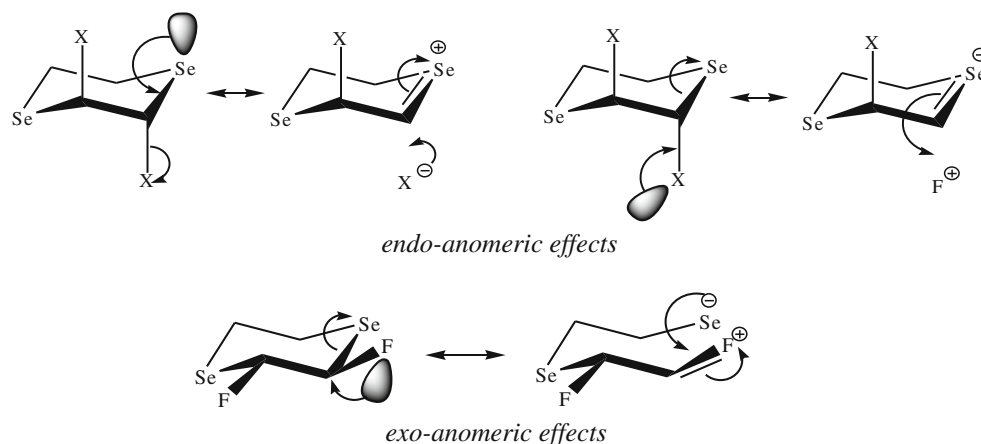
(US) package of programs [29] for optimizing the initial estimated structural geometries of the axial and equatorial conformations of compounds **1-6**. Also, composite complete basis set (CBS) calculations were carried out using the CBS-4 levels of theory with the GAUSSIAN 98 package of programs to optimize the structures of above compounds [30, 36–42].

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 [36–42]. CBS-4 is a six-step method. The CBS-4 model chemistry employs the very fast UHF/3-21G* method for geometry optimization and zero point energies. This model chemistry is followed by UHF (to calculate the SCF energies), CBS2 (to extrapolate the complete basis set second-order limit using the N-1 asymptotic convergence of N-configuration pair natural orbital expansions), MP4(SDQ) (to include the effect of adding polarization functions), and empirical corrections (a size-consistent empirical correction and spin contamination correction) [42].

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

4: X=F, **5**: X=Cl, **6**: X=Br
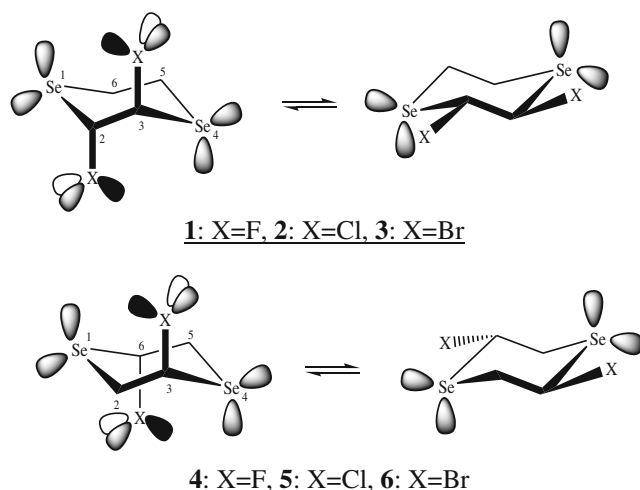
Scheme 3 Schematic representation of the axial and equatorial conformations of compounds **1-6**

The NBO analyses were performed for the axial and equatorial conformations **1-6** by the NBO 5.G program contained in the PC-GAMESS interface [35]. Accordingly, the magnitude of the donor-acceptor hyperconjugative interactions in compounds **1-6** can be quantitatively estimated. In the NBO analysis the electronic wavefunctions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization effects (or donor–acceptor charge transfers) can be estimated from the off-diagonal elements of the Fock matrix in the NBO basis. The NBO program searches for an optimal natural Lewis structure, which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula. Therefore, the new orbitals are more stable than pure Lewis orbitals, stabilizing the wave function and giving a set of molecular orbitals equivalent to canonical molecular orbitals.

The stabilization energies associated with *endo-* and *exo-anomeric effects*, bonding, nonbonding, and antibonding orbital occupancies and energies in the axial and equatorial conformations of compounds **1-6** were calculated using NBO analysis. The stabilization energies associated with the donor-acceptor electron delocalizations are proportional to $S^2/\Delta E$ where S is the orbital overlap and ΔE is the energy difference between the donor and acceptor orbitals [8, 9]. The stabilization energy (E_2) associated with $i \rightarrow j$ delocalization, is explicitly estimated by the following equation:

$$E_2 = q_i \frac{F^2(i,j)}{\varepsilon_j - \varepsilon_i},$$

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

The stabilization energies (E_2) associated with $LP_{ax}Se_1 \rightarrow \sigma^*_{C2-X}$, $LP_{eq}Se_1 \rightarrow \sigma^*_{C2-X}$ (*endo- anomeric effect*), $LP_1X \rightarrow$

$\sigma^*_{C2\text{-}Se1}$, $LP_2X \rightarrow \sigma^*_{C2\text{-}Se1}$ and $LP_3X \rightarrow \sigma^*_{C2\text{-}Se1}$ (*exo-anomeric effect*) electron delocalizations and their influences on the conformational properties of compounds **1-6** were investigated quantitatively by the NBO analysis [35]. It should be noted that the NBO analysis is a sufficient approach to investigate the effect of stereoelectronic interactions on the reactivity and dynamic behaviors of chemical compounds [43].

