



IAU-ARAK

J. Iran. Chem. Res. 4 (2011) 207-217

Journal of the
Iranian
Chemical
Research

www.iau-jicr.com

Hybrid-DFT study and NBO interpretations of the conformational behavior of 1,2-dihalodisilanes

Davood Nori-Shargh^{*,1}, Seiedeh Negar Mousavi¹, Hooriye Yahyaei², Somayye Yazdani¹ and Bahareh Ahmadi¹

¹ Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran

² Department of Chemistry, Zanjan Branch, Islamic Azad University, Zanjan, Iran

Received 1 January 2011; received in revised form 20 November 2011; accepted 25 November 2011

Abstract

Hybrid-density functional theory (B3LYP/Def2-TZVPP) based method and NBO interpretation were used to investigate the conformational behavior of 1,2-dihalodisilanes [halo=F (**1**), Cl (**2**), Br (**3**), I (**4**)]. The B3LYP/Def2-TZVPP results showed that the anti conformations of compounds **1-4** are more stable than their corresponding gauche conformations. The stability of the anti conformation compared to the gauche conformation increases from compound **1** to compound **4**. The NBO analysis of donor-acceptor interactions showed that the generalized anomeric effect (*GAE*) is in favor of the gauche conformations of compounds **1** and **2**. Contrary to compounds **1** and **2**, *GAE* is in favor of the anti conformations of compounds **3** and **4**. The *GAE* values calculated (i.e. $GAE_{\text{anti}}-GAE_{\text{gauche}}$) increase from compound **1** to compound **4**. On the other hand, the calculated dipole moment values for the gauche conformations increase from compound **1** to compound **3** but decreases from compound **3** to compound **4**. Based on the results obtained, there is no conflict between the *GAE* and the electrostatic model impacts on the conformational preferences in compounds **1-3** but the electrostatic model can not rationalize the increase of the instability of the gauche conformation of compound **4** compared to its anti conformation on going from compound **3** to compound **4**. Consequently, in the conflict between the *GAE* and the electrostatic model, the former succeeded in accounting for the increase of the anti conformation stability from compound **1** to compound **4**. There is a direct correlation between the calculated *GAE*, $\Delta[r_{\text{Si-Si}}(\text{G})-r_{\text{Si-Si}}(\text{A})]$ parameters. The correlations between the *GAE*, bond orders, $\Delta G_{\text{Anti-Gauche}}$, $\Delta G^{\ddagger}(\text{Gauche} \rightarrow \text{Gauche}', C_{2v})$, $\Delta G^{\ddagger}(\text{Anti} \rightarrow \text{Gauche}, C_2)$, dipole-dipole interactions, structural parameters and conformational behaviors of compounds **1-4** have been investigated.

Keywords: generalized anomeric effects; stereoelectronic interactions; ab initio; NBO; 1,2-dihalodisilanes.

1. Introduction

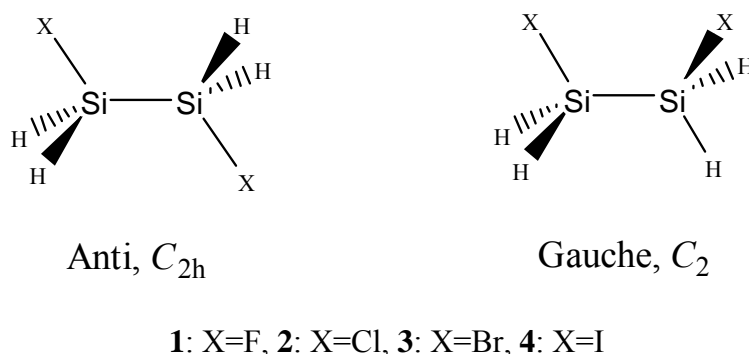
Haloethanes are an alternative to chlorofluorocabons, CFCs, believed to be major contributors to the seasonal ozone depletion over the Antarctic continent [1-5]. The widespread use of these CFC replacements makes it desirable to investigate their properties [6]. The

* Corresponding author. Tel. & fax: +98 861 3670017.

E-mail address: d-norishargh@iau-arak.ac.ir & nori_ir@yahoo.com

structures and rotational barriers about the C-C bonds of 1,2-difluoroethane and 1,2-dichloroethane have been investigated experimentally [7-17] and theoretically [17-19].

Although the impacts of the anomeric effect associated with the electron delocalization and the electrostatic model on the structures, conformational behaviors 1,2-difluoro-, -chloro-, -bromo and -iodoethane have examined by using CBS-4, hybrid-DFT and NBO interpretations, there is no published experimental or theoretical data about the analogs of 1,2-dihaloethanes containing Si atoms (i.e. 1,2-difluoro-1,2-disilane (**1**), 1,2-dichloro-1,2-disilane (**2**), 1,2-dibromo-1,2-disilane (**3**) and 1,2-diiodo-1,2-disilane (**4**)). In this work, the stereoelectronic interactions associated with the generalized anomeric effect (*GAE*) and also the conformational and structural properties of compounds **1-4** are investigated computationally using the hybrid-DFT based method (B3LYP/Def2-TZVPP) and natural bond orbital (NBO) analysis (see scheme 1) [20-25].



Scheme 1. Schematic representation of conformations of compounds **1-4**.