Results and discussion

Conformation preference

The resulted Gibbs free energy, enthalpy, and entropy differences (i.e., ΔG, ΔH, and ΔS) for the axial and equatorial conformations of compounds **1-6** from the CBS-4 and B3LYP/6-311+G** levels of theory are given in Table 1. Both methods show that the axial conformations of compounds **1** and **4** are more stable than their corresponding equatorial conformations and the axial conformation stability, compared to the corresponding equatorial conformation, decreases from compounds **1→3** and **4→6**.

The CBS-4 method shows that the Gibbs free energy differences for compounds **1-3** and **4-6** come from the corresponding enthalpic term. Based on the results obtained at the CBS-4 level, the entropies of the equatorial conformations are greater than those of their axial conformations. Also, this level of theory shows that the entropy difference (ΔS) between the equatorial axial conformations increases from compounds **1→3** and **4→6**. Interestingly, this fact can be explained by the *anomeric effect* associated with the electron delocalization.

Table 1 CBS-4 and B3LYP/6-311+G** calculated thermodynamic parameters [ΔH, ΔG (in kcal mol^{-1}) and ΔS (in cal mol^{-1} K^{-1})], for the axial and equatorial conformations of compounds **1-6**

Geometries	CBS-4			B3LYP/6-311+G**		
	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a
1-Eq	1.21	0.000	1.57	1.92	0.777	1.68
1-Ax	0.00	1.195	0.00	0.00	0.000	0.00
2-Eq	0.00	0.789	0.00	0.00	0.000	0.02
2-Ax	0.50	0.000	0.74	0.24	0.876	0.00
3-Eq	0.00	0.890	0.00	0.00	1.743	0.00
3-Ax	1.98	0.000	2.24	0.41	0.000	0.93
4-Eq	0.33	0.000	0.91	1.35	0.000	1.46
4-Ax	0.00	1.947	0.00	0.00	0.356	0.00
5-Eq	0.00	1.004	0.00	0.00	0.850	0.00
5-Ax	1.47	0.000	1.76	1.72	0.000	1.97
6-Eq	0.00	1.318	0.00	0.00	0.716	0.00
6-Ax	2.86	0.000	3.25	2.81	0.000	3.03

^{a} Relative to the most stable forms

Our results demonstrate that the greater C_2-Se bond orders in the axial conformations of compounds **1-6**, compared to their corresponding equatorial conformations increases the rigidity of the corresponding rings (see Scheme 4). Consequently, the entropies of the axial conformations decrease from compounds **1→3** and **4→6** increase in the equatorial conformations.

Both levels of theory show that the axial and conformations of compounds **4-6** are more stable than their corresponding conformations in compounds **1-3** (see Table 2). This fact may be attributed to the dipole moments of the axial and equatorial conformations of compounds **1-3**.

Stabilization energies

The stabilization energies associated with the electron delocalizations contribute to the energy differences between the axial and equatorial conformations of compounds **1-6**, and in the NBO scheme they arise from nonbonding-antibond and bond-antibond charge transfers. The NBO analysis was performed on lone pair-antibond and bond–antibond interactions for the axial and equatorial conformations of compounds **1-6**. These delocalization energies are decomposed with various lone pair-antibond and bond-antibond interaction energies as shown in Table 3. Since the $LP_{ax}Se$ and $LP_{eq}Se$ nonbonding and C_2–X antibonding orbitals are the electron abundant and the electron-deficient components, the $LP_{ax}Se \rightarrow \sigma^*_{C2\text{-}X}$, $LP_{ax}Se \rightarrow \sigma^*_{C2\text{-}X}$ and $\sigma_{C2\text{-}X} \rightarrow \sigma^*_{C3\text{-}X}$ electron transfers are favorable filled-empty interactions such as the donor–acceptor interaction and are the dominant term in determining delocalization energy (see Scheme 2).

Based on the optimized ground state geometries obtained from the B3LYP/6-311+G** method, the NBO analysis of donor-acceptor interactions showed that the stabilization energies associated with $LP_{ax}Se_1 \rightarrow \sigma^*_{C2\text{-}X}$ delocalizations (*endo-anomeric effect*) for the axial conformations decrease from compound **1** to compound **2** but increases from compound **2** to compound **3** (see Table 3). This trend is also observed for the axial conformations of compounds **4-6**.

In addition, the stabilization energy associated with the $LP_{eq}Se_1 \rightarrow \sigma^*_{C2\text{-}X}$ electronic delocalization (*endo-anomeric effect*) for the equatorial conformations of compounds **1** and **4** are 1.30 and 1.10 kcal mol^{-1}, respectively, while this kind of
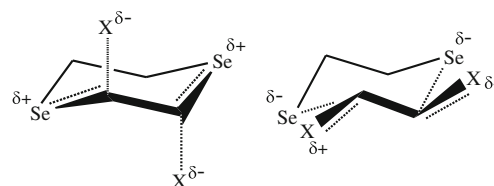
Scheme 4 Schematic representation of the variation of the bond orders in the axial and equatorial conformations of compounds **1-6**

Table 2 CBS-4 and B3LYP/6-311+G** calculated thermodynamic parameters [ΔH, ΔG (in kcal mol^{-1}) and ΔS (in cal mol^{-1} K^{-1})], for the axial and equatorial conformations of compounds **1-6**

Geometries	B3LYP/6-311+G**			CBS-4		
	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a
1-Ax	1.11	0.000	1.73	1.29	0.000	2.01
4-Ax	0.00	2.052	0.00	0.00	2.404	0.00
2-Ax	0.54	0.000	0.97	1.10	0.231	1.03
5-Ax	0.00	1.442	0.00	0.00	0.000	0.00
3-Ax	0.61	0.000	1.00	0.77	0.000	1.20
6-Ax	0.00	1.315	0.00	0.00	1.442	0.00
1-Eq	2.00	0.000	2.39	1.85	0.000	2.23
4-Eq	0.00	1.301	0.00	0.00	1.271	0.00
2-Eq	1.51	0.000	2.00	2.57	0.000	3.02
5-Eq	0.00	1.656	0.00	0.00	1.495	0.00
3-Eq	1.49	0.000	2.01	3.17	0.000	3.30
6-Eq	0.00	1.743	0.00	0.00	0.415	0.00

^{a} Relative to the most stable forms

electronic delocalization does not exist for the equatorial conformations of compounds **2**, **3**, **5**, and **6**. The NBO results show that the stabilization energies associated with LP$_3$ X→ σ*$_{C2-Se1}$ (*exo-anomeric effect*) in the axial conformations decrease from compounds **1**→**3** and **4**→**6** (see Table 3).

Based on Eq. 1, the *anomeric effect* associated with LP$_{ax}$Se$_1$→σ*$_{C2-X}$, LP$_{eq}$Se$_1$→σ*$_{C2-X}$ (*endo-anomeric effect*), LP$_1$X→σ*$_{C2-S1}$, LP$_2$X→σ*$_{C2-S1}$, LP$_3$X→σ*$_{C2-S1}$ (*exo-anomeric effect*) and σ$_{C2-X}$→σ*$_{C3-X}$ electron delocalization for compounds **1-3** increases from compounds **1**→**3** and **4**→**6** (see Table 3 and Scheme 5). Based on the calculated Gibbs free energy differences between the axial and equatorial conformations of compounds **1-3** and **4-6**, the axial conformation stability compared to the corresponding equatorial conformation decreases from compounds **1**→**3** and **4**→**6** (see Table 1). The rationalization of the conformational preference solely in terms of the *anomeric effect* fails to account for compounds **1-6**. Obviously, other factors (steric effect and dipole-dipole interactions) have determinant impacts on the conformational preferences in compounds **1-6**.

Orbital occupancies

The orbital occupancies of the most effective electron delocalization which has the most impact on the *anomeric effects* of the axial conformations of compounds **1-6** (i.e., LP$_{ax}$Se$_1$→ σ*$_{C2-X}$ and LP$_3$X→σ*$_{C2-Se1}$) have been investigated. The NBO results showed that the LP$_{ax}$Se$_1$ non-bonding orbital occupancies in the axial conformations increase from compound **1** to compound **2** but decrease from compound **2** to

compound **3**. This trend is also observed for compounds **4-6** (see Table 3). This fact can be explained by the variation of the LP$_{ax}$Se$_1$→σ*$_{C2-X}$ electron delocalizations in these compounds.

Interestingly, the σ*$_{C2-X}$ antibonding orbital occupancies increase from compounds **1**→**3** and **4**→**6** (see Table 3). The increase of the *endo-anomeric effect* from compounds **1**→**3** and **4**→**6** can explain this observation.

The LP$_3$X nonbonding orbital occupancies increase from the axial conformations of compounds **1**→**3** and **4**→**6** which result from the decrease of the electron transfer from the LP$_3$X nonbonding orbitals to the σ*$_{C2-X}$ antibonding orbitals of compounds **1**→**3** and **4**→**6**.

Orbital energies and off-diagonal elements

It should be noted that the stabilization energies associated with electron delocalization are proportional to $F_{ij}^2/\Delta E_{ij}$ where F_{ij} is the orbital overlap integral (or off-diagonal elements of the secular determinant) and ΔE_{ij} is the energy difference between the donor bonding (or nonbonding) and σ* (or π*) antibonding orbitals. 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. Also, the stabilization (resonance) energy associated with the electron delocalization may increase as the acceptor orbital energy decreases and the donor orbital energy increases [8–28].