Since the preferred geometry of many molecules can be viewed as the result of the maximization of an interaction between the best donor and the best acceptor bonds [26], the stereoelectronic interactions are expected to play an important role in the conformational properties of these compounds [27-29].

The generalized anomeric effect (*GAE*), observable in acyclic compounds (such as dimethoxymethanes), as well as within rings, is a generalized manifestation of the preference of axial over equatorial C-1 alkoxy groups in pyranose sugars which has long been known as the anomeric effect [30].

2. Computational details

B3LYP/Def2-TZVPP levels of theory with the GAUSSIAN 98 package of programs [20]. The NBO analysis was performed at the B3LYP/Def2-TZVPP level for the gauche and anti conformations of compounds **1-4** by the NBO 5.G program contained in the PC-GAMESS interface [25]. The bonding and antibonding orbital occupancies in the axial and equatorial conformations of compounds **1-4**, and also the stabilization energies associated with donor-acceptor electron delocalization were calculated using NBO analysis. The stabilization energies 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 [26,29].

In addition, 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 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 GAE associated with the electron delocalizations shown in Fig. 1 can have negative or positive values which depend on the relative magnitude of the various GAE_{anti} and GAE_{gauche} contributions. Therefore, we can calculate the total GAE for compounds **1-4** as follow (equation 1):

$$GAE = \Sigma (GAE_{\text{anti}}) - \Sigma (GAE_{\text{gauche}}) \quad (\text{Eq. 1})$$

The influence of the GAE associated with $\sigma_{\text{Si1-H}} \rightarrow \sigma^*_{\text{Si2-X}}$, $\sigma_{\text{Si1-X}} \rightarrow \sigma^*_{\text{Si2-X}}$ and $\text{LP}_3\text{X}_{\text{Si1}} \rightarrow \sigma^*_{\text{Si2-X}}$ electron delocalizations (see Fig. 1) and electrostatic interactions on the conformational properties of compounds **1-4** were quantitatively investigated by the NBO analysis [25]. Our recent studies have shown that the NBO analysis is a sufficient approach to investigate the effect of the stereoelectronic interactions on the stability, reactivity and dynamic behaviors of chemical compounds [31-37].

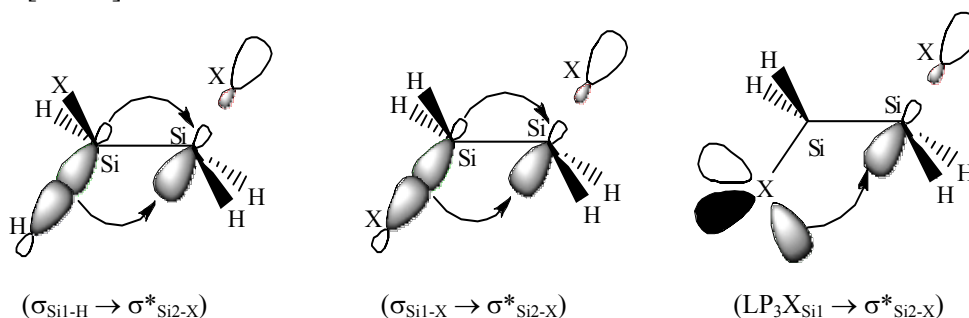


Fig. 1. Schematic representation of the electronic delocalization between bonding, non-bonding and anti-bonding orbitals ($\sigma_{\text{Si1-H}} \rightarrow \sigma^*_{\text{Si2-X}}$, $\sigma_{\text{Si1-X}} \rightarrow \sigma^*_{\text{Si2-X}}$, $\text{LP}_3\text{X}_{\text{Si1}} \rightarrow \sigma^*_{\text{Si2-X}}$) in compounds **1-4**.

3. Results and Discussion

3.1. Conformation preference

The Gibbs free energy, enthalpy and entropy differences (i.e. ΔG , ΔH and ΔS) for the gauche, anti and corresponding interconversional transition state conformations of compounds **1-4**, as calculated at the B3LYP/Def2-TZVPP level of theory are given in Table 1. The absolute values of the thermodynamic properties certainly can not be calculated at the accuracy level shown in this table; the correction for anharmonicity in a C-H bond may alone be on the order of 0.2 kcal mole⁻¹ (the value in the C-H radical). However, the quantities of interest here are the relative values of the thermodynamic functions for different conformations of the same molecule. We expect that the errors in such differences will be very small and that even the corresponding errors between the different closely related compounds will be minimal. The smooth variation among the calculated values supports this expectation.

The B3LYP/Def2-TZVPP method was used for compounds **1-4** (see Table 1). The calculated Gibbs free energy difference ($G_{\text{gauche}} - G_{\text{anti}}$) values between the anti and gauche conformations (i.e. $\Delta G_{\text{gauche-anti}}$) of compounds **1-3** are 0.05, 0.57, 0.83 and 1.27 kcal mol⁻¹, respectively, as calculated at the B3LYP/Def2-TZVPP level of theory.

Similar to trend observed for 1,2-dihaloethane [38], two distinct transition states (excluding the mirror image pathways), are required to describe the dynamic conformational properties of compounds **1-4** (see Fig. 2). The racemization processes of the gauche (C_2 point group) ground state conformation could take place by passing through the eclipsed (C_2 point group) or the plane symmetrical (C_{2v} point group) transitions state conformations as shown in Fig. 2.