The energy differences between donor (E LP$_{ax}$Se$_1$) and acceptor (E σ*$_{C2-X}$) orbitals [i.e., $\Delta(E$ σ*$_{C2-X}$ - E LP$_{ax}$Se$_1$)] for the axial conformations decrease from compounds **1**→**3** and **4**→**6**. The strong acceptor antibonding orbital of the axial conformation of compound **3** (E σ*$_{C2-X}$: 0.00451 a.u.), compared to those in compounds **2** and **1** (0.06080 and 0.18781 a.u., respectively) gives rise to strong LP$_{ax}$Se$_1$→ σ*$_{C2-X}$ electron delocalization. On the other hand, the decrease of the *orbital overlap integral* (S) [i.e., off-diagonal elements (F_{ij})] values could reduce the LP$_{ax}$Se$_1$→σ*$_{C2-X}$ electron delocalization (see Table 3). The decrease of F_{ij} values could be justified by the increase of the X atom radius from compound **1** to compound **3**. Consequently, it seems that in the axial conformations of compounds **1-3**, F_{ij} affect and control the order of the stabilization energies associated with LP$_{ax}$Se$_1$→σ*$_{C2-X}$ electron delocalizations. This conclusion can be generalized for compounds **4-6**.

Dipole moments

In the gas phase, it is generally found that the conformation with the larger electrostatic energy (i.e., the larger dipole moment) has an increased overall energy [44].
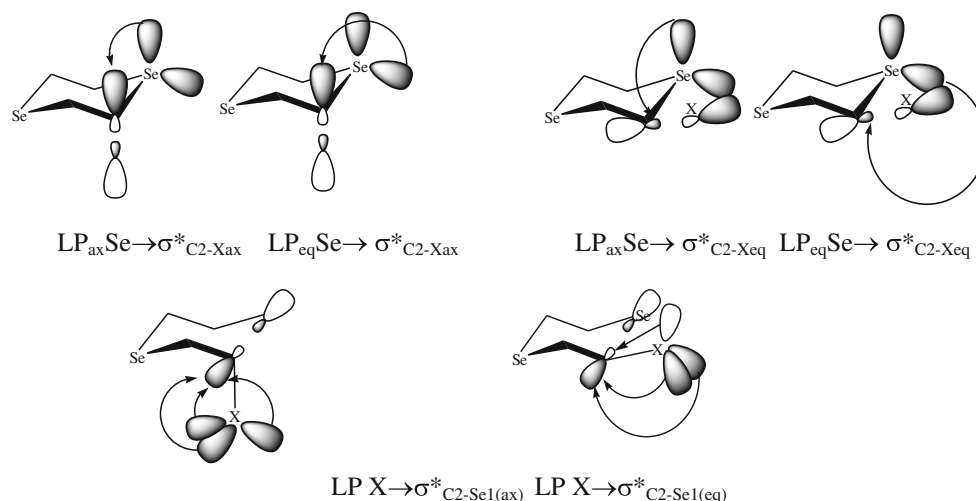
Based on the results of the extended block-localized wavefunction (*BLW*) method, it has been noted that

Table 3 NBO calculated stabilization energies (E_2, in kcal mol^{-1}), off-diagonal elements (F_{ij}, in a.u.), orbital energies (in a.u.) and orbital occupancies (e), bond orders (Wiberg Bond Index, *WBI*) and dipole moments (μ, in debye), based on the calculated geometries using B3LYP/6-311+G** level of theory, for the axial and equatorial conformations of compounds **1-6**