The calculated Gibbs free energy barriers for the interconversion processes in compound **1** between the gauche ground state conformation and its eclipsed and plane symmetrical transition state conformations are 1.53 and 2.29 kcal mol⁻¹, respectively, as calculated by the B3LYP/Def2-TZVPP level.

Based on the results obtained from the B3LYP/Def2/TZVPP method, the calculated activation Gibbs free energy values for the conformational interconversion processes between the anti and gauche conformations by passing from the axial symmetrical transition state structures (i.e. ΔG_1^\ddagger) increase from compound **1** to compound **3** but decrease slightly from compound **3** to compound **4** (see Fig. 1 and Table 1). In addition, the calculated Gibbs free energy differences between the anti conformations and their axial-plane symmetrical transition state conformations (C_{2v} symmetry) in compounds **1-4** (i.e. ΔG_2^\ddagger) increase from compound **1** to compound **4** (see Fig. 1 and Table 1).

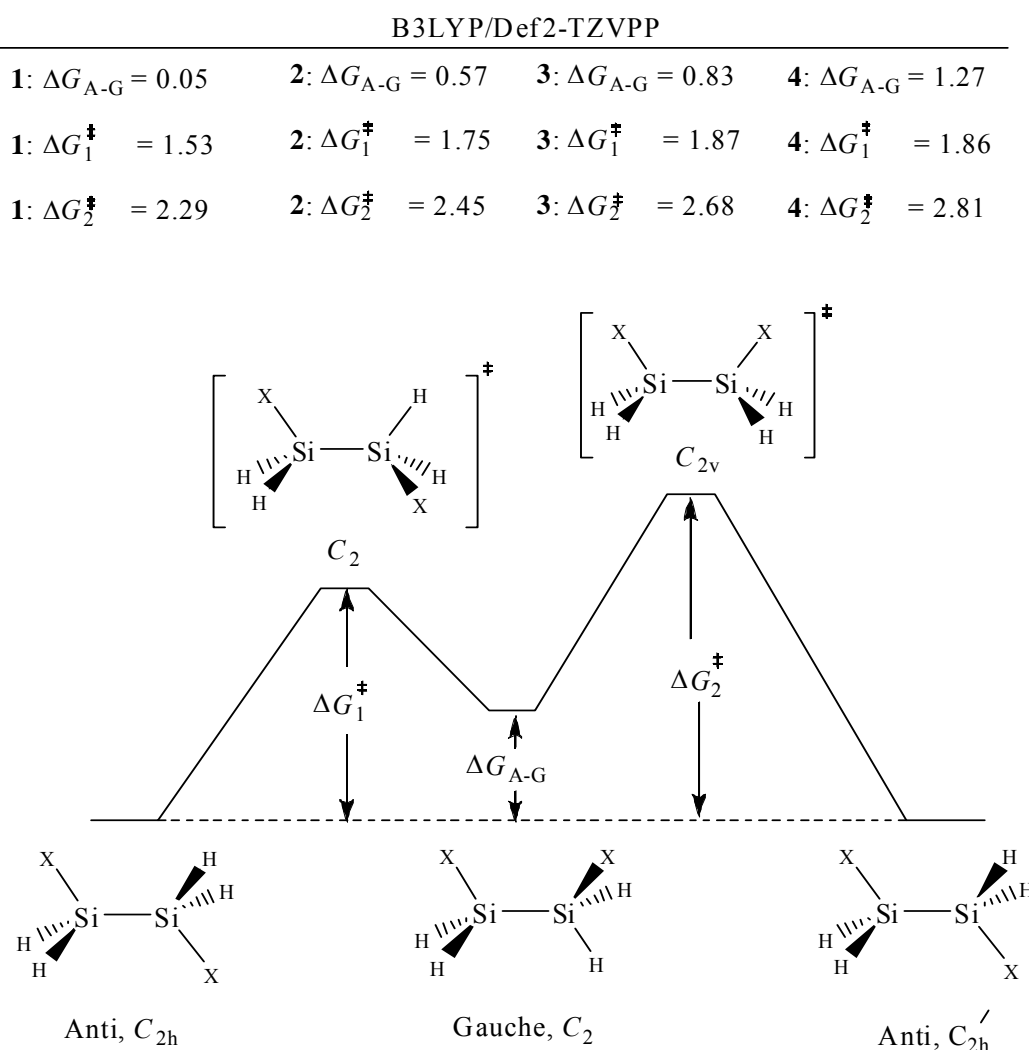


Fig. 2. B3LYP/Def2-TZVPP calculated free energy profiles of the conformational interconversion processes for compounds **1-4**.

Table 1B3LYP/Def2-TZVPP calculated thermodynamic parameters [ΔH , ΔG (in hartree) and ΔS (in cal mol⁻¹K⁻¹)], for the ground and transition state conformations of compounds **1-4**.