E_2	1 Eq	1 Ax	2 Eq	2 Ax	3 Eq	3 Ax	4 Eq	4 Ax	5 Eq	5 Ax	6 Eq	6 Ax
(LP$_{eq}$Se$_1$→σ*$_{C2-X}$)×2: *endo-AE*	1.30	–	–	2.22	–	2.88	1.10	–	–	2.32	–	3.02
(LP$_{ax}$Se$_1$→σ*$_{C2-X}$)×2: *endo-AE*	2.52	19.04	2.96	17.72	3.36	21.44	2.70	18.28	3.02	17.88	3.46	21.28
(LP$_1$X→σ*$_{C2-Se1}$)×2: *endo-AE*	–	–	1.16	1.40	1.12	1.44	–	–	1.10	1.24	1.10	1.32
(LP$_2$X→σ*$_{C2-Se1}$)×2: *exo-AE*	1.50	–	1.18	2.86	1.28	4.60	1.94	–	1.68	–	1.36	–
(LP$_3$X→σ*$_{C2-Se1}$)×2: *exo-AE*	15.76	18.98	7.58	10.10	4.60	4.48	16.50	19.36	8.96	13.22	5.58	9.72
(σ$_{C1-X}$→σ*$_{C2-X}$)×2	–	3.34	–	7.04	–	9.68	–	–	–	–	–	–
endo-AE+ *exo-AE*	21.08	41.36	12.88	41.34	10.36	44.52	22.24	37.64	14.76	34.66	11.5	35.34
anomeric effect	−20.28		−28.46		−34.16		−15.4		−19.9		−23.84	
anomeric effect^X/ *anomeric effect*^{F}	1		1.40		1.68		1		1.29		1.55	
Orbital occupancy												
LP$_2$Se$_1$	**1.94450**	**1.90896**	**1.93614**	**1.90969**	**1.93141**	**1.89710**	**1.94563**	**1.91748**	**1.93743**	**1.91847**	**1.93226**	**1.89909**
LP$_3$X	**1.95642**	**1.95666**	**1.95722**	**1.96034**	**1.96114**	**1.96583**	**1.95795**	**1.95593**	**1.95980**	**1.96210**	**1.96473**	**1.97014**
σ*$_{C2-X}$	0.04576	0.06634	0.05035	0.07755	0.06018	0.10153	0.04680	0.06783	0.05088	0.07550	0.06034	0.09245
σ*$_{C2-Se1}$	0.04705	0.05557	0.04681	0.05226	0.04391	0.04638	0.01937	0.02787	0.03489	0.02671	0.04224	0.02598
Orbital energy												
E LP$_2$Se$_4$	−0.24974	−0.24049	−0.25097	−0.24643	−0.25138	−0.25169	−0.24934	−0.24005	−0.25241	−0.24843	−0.25329	−0.25478
E LP$_3$X	−0.42705	−0.43407	−0.32850	−0.33051	−0.30328	−0.29981	−0.43158	−0.43243	−0.33495	−0.34342	−0.30911	−0.32491
E σ*$_{C2-X}$	0.18674	0.18781	0.06797	0.06080	0.01555	0.00451	0.18286	0.19161	0.06490	0.06677	0.01176	0.01383
E σ*$_{C2-Se1}$	0.05329	0.07229	0.04786	0.06527	0.04982	0.06922	0.07405	0.07545	0.06771	0.07381	0.06577	0.07337
Δ(E σ*$_{C2-X}$ - E LP$_2$Se$_1$)	0.43648	0.4283	0.31894	0.30723	0.26693	0.2562	0.4322	0.43166	0.31731	0.3152	0.26505	0.26861
Δ(E σ*$_{C2- Se1}$ - E LP$_3$X)	0.61379	0.62188	0.39647	0.39131	0.31883	0.30432	0.61444	0.62404	0.39985	0.41019	0.32087	0.33874
F_{ij}												
LP$_2$Se$_1$→σ*$_{C1-X}$	0.021	0.057	–	0.047	–	0.047	–	0.056	–	0.048	–	0.048
LP$_3$X$_{C2}$→σ*$_{C1-Se4}$	0.055	0.062	0.034	0.040	0.025	0.026	0.057	0.063	0.037	0.047	0.029	0.039
(σ$_{C1-X}$→σ*$_{C2-X}$)×2	–	0.040	–	0.046	–	0.049	–	–	–	–	–	–
Dipole moment												
μ(Debye)	3.9404	1.5259	3.6855	1.8604	3.4651	2.1122	0.0	0.0	0.0	0.0	0.0	0.0
Δ(μ_{eq} - μ_{ax})	2.4145		1.8251		1.3529		0.0		0.0		0.0	
Bond order (Wiberg Bond Index)												
C$_2$-Se$_1$	0.9423	1.0105	0.9257	0.9840	0.9279	0.9992	0.9502	1.0017	0.9469	0.9834	0.9577	0.9976
C$_2$-X	0.8349	0.8248	0.9881	0.9659	0.9631	0.9246	0.8274	0.8258	0.9826	0.9762	0.9594	0.9483
Δ(WBI $_{ax-eq}$), C$_2$-Se$_1$	0.0682		0.0583		0.0713		0.0515		0.0365		0.0399	
Δ(WBI $_{eq-ax}$), C$_2$-X	0.0101		0.0222		0.0385		0.0016		0.0064		0.0111	

Bold numbers show the variation of the electron occupancy with the variation of the corresponding electron delocalization

Scheme 5 Schematic representation of the electron delocalization between non-bonding and anti-bonding orbitals in compounds **1-6**

$LP_{ax}Se \rightarrow \sigma^*_{C2-Xax}$ $LP_{eq}Se \rightarrow \sigma^*_{C2-Xax}$ $LP_{ax}Se \rightarrow \sigma^*_{C2-Xeq}$ $LP_{eq}Se \rightarrow \sigma^*_{C2-Xeq}$

$LP\ X \rightarrow \sigma^*_{C2-Se1(ax)}$ $LP\ X \rightarrow \sigma^*_{C2-Se1(eq)}$

hyperconjugative interactions are not responsible for the *anomeric effect* and the *anomeric effect* is better interpreted in terms of electrostatic interactions [45]. The total dipole moment changes, are one of the reasonable descriptors of the total energy differences, however, the correlations between them are not strong enough. It seems using any of the electron delocalization and electrostatic interactions alone is not adequately convincing to explain the general validity of the *anomeric effect* [46, 47].

In this work, we have examined the contribution of the electrostatic interactions (by the calculation of the total dipole moment values) [45–47] to the total energy differences between the axial and equatorial conformations of compounds **1-3**. The calculated dipole moments for the axial and equatorial conformations of compounds **1-3** are given in Table 3. Based on the results obtained, the calculated dipole moments of the axial conformations are fewer than those in their equatorial conformations. The dipole moment values decrease from the equatorial conformations of compound **1** to compound **3** but increase for their corresponding axial conformations.