Geometries	B3LYP/Def2-TZVPP					
	<i>H</i>	<i>S</i>	<i>G</i>	ΔH^a	ΔS^a	ΔG^a
1-A , <i>C</i> _{2h}	781.297502-	79.876	-781.335454	0.000062 (3.89) ^b	0.309	0.000000 (0.00) ^b
1-G , <i>C</i> ₂	781.297564-	79.567	781.335369-	0.000000 (0.00) ^b	0.000	0.000085 (0.05) ^b
[1-G → 1-G'] [‡] , <i>C</i> _{2v}	781.297391-	74.797	781.332929-	0.000111 (0.06) ^b	5.079	0.00244 (1.53) ^b
[1-A → 1-G'] [‡] , <i>C</i> ₂	781.296124-	74.884	-781.331704	0.001378 (0.86) ^b	4.992	0.003665 (2.29) ^b
2-A , <i>C</i> _{2h}	1501.958951-	85.370	-1501.999513	0.000000 (0.00) ^b	0.074	0.000000 (0.00) ^b
2-G , <i>C</i> ₂	1501.958064-	85.296	1501.998591-	0.000887 (0.55) ^b	0.000	0.000922 (0.57) ^b
[2-G → 2-G'] [‡] , <i>C</i> _{2v}	-1501.957879	79.790	-1501.995790	0.000185 (0.11) ^b	5.580	0.002801 (1.75) ^b
[2-A → 2-G'] [‡] , <i>C</i> ₂	-1501.956742	79.857	-1501.994685	0.001322 (0.82) ^b	5.513	0.003906 (2.45) ^b
3-A , <i>C</i> _{2h}	-5729.864883	90.987	-5729.908114	0.000000 (0.00) ^b	0.044	0.000000 (0.00) ^b
3-G , <i>C</i> ₂	-5729.863577	90.943	-5729.906787	0.001306 (0.81) ^b	0.000	0.001327 (0.83) ^b
[3-G → 3-G'] [‡] , <i>C</i> _{2v}	-5729.863455	84.919	-5729.903802	0.000122 (0.07) ^b	6.068	0.002985 (1.87) ^b
[3-A → 3-G'] [‡] , <i>C</i> ₂	-5729.862027	85.213	-5729.902514	0.00155 (0.97) ^b	5.774	0.004273 (2.68) ^b
4-A , <i>C</i> _{2h}	-1177.092196	95.469	-1177.137557	0.000000 (0.00) ^b	0.755	0.000000 (0.00) ^b
4-G , <i>C</i> ₂	-1177.090518	94.714	-1177.135520	0.001678 (1.05) ^b	0.000	0.002037 (1.27) ^b
[4-G → 4-G'] [‡] , <i>C</i> _{2v}	-1177.090446	88.608	-1177.132547	0.00175 (1.09) ^b	6.861	0.002973 (1.86) ^b
[4-A → 4-G'] [‡] , <i>C</i> ₂	-1177.088682	89.150	-1177.131040	0.001836 (1.15) ^b	6.319	0.00448 (2.81) ^b

^a Relative to the most stable form. ^b Numbers in parenthesis are in kcal mol⁻¹.

3.2. Stabilization energies and GAE

The NBO analysis shows that the anti and gauche conformations of compounds **1-4** benefit from donor-acceptor electron delocalizations. It has to be noted that the stabilization energies associated with the electron delocalizations in 1,2-dihaloethanes [19] are greater than those obtained for compounds **1-4**. Based on the optimized ground state geometries using the B3LYP method, the NBO analysis of donor-acceptor (bond-antibond, nonbond-antibond) interactions showed that the stabilization energies associated with $\sigma_{\text{Si1-H}} \rightarrow \sigma_{\text{Si2-X}}^*$ for the gauche conformations of compounds **1-4** are 1.74, 1.82, 2.04 and 2.34 kcal mol⁻¹, respectively. There is no $\sigma_{\text{Si1-H}} \rightarrow \sigma_{\text{Si2-X}}^*$ electron delocalization for the anti conformations of these compounds (see Table 2). Importantly, the stabilization energies associated with $\sigma_{\text{Si1-H}} \rightarrow \sigma_{\text{Si2-X}}^*$ electron delocalizations can not control the conformational behaviors of compounds **1-4**. If there were only $\sigma_{\text{Si1-H}} \rightarrow \sigma_{\text{Si2-X}}^*$ electron delocalizations, the gauche conformation stabilities would increase from compound **1** to compound **4**. However, there are also interesting $\sigma_{\text{Si1-X}} \rightarrow \sigma_{\text{Si2-X}}^*$ and LP₃X_{Si1} $\rightarrow \sigma_{\text{Si2-X}}^*$ electron delocalizations in the anti conformations of compounds **1-4** which increase the stability of the anti conformations from compound **1** to compound **4**, compared to their corresponding gauche conformations.

Based on Eq. 1, the *GAE* values calculated (i.e. $GAE_{\text{anti}} - GAE_{\text{gauche}}$) associated with $\sigma_{\text{Si1-H}} \rightarrow \sigma_{\text{Si2-X}}^*$, $\sigma_{\text{C1-X}} \rightarrow \sigma_{\text{Si2-X}}^*$ and LP₃X_{Si1} $\rightarrow \sigma_{\text{Si2-X}}^*$ electron delocalization for compounds **1-4** are -1.74, -0.64, 0.52 and 1.48 kcal mol⁻¹, respectively (see Table 2). The *GAE* increases from compound **1** to compound **4**. Since the anti conformation stability increases from compound **1** to compound **4** (compared to the corresponding gauche conformations), the rationalization of the conformational preference can be accounted for solely in terms of the *GAE*.

3.3. Orbital occupancies

The NBO results showed that the $\sigma_{\text{C1-H}}$ bonding orbital occupancies in the gauche conformations of compounds **1-4** are 1.98241, 1.97785, 1.97479 and 1.97231, respectively (see Table 2). Also, the $\sigma_{\text{C1-X}}$ bonding orbital occupancies in the anti conformations of compounds **1-4** are 1.99554, 1.98506, 1.97613 and 1.96352, respectively. In addition, the NBO results revealed that the $\sigma_{\text{C1-X}}^*$ anti-bonding orbital occupancies in the gauche conformations of compounds **1-4** are 0.02241, 0.02241, 0.02671 and 0.03058, respectively. Further, the $\sigma_{\text{C1-X}}^*$ anti-bonding orbital occupancies in the anti conformations of compounds **1-4** are 0.01253, 0.02468, 0.03628 and 0.05130, respectively. These trends can be justified by the increase of the $\sigma_{\text{C1-H}} \rightarrow \sigma_{\text{C2-X}}^*$, $\sigma_{\text{C1-X}} \rightarrow \sigma_{\text{C2-X}}^*$ electronic delocalization from the gauche and anti conformations of compound **1** to compound **4**.

3.4. Orbital energies and off-diagonal elements

The stabilization energies associated with donor-acceptor electron delocalizations are proportional to $S^2/\Delta E$ where *S* is the orbital overlap and ΔE is the energy differences between the donor and acceptor orbitals. 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, and the stabilization should increase as the acceptor orbital energy decreases and the donor orbital energy increases.

The NBO analysis showed that the energy differences between donor ($E\sigma_{\text{Si1-H}}$) and acceptor ($E\sigma_{\text{Si2-X}}^*$) orbitals [i.e. $\Delta(E\sigma_{\text{Si2-X}}^* - E\sigma_{\text{Si1-H}})$] for the gauche conformations of compounds **1-4** are 0.63, 0.54, 0.50 and 0.46 a.u., respectively. Also, the NBO results showed that the calculated $\Delta(E\sigma_{\text{Si2-X}}^* - E\sigma_{\text{Si1-X}})$ values for the anti conformations of compounds **1-4** are 1.22, 0.76, 0.65 and 0.52 a.u., respectively. Based on the NBO results, the energy difference between donor ($E\sigma_{\text{Si1-H}}$) and acceptor ($E\sigma_{\text{Si2-X}}^*$) orbitals [i.e. $\Delta(E\sigma_{\text{Si2-X}}^* - E\sigma_{\text{Si1-H}})$] decrease from the gauche

conformations of compound 1 to compound 4. Also, the $\Delta(E\sigma_{Si_2-X}^* - E\sigma_{Si_1-X})$ calculated values decrease from the anti conformations of compound 1 to compound 4.

Table 2

NBO calculated stabilization energies (E_2 , in kcal mol⁻¹), generalized anomeric effect (GAE , in kcal mol⁻¹), off-diagonal elements (F_{ij} , in a.u.), orbital energies (in a.u.) and orbital occupancies and bond orders (Wiberg Bond Index, WBI) based on the geometries optimized at the B3LYP/Def2-TZVPP level of theory, for the anti and gauche conformations of compounds 1-4.

	1		2		3		4	
	A	G	A	G	A	G	A	G
Donor→acceptor								
$(\sigma_{Si_1-H} \rightarrow \sigma_{Si_2-X}^*) \times 2$	-	1.74	-	1.82	-	2.04	-	2.34
$(\sigma_{Si_1-X} \rightarrow \sigma_{Si_2-X}^*) \times 2$	-	0.00	-	-	1.16	-	2.16	-
$(LP_3 X_{Si_1} \rightarrow \sigma_{Si_2-X}^*) \times 2$	-	0.00	1.18	-	1.40	-	1.66	-
Σ	-	1.74	1.18	1.82	2.56	2.04	3.82	2.34
GAE		-1.74		-1.64		0.52		1.48
Orbital occupancy								
σ_{Si_1-H}	1.97839	1.97785	1.98148	1.98130	1.98169	1.98161	1.98215	1.98219
σ_{Si_1-X}	1.99422	1.99450	1.98837	1.98939	1.98495	1.98661	1.97919	1.98235
$LP_3 X_{Si_1}$	1.95661	1.95593	1.94851	1.94841	1.94758	1.94893	1.94560	1.94927
$\sigma_{Si_2-X}^*$	0.03003	0.03170	0.02998	0.02628	0.03364	0.02692	0.03928	0.02709
Orbital energy								
$E \sigma_{Si_1-H}$	-0.44573	-0.44627	-0.45378	-0.45319	-0.45699	-0.45573	-0.45739	-0.45588
$E \sigma_{Si_1-X}$	-1.04450	-1.04715	-0.67304	-0.67484	-0.60669	-0.60977	-0.51506	-0.51606
$E LP_3 X_{Si_1}$	-0.42820	-0.42734	-0.33826	-0.33548	-0.31311	-0.31183	-0.28451	-0.28221
$E \sigma_{Si_2-X}^*$	0.17979	0.17893	0.08585	0.08756	0.04465	0.04682	0.01881	0.02188
$\Delta(E \sigma_{Si_2-X}^* - E \sigma_{Si_1-H})$	0.62552	0.6252	0.53963	0.54075	0.50164	0.50255	0.45739	0.45588
$\Delta(E \sigma_{Si_2-X}^* - E \sigma_{Si_1-X})$	1.22429	1.22608	0.75889	0.7624	0.65134	0.65659	0.51506	0.51606
$\Delta(E \sigma_{Si_2-X}^* - E LP_3 X_{Si_1})$	0.60799	0.60630	0.42411	0.42304	0.35776	0.35865	0.28451	0.28221
F_{ij} (off-diagonal element)								
$\sigma_{Si_1-H} \rightarrow \sigma_{Si_2-X}^*$	-	0.021	-	0.020	-	0.020	-	0.021
$\sigma_{Si_1-X} \rightarrow \sigma_{Si_2-X}^*$	-	-	-	-	0.017	-	0.022	-
$LP_3 X_{Si_1} \rightarrow \sigma_{Si_2-X}^*$	-	-	0.014	-	0.014	-	0.014	-
μ (Debye)	0.0000	1.8503	0.0002	1.8659	0.0002	1.8822	0.0001	1.5404
$\Delta \mu$		1.8503		1.8657		1.8820		1.5403
Bond order (Wiberg Bond Index)								
Si1-Si2	0.9049	0.9069	0.9123	0.9112	0.9171	0.9152	0.9269	0.9227
Si1-X	0.5720	0.5763	0.8724	0.8856	0.9238	0.9417	0.9802	1.0033
$\Delta(WBI_{anti-gauche}, Si1-Si2)$		-0.0020		0.0011		0.0019		0.0042
$\Delta(WBI_{gauche-anti}, Si1-X)$		0.0043		0.0132		0.0179		0.0231