Using the dipole moments a "Δ" parameter was defined as $\Delta\mu_{eq-ax}$. $\Delta\mu_{eq-ax}$ values decrease from compounds **1→3**. Therefore, the variations of the calculated $\Delta\mu_{eq-ax}$ values are in the same trend observed for the corresponding ΔG_{ax-eq} values (i.e., the total energy differences). Since the calculated dipole moment values of the axial conformations of compounds **1-3** are smaller than those of their equatorial conformations, the *electrostatic model* associated with the dipole-dipole interactions explains the increase of the equatorial conformation stability compared to the corresponding axial conformations ongoing from compound **1** to compound **3**. Although $\Delta\mu_{eq-ax}$ value decreases from compound **1** to compound **3**, the dipole moment values of the axial conformations are smaller than those of their corresponding equatorial conformations. Consequently, the *electrostatic model* plays a role

on the decrease of the axial conformation stability compared to its equatorial conformation but has no determinant impact here. Since the *anomeric effect* associated with the electron delocalization fails to account for the decrease of the axial conformation stability compared to its equatorial conformation ongoing from compound **1** to compound **3**, it seems that steric repulsions could be a reasonable descriptor of the total energy differences between the axial and equatorial conformations of compounds **1-3**.

Bond orders

The *endo-anomeric effect* associated with the $LP_{ax}Se_1 \rightarrow \sigma^*_{C2-X}$ and $LP_{eq}Se_1 \rightarrow \sigma^*_{C2-X}$ electron delocalizations can affect the bond orders [e.g., Wiberg Bond Index, *WBI*: the sum of squares of off-diagonal density matrix elements between atoms, as formulated in terms of the natural atomic orbital (NAO) basis set] of C_2-X bonds. The differences between the *WBI* of C_2-X bonds in the axial and equatorial conformations [i.e., $\Delta(WBI(C_2-X)_{ax-eq}]$ increase from compounds **1→3**, and also from compounds **4→6** (see Table 3). The variations of the calculated $\Delta(WBI(C_2-X)_{ax-eq}$ parameter are in accordance with the increase of the *endo-anomeric effect* from compounds **1→3** and also from compounds **4→6** (see Table 3).

Also, the increase of the *endo-anomeric effect* associated with the $LP_{ax}Se_1 \rightarrow \sigma^*_{C2-X}$ and $LP_{eq}Se_1 \rightarrow \sigma^*_{C2-X}$ electron delocalizations justifies the increase of the differences between the *WBI* of C_2-Se$_1$ bonds in the equatorial and axial conformations [i.e., $\Delta(WBI(C_2-Se_1)_{ew-ax}]$ of compounds **1-3** and **4-6** (see Table 3).

Structural parameters

Representative structural parameters for the axial and equatorial conformations of compounds **1-6**, as calculated at the

Table 4 B3LYP/6-311+G** calculated structural parameters for the equatorial and axial conformations of compounds **1-6**

| State	1 Eq	1 Ax	2 Eq	2 Ax	3 Eq	3 Ax	4 Eq	4 Ax	5 Eq	5 Ax	6 Eq	6 Ax
Bond lengths (Å)												
r_{1-2}	1.995	1.963	1.995	1.966	1.992	1.958	1.997	1.971	1.989	1.969	1.983	1.962
r_{2-3}	1.510	1.529	1.515	1.533	1.510	1.527	1.511	1.515	1.512	1.520	1.509	1.520
r_{3-4}	1.995	1.963	1.995	1.966	1.992	1.958	1.979	1.981	1.985	1.977	1.991	1.976
r_{4-5}	1.980	1.982	1.980	1.979	1.982	1.977	1.997	1.971	1.989	1.969	1.983	1.962
r_{5-6}	1.518	1.517	1.517	1.518	1.517	1.519	1.511	1.515	1.512	1.520	1.509	1.520
r_{6-1}	1.980	1.982	1.980	1.979	1.982	1.977	1.979	1.981	1.985	1.977	1.991	1.976
r_{2-X}	1.392	1.393	1.817	1.828	1.989	2.012	1.398	1.395	1.822	1.826	1.993	2.002
$\Delta[r_{2-X}(Ax)- r_{2-X}(Eq)]$	0.001		0.011		0.023		-0.003		0.004		0.009	
Bond angles (°)												
θ_{1-2-3}	112.7	117.0	112.6	116.8	112.5	117.5	113.9	114.8	113.7	113.8	114.0	114.1
θ_{2-3-4}	112.7	117.0	112.6	116.8	112.5	117.5	112.5	116.3	112.4	117.0	112.0	117.2
θ_{3-4-5}	98.9	99.0	99.7	99.0	99.8	99.3	97.6	98.9	98.1	98.8	98.1	99.0
θ_{4-5-6}	113.3	113.7	113.0	113.6	113.0	113.6	113.9	114.8	113.7	113.8	114.0	114.1
θ_{5-6-1}	113.3	113.7	113.0	113.6	113.0	113.6	112.5	116.3	112.4	117.0	112.0	117.2
θ_{6-1-2}	98.9	99.0	99.7	99.0	99.8	99.3	97.6	98.9	98.1	98.8	98.1	99.0
θ_{x-2-1}	104.1	111.8	103.9	113.3	103.2	113.5	104.4	111.5	105.8	113.8	105.6	114.3
$\Delta[\theta_{x-2-1}(Ax)-\theta_{x-2-1}(Eq)]$	7.7		9.4		10.3		7.1		8.0		8.7	
Torsion angles (°)												
$\phi_{1-2-3-4}$	−69.1	−60.2	−68.1	−60.0	−68.5	−58.4	−70.1	−65.2	−69.7	−65.6	−69.7	−64.0
$\phi_{2-3-4-5}$	60.6	53.4	60.3	53.5	60.6	52.2	60.1	65.5	60.2	57.5	60.0	56.9
$\phi_{3-4-5-6}$	−59.9	−58.8	−59.0	−59.2	−59.8	−58.7	−61.2	−55.4	−61.1	−55.2	−61.5	−54.7
$\phi_{4-5-6-1}$	68.3	70.2	67.9	70.8	67.5	70.4	70.1	65.2	69.7	65.6	69.7	65.0
$\phi_{5-6-1-2}$	−59.9	−58.8	−59.0	−59.2	−59.8	−58.7	−60.1	−65.5	−60.2	−57.5	−59.0	−56.9
$\phi_{6-1-2-3}$	60.6	53.4	60.3	53.5	60.6	52.2	61.2	55.4	61.1	55.2	61.5	54.7
$\phi_{x-c-c-x}$	60.6	−166.9	59.5	−161.0	59.9	−158.3	–	–	–	–	–	–
$\phi_{x-2-1-6}$	−178.7	−71.2	−178.0	−73.8	−178.3	−75.2	−179.9	−70.5	−178.4	−73.9	−178.0	−74.9
$\Delta[\phi_{x-2-1-6}(Eq)- \phi_{x-2-1-6}(Ax)]$	−107.5		−104.2		−103.1		−109.4		−104.5		−103.1	