The decrease of the calculated $\Delta(E\sigma_{Si_2-X}^* - E\sigma_{Si_1-H})$, $\Delta(E\sigma_{Si_2-X}^* - E\sigma_{Si_1-X})$ and $\Delta(E\sigma_{Si_2-X}^* - E_{LP_3 X_{Si_1}})$ can be resulted from the decrease of the acceptor $\sigma_{Si_2-X}^*$ antibonding orbital energies from the anti and gauche conformations of compound 1 to compound 4 [may give rise to strong electron delocalization (see Table 2)]. It should be noted that there is no significant differences between the orbital overlap (S) [off-diagonal elements (F_{ij})] values for the $\sigma_{Si_1-H} \rightarrow \sigma_{Si_2-X}^*$, $\sigma_{C1-X} \rightarrow \sigma_{Si_2-X}^*$ and $LP_3 X_{Si_1} \rightarrow \sigma_{Si_2-X}^*$ electron delocalizations (see Table 2). Consequently, in the gauche and anti conformations of compounds 1-4, the $\Delta(E\sigma_{Si_2-X}^* - E\sigma_{Si_1-H})$, $\Delta(E\sigma_{Si_2-X}^* - E\sigma_{Si_1-X})$ and $\Delta(E\sigma_{Si_2-X}^* -$

$E_{LP_3-XSi_1}$) could affect and control the order of the stabilization energies associated with $\sigma_{Si_1-H} \rightarrow \sigma_{Si_2-X}^*$, $\sigma_{C_1-X} \rightarrow \sigma_{Si_2-X}^*$ and $LP_3X_{Si_1} \rightarrow \sigma_{Si_2-X}^*$ electron delocalizations.

3.5. Dipole moments

It has to be noted that there is a preference for the conformation with the smallest resultant dipole moment especially in the gas phase [38]. Table 2 presents the calculated dipole moments for the gauche conformations of compounds **1-4**. The anti conformations of compounds **1-4** have central symmetry (C_i), therefore, they do not possess dipole moments.

Based on the results obtained at the B3LYP/Def2/TZVPP level of theory, the dipole moments of the gauche conformations increase from compound **1** to compound **3** but decrease from compound **3** to compound **4** (see Table 2). It can be expected that the increase of the dipole moments from the gauche conformations of compound **1** to compound **3** may decrease their relative stabilities compared to their corresponding anti conformations. Interestingly, the trend observed for the variation of the calculated dipole moment values for compounds **1-3** is the same with the observed for the variation of the calculated *GAE* values. Since the calculated dipole moment value decreases from the anti conformation compound **3** to compound **4**, the electrostatic model can not explain the increase of the anti conformation stability of compound **4** compared to its gauche conformation in comparison to compound **3**. Consequently, the *GAE* (i.e. $GAE_{anti} - GAE_{gauche}$) succeeds in accounting for the increase of the anti conformation stabilities from compound **1** to compound **4**.

3.6. Bond orders

The bond orders of Si1-Si2 and Si-X bonds can be affected from $\sigma_{Si_1-H} \rightarrow \sigma_{Si_2-X}^*$, $\sigma_{Si_1-X} \rightarrow \sigma_{Si_2-X}^*$ and $LP_3X_{Si_1} \rightarrow \sigma_{Si_2-X}^*$ electron delocalizations. Based on the NBO results, the calculated bond orders [Wiberg Bond Index (*WBI*)] for Si1-Si2 bonds of the gauche conformations increase from compound **1** to compound **4** (see Table 2). Also, the differences between the *WBI* of Si1-Si2 and also Si-X bonds in the anti and gauche conformations [i.e. $\Delta(WBI(Si_1-Si_2)_{anti-gauche})$ and $\Delta(WBI(Si-X)_{gauche-anti})$] increase from compound **1** to compound **4**. The NBO analysis showed that the calculated $\Delta(WBI(Si_1-Si_2)_{anti-gauche})$ parameters in compounds **1-4** are -0.0120, 0.0011, 0.0019 and 0.0042 respectively. Also, the calculated $\Delta(WBI(Si-X)_{gauche-anti})$ parameters in compounds **1-4** are 0.0043, 0.0132, 0.0179 and 0.0231, respectively (see Table 2). The variation of the calculated $\Delta(WBI(Si_1-Si_2)_{anti-gauche})$ and $\Delta(WBI(Si-X)_{gauche-anti})$ parameters are in accordance with the increase of the calculated *GAE* from compound **1** to compound **4** (see Table 2).

3.7. Structural parameters

Representative structural parameters for the gauche and anti conformations of compounds **1-4** and their corresponding transition state structures, as calculated at the B3LYP/Def2-TZVPP level of theory, are shown in Table 3. The structures of compounds **1-4** give evidence that in the gauche conformation of compound **1**, the Si₁-Si₂ bond length is significantly contracted compared to that in its anti conformation (see Table 3). Contrary to compound **1**, the Si₁-Si₂ bond lengths in the anti conformations of compounds **2-4** are longer than those in their corresponding gauche conformations. These facts can be explained by the increase of the non-bonded attractive interactions (i.e. $\sigma_{Si_1-X} \rightarrow \sigma_{Si_2-X}^*$ and $LP_3 X_{Si_1} \rightarrow \sigma_{Si_2-X}^*$ electron delocalizations) from the anti conformations of compound **1** to compound **4** (see Table 2).

Using the structural parameters obtained, "Δ" parameters were defined as $\Delta[r_{Si-Si}(G) - r_{Si-Si}(A)]$ and $\Delta[r_{Si-X}(A) - r_{Si-X}(G)]$. There is a direct correlation between the calculated *GAE* and $\Delta[r_{Si-Si}(G) - r_{Si-Si}(A)]$ and $\Delta[r_{Si-X}(A) - r_{Si-X}(G)]$ parameters (see Tables 2, 3). These results indicate that with the increase of $\Delta[r_{Si-Si}(G) - r_{Si-Si}(A)]$ and $\Delta[r_{Si-X}(A) - r_{Si-X}(G)]$ parameters from compound **1** to

compound **4**, the corresponding *GAE* values decrease. Consequently, the calculated $\Delta[r_{\text{Si-Si}}(\text{G}) - r_{\text{Si-Si}}(\text{A})]$ and $\Delta[r_{\text{Si-x}}(\text{A}) - r_{\text{Si-x}}(\text{G})]$ parameters could be proposed as a criterion for the evaluation of the *GAE* values in compounds **1-4**.

Table 3

B3LYP/Def2/TZVPP calculated structural parameters for the ground and transition state conformations of compounds **1-4**.

	Bond lengths (Å)				Bond angle (°)	Torsion angle (°)
	$r_{\text{Si-Si}}$	$r_{\text{Si-x}}$	$\Delta[r_{\text{Si-Si}}(\text{G}) - r_{\text{Si-Si}}(\text{A})]$	$\Delta[r_{\text{Si-x}}(\text{A}) - r_{\text{Si-x}}(\text{G})]$	$\theta_{\text{x-Si-Si}}$	$\phi_{\text{x-c-c-x}}$
1-A , C_{2h}	2.362	1.614			107.7	180.0
1-G , C_2	2.358	1.612	-0.004	0.002	110.2	69.0
[1-G → 1-G'] [‡] , C_{2v}	2.370	1.613			108.	122.9
[1-A → 1-G'] [‡] , C_2	2.375	1.610			109.2	0.0
2-A , C_{2h}	2.350	2.076			108.1	180.0
2-G , C_2	2.353	2.073	0.003	0.003	109.9	65.2
[2-G → 2-G'] [‡] , C_{2v}	2.365	2.076			109.4	116.6
[2-A → 2-G'] [‡] , C_2	2.372	2.069			110.9	0.003
3-A , C_{2h}	2.347	2.249			108.0	180.0
3-G , C_2	2.351	2.242	0.004	0.007	109.9	65.8
[3-G → 3-G'] [‡] , C_{2v}	2.363	2.247			109.4	115.3
[3-A → 3-G'] [‡] , C_2	2.372	2.238			112.2	0.001
4-A , C_{2h}	2.346	2.473			108.3	180.0
4-G , C_2	2.351	2.465	0.0052	0.008	110.3	66.8
[4-G → 4-G'] [‡] , C_{2v}	2.362	2.470			109.9	112.2
[4-A → 4-G'] [‡] , C_2	2.372	2.461			114.0	0.0

4. Conclusions

The CBS-QB3, B3LYP/Def2-TZVPP calculations reported above and NBO analysis provided a reasonable picture from energetic, structural, bonding and stereoelectronic points of view for the conformational preference in compounds **1-4**. Effectively, the CBS-QB3 and B3LYP/Def2-TZVPP results showed that the calculated Gibbs free energy difference ($G_{\text{gauche}} - G_{\text{anti}}$) values between the anti and gauche conformations (i.e. $\Delta G_{\text{gauche-anti}}$) increase from compound **1** to compound **4**. This fact can be explained by the decrease of the *GAE* values (i.e.