B3LYP/6-311+G** level of theory, are shown in Table 4. Although it is not expected, in principle, to obtain values exactly the same as the experimental ones because of the differences in definition of bond length values, it is possible to carry out theoretical calculations, from which many properties and structures can be obtained with an accuracy that is competitive with experiments. From a comparison of the calculated corresponding structural parameters, it follows that the molecular symmetry of compounds **1-3** is C_2 (a twofold axis running through the midpoints of the C_2-C_3 and the C_5-C_6 bonds). The molecular symmetry of compounds **4-6** is C_i (see Table 4).

Importantly, B3LYP/6-311+G** results showed that the σ_{Se1-C2} and σ_{Se4-C3} bond lengths are significantly contracted compared to those in their equatorial conformations. The *endo-anomeric effect* associated with the $LP_{ax}Se_1 \rightarrow \sigma^*_{C2-X}$

and $LP_{eq}Se_1 \rightarrow \sigma^*_{C2-X}$ electron delocalizations justifies the shorter σ_{Se1-C2} and σ_{Se4-C3} bond lengths in the axial conformations of compounds **1-6**, compared to those in their equatorial conformations (see Table 4).

The B3LYP/6-311+G** results showed that the σ_{Se1-C2} bond length in the equatorial conformations of compounds **1-6** are longer compared to those in their axial conformations. This fact can be explained by the *exo-anomeric effect* associated with the $LP_1X \rightarrow \sigma^*_{C2-Se1}$, $LP_2X \rightarrow \sigma^*_{C2-Se1}$ and $LP_3X \rightarrow \sigma^*_{C2-Se1}$ electron delocalizations.

Using the structural parameters obtained, a "Δ" parameter was defined as $\Delta[r_{2-X}(ax)- r_{2-X}(eq)]$. There is a direct correlation between the *anomeric effect* and $\Delta[r_{2-X}(ax)- r_{2-X}(eq)]$ (see Tables 3, 4). Based on the results obtained, with the increase of the $\Delta[r_{2-X}(ax)- r_{2-X}(eq)]$ parameters from compounds **1→3** and compounds **4→6**, the corresponding *anomeric effect*
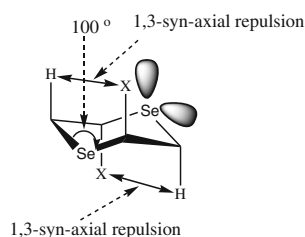
Scheme 6 Schematic representation of the 1,3-syn-axial repulsions in the axial confirmation of compounds **1-6**

values increase. Consequently, the calculated $\Delta[r_{2\text{-}X}(ax)\text{-}r_{2\text{-}X}(eq)]$ parameters could be proposed as a criterion for the evaluation of the *anomeric effect* in compounds **1-6**.