$GAE_{\text{anti}}-GAE_{\text{gauche}}$) from compound **1** to compound **4**. Based on the results obtained, there is no conflict between the GAE and the electrostatic model impacts on the conformational preferences in compounds **1-3** but the electrostatic model can not rationalize the increase of the instability of the gauche conformation of compound **4** compared to its anti conformation on going from compound **3** to compound **4**.

References

- [1] J.E. Lovelock, *Nature*. 230 (1971) 379-381.
- [2] M.J. Molina, F.S. Rowland, *Nature*. 249 (1974) 810-812.
- [3] F.S. Rowland, *Am Sci.* 77 (1989) 36-45.
- [4] D.A. Keller, D.C. Roe, P.H. Lieder, *Fundam. Appl. Toxicol.*, 30 (1996) 213-219.
- [5] IARC Monographs on the Evaluation on the Carcinogenic Risk of Chemicals to Man, World Health Organization, International Agency for Research on Cancer: Geneva 20, (1979).
- [6] B.M. Wong, M.M. Fadri, S. Raman, *J. Comput. Chem.*, and references therein, 29 (2008) 481-487.
- [7] T. Hirano, S. Nonoyama, T. Miyajima, Y. Kurita, T. Kawamura, H. Sato, *J. Chem. Soc. Chem. Commun.*, (1986) 606-607
- [8] P. Huber-Walchli, H.H. Gunthard, *Spectrochim. Acta Part A*. 37A (1981) 285-304.
- [9] W.D. Gwinn, K.S. Pitzer, *J. Chem. Phys.* 16 (1948) 303-309.
- [10] K. Kveseth, *Acta Chem. Scand. A*. 29 (1975) 307-311.
- [11] H.J. Bernstein, *J. Chem. Phys.* 17 (1949) 258- 261.
- [12] K. Tanabe, *Spectrochim. Acta Part A*. 28A (1972) 407-424.
- [13] Y. A. Pentin and V. M. Tatevskii, *Dokl. Akad. Nauk SSSR*, 108 (1956) 290.
- [14] T.H. Can, J.B. Peel, G.D. Willett, *J. Chem. Soc. Faraday Trans. 2* (1977) 965- 290.
- [15] S. Mizushima, I. Watanabe, T. Simanouti, S. Yamaguchi, *J. Chem. Phys.* 17 (1949) 591-594.
- [16] H. Takeo, C. Matsumura, Y. Morino, *J. Chem. Phys.* 84 (1986) 4205-4210.
- [17] K.B. Wiberg, T.A. Keith, M.J. Frisch, M. Murcko, *J. Phys. Chem.* 99 (1995) 9072-9079.
- [18] K.B. Wiberg, M.A. Murcko, *J. Phys. Chem.* 91 (1987) 3616-3620.
- [19] D. Nori-Shargh, J.E. Boggs, *Struct. Chem.*, 22 (2011) 253-262.
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03*, Revision B.03, Gaussian, Inc, Wallingford (2004).
- [21] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648-5652.
- [22] C. Lee, W. Yang, R.G. Parr, *Phys Rev B*. 37 (1988) 785-789
- [23] W.J. Hehre, L. Radom, P.R. Schleyer, J.A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York. (1986).
- [24] J.M. Seminario, P. Politzer, (Eds) *Modern Density Function Theory, A Tool for Chemistry*, Elsevier, Amsterdam. (1995).
- [25] E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, J.A. Bohmann, C.M. Morales, Weinhold F, *Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, NBO Version 5.G.* (2004).
- [26] N.D. Epiotis, R.L. Yates, R.J. Larson, C.R. Kirmayer, F. Bernardi, *J Am Chem Soc.* 99 (1977) 8379-8388.
- [27] E.L. Eliel, S.H. Wilen, *Stereochemistry of organic compounds*, Wiley, New York. (1994).
- [28] E. Juaristi, G. Cuevas, *The anomeric effect*, CRC Press. Inc, Florida. (1995).
- [29] P. Dionne, M. St-Jacques, *J Am Chem Soc.* 109 (1987) 2616-2623.
- [30] W.F. Bailey, E.L. Eliel, *J Am Chem Soc.* 96 (1974) 1798-1806.

- [31] D. Nori-Shargh, F. Roohi, F. Deyhimi, R. Naeem-Abyaneh. *J Mol Struct (THEOCHEM)*. 763 (2006) 21-28.
- [32] D. Nori-Shargh, F. Deyhimi, J.E. Boggs, S. Jameh-Bozorgh, R. Shakibazadeh, *J Phys Org Chem*. 20 (2007) 355-364.
- [33] D. Nori-Shargh, H. Yahyaei, *J Mol Struct (THEOCHEM)*. 913 (2009) 8-15.
- [34] D. Nori-Shargh, N. Hassanzadeh, M. Kosari, S. Sharifi, *J Mol Struct (THEOCHEM)*. 940 (2010) 129-134.
- [35] A. Zeinalinezhad A, Nori-Shargh D, Abbasi-Bakhtiari Z, Boggs JE *J Mol Struct (THEOCHEM)*. 947 (2010) 52-57.
- [36] D. Nori-Shargh, H. Yahyaei, J.E. Boggs, *J. Mol. Graph. Model*. 28 (2010) 807-813.
- [37] D. Nori-Shargh, J.E. Boggs, *J Phys Org Chem*. Doi:10.1002/poc.1728. (2010).
- [38] K.B. Wiberg, M. Murcko, *J. Phys. Chem*. 91 (1987) 3616-3620.