Also, the $\theta_{x\text{-}2\text{-}1}$ bond angles increase from the axial conformations of compounds **1→3** and compounds **4→6**. Using the $\theta_{x\text{-}2\text{-}1}$ bond angles, another "Δ" parameter was defined as $\Delta[\theta_{x\text{-}2\text{-}1}(ax)\text{-}\theta_{x\text{-}2\text{-}1}(eq)]$. Based on the results obtained, $\Delta[\theta_{x\text{-}2\text{-}1}(Ax)\text{-}\theta_{x\text{-}2\text{-}1}(Eq)]$ values increase from compounds **1→3** and compounds **4→6**. This fact can be reasonably justified by the increase of the *endo-anomeric effect* associated with $LP_{ax}Se_1 \rightarrow \sigma^*_{C2\text{-}X}$ and $LP_{eq}Se_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalizations from compounds **1→3** and compounds **4→6** by increasing the corresponding $\Delta(WBI(C_2\text{-}Se_1)_{eq\text{-}ax}$ parameters.

In addition, the $\phi_{x\text{-}2\text{-}1\text{-}6}$ values increase from the axial conformations of compound **1** to compound **3** and from compound **4** to compound **6**. The increase of the *exo-* and *endo-anomeric* effects cannot justify the decrease of the $\Delta[\phi_{x\text{-}2\text{-}1\text{-}6}(eq)\text{-}\phi_{x\text{-}2\text{-}1\text{-}6}(ex)]$ parameters; therefore, it seems another factor may have significant impact and play the more important role here.

Because of the smaller $\theta_{2\text{-}1\text{-}6}$ bond angle ($\sim100°$), compared to the normal bond angle around the sp^3 hybridized center ($\sim110°$), one may expect that the 1,3-syn-axial repulsion can be increased on going from the axial conformations of compounds **1→3** (see Scheme 6). Accordingly, based on the results obtained, the Gibbs free energy differences between the axial and equatorial conformations (i.e., $\Delta G_{eq\text{-}ax}$) in general are dictated by the steric hindrance factor associated with the 1,3-syn-axial repulsions.

Conclusions

The CBS-4, B3LYP/6-311+G** calculations reported above and NBO interpretations provided a reasonable picture from energetic, structural, bonding, and stereoelectronic points of view for the conformational preferences in *trans*-2,3-dihalo-1,4-diselenane (**1-3**) and *trans*-2,5-dihalo-1,4-diselenane (**4-6**). Effectively, the CBS-4 and B3LYP/6-311+G** results showed that the equatorial conformation stability

compared to its corresponding axial conformation, increases from compounds **1→3** and **4→6**. $\Delta G_{ax\text{-}ax}$ values between the axial and equatorial conformations increase from compounds **1→3** and **4→6**. In addition, NBO results revealed that

– the *anomeric effect* (i.e., *endo-anomeric effect + exo-anomeric effect*) increases from compounds **1→3** and **4→6**,

– the rich acceptor antibonding orbitals of compound **3** and compound **6**, compared to those in compounds **1** and **2** and compounds **4** and **5** gives rise to a strong *endo-anomeric effect*,

– the *anomeric effect* and the *electrostatic model* associated with the dipole-dipole interactions fails to account quantitatively for the conformation preferences in compounds **1-6**; therefore, in general it is dictated by the steric hindrance factor associated with the 1,3-syn-axial repulsions,

– F_{ij} off-diagonal elements of secular determinants could affect and control the order of the stabilization energies associated with $LP_{ax}Se_1 \rightarrow \sigma^*_{C2\text{-}X}$ electron delocalizations in compounds **1-6**. Importantly, there is a conflict between the F_{ij} and $\Delta E_{acceptor\text{-}donor}$ and donor orbital occupancy for the exo-*anomeric effect* in the axial conformations of compounds **1-3** and compounds **4-6**,

– the increase of the *endo-anomeric effect* from compound **1** to compound **3** and compound **4** to compound **6** is in accordance with the variation of the calculated $\Delta(WBI_{eq\text{-}ax})$ values for $C_2\text{-}X$ bonds.

It should be noted that the anomeric effect and electrostatic model cannot justify the Gibbs free energy differences between the axial and equatorial conformations (i.e., $\Delta G_{eq\text{-}ax}$). Therefore, $\Delta G_{eq\text{-}ax}$ values for compounds 1-6 are dictated by the steric hindrance factor associated with the 1,3-syn-axial repulsions.

Effectively, with the increase of the *anomeric effect*, the $\Delta[r_{2\text{-}X}(ax)\text{-}r_{2\text{-}X}(eq)]$ and $\Delta[\theta_{x\text{-}2\text{-}1}(Ax)\text{-}\theta_{x\text{-}2\text{-}1}(Eq)]$ parameters increase from compounds **1→3** and compounds **4→6**. It should be noted that the increase of the exo- and endo-anomeric effects can not justify the decrease of the $\Delta[\phi_{x\text{-}2\text{-}1\text{-}6}(eq)\text{-}\phi_{x\text{-}2\text{-}1\text{-}6}(ex)]$ parameters. Accordingly, the decrease is caused by the steric hindrance factor associated with the 1,3-syn-axial repulsions.

Importantly, the CBS-4 results show that the entropies of the equatorial conformations are greater than those of their axial conformations and the entropy difference (ΔS) between the equatorial axial conformations increases from compounds **1→3** and **4→6**. The *anomeric effect* associated with the electron delocalization justifies this observation.

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