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DFT and NBO analysis on conformers of dioxaphosphinane derivatives

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ABSTRACT: The structural and thermodynamic parameters for dioxaphosphinane derivatives are investigated by DFT: B3LYP methods for axial and equatorial conformations. The stabilization of energy electrons delocalization in the axial conformation is higher than that of the equatorial one, indicating that the electrons delocalization transfer occurs more in the axial conformation. Stereoelectronic interactions associated with anomeric effect (AE) and electrostatic effect on the conformational behaviors of 2,5,5-trimethyl-1,3,2-dioxaphosphinane 2-sulfide (**1**),-dithiaphosphinane 2-sulfide (**2**) and -diselenaphosphinane 2-sulfide (**3**) were investigated using quantum mechanical methods. These compounds have been analyzed by means of DFT method and natural bond orbital (NBO) interpretation. Our results show that the AE is more considerable for the justification of the conformational preferences of compounds than the other factors.

Keywords: *Anomeric effect, Conformation, DFT method, Dioxaphosphinane, Electrostatic effect, Interaction, NBO analysis.*

INTRODUCTION

Chemical reactions involve interactions between molecular orbitals accounting for the increasingly important role of the concept of stereoelectronic effects in chemistry [1, 2]. There are many examples of anomeric behavior of cyclohexanes and heterocyclohexanes, and in the presence of almost constant steric effects, hyperconjugation seems a reasonable explanation [3]. The anomeric effect was initially defined as the preference of a polar substituent at the anomeric carbon (C_1) of a pyranosides ring to the axial orientation over the equatorial one [4]. Although the most common examples of anomeric effect have been observed in cyclic oxygen-containing carbohydrates, there have been recent studies which examine such an effect in phosphorus, sulfur, silicon, and nitrogen containing compounds [5]. The importance of such stereoelectronic effect extends to organometallic chemistry, as well as biochemistry [6]. The research of carbocyclic and heterocyclic compounds is led to the study of stereoelectronic interactions because their rigid cyclic geometry retains interacting orbitals in a well-defined geometry [7]. The source of the generalized anomeric effect [8, 9] rises from the tendency of R'-X-CH_2-Y-R'' segment (where R' and R'' are functional groups and X and Y as heteroatoms, which are often more electronegative than carbon) to be a gauche orientation rather than the anti-conformation [10-14]. Especially important are interactions that arise when the best donor orbital (bond or lone pair) is oriented antiperiplanar to the best acceptor orbital [15-18]. Historically, when Edward appointed the anomeric effect, he proposed that this effect

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is related to oxygen lone pairs of pyranose ring [4]. The cause of both anomeric and generalized anomeric effects is known, which is due to the introduction of an electronegative heteroatom, and the consequence is known as well, which is the order change in stability among different isomers of the same molecule. The anomeric effect influences conformational equilibrium around the anomeric center and affects the stereochemical output of many reactions occurring at the anomeric center. Well identified consequences of stereoelectronic interactions in conformational equilibrium are the anomeric effect [9-14] and the generalized anomeric effects [14, 15], and the accumulated evidence suggests the importance of the relevance of anomeric $n(X) \rightarrow \sigma^*(P\text{-}S)_{app}$ (the orientation of P=S is axial) and $n(X) \rightarrow \sigma^*(P\text{-}C)_{app}$ (the orientation of is equatorial) (X= O, S and Se) stereoelectronic interactions, respectively. The 1,3,2-dioxaphosphorinane derivatives are interesting compounds because of their biological activities [15-19]. Numerous studies of structures and conformations of 1,3,2-dioxaphosphorinanes and related heterocycles have been reported [20-24]. These studies on heterocyclic organo-phosphorus compounds have provided evidence the participation of antibonding orbitals even in molecules with low acceptor orbitals such as P=O and P=S groups [25-27].

In the present study, the stereoelectronic effects, electrostatic interactions and also the conformational behaviors of three compounds of 2,5,5-trimethyl-1,3,2-dioxaphosphinane 2-sulfide (**1**-ax⇆**1**-eq), 2,5,5-trimethyl-1,3,2-dithiaphosphinane 2-sulfide (**2**-ax⇆**2**-eq) and 2,5,5-trimethyl-1,3,2-diselenaphosphinane 2-sulfide (**3**-ax⇆**3**-eq) have been studied computationally using modern density functional theory, (DFT) [28, 29] methods and natural bond orbital, NBO analysis [30], analyses have been used to study the influences of various hetero atoms in ring with different P=S orientations on the anomeric effect in 1,3,2-dihetereo 2-sulfide.

COMPUTATIONAL DETAILS

All structures were fully optimized at B3LYP Methods using the Gaussian 09 package [31] and with the aid of GAUSSVIEW 5.0 molecular visualization program [32]. The modern density functional theory, DFT, method using hybrid gradient-corrected (three parameter nonlocal) exchange functional by Becke [33] with the gradient corrected (nonlocal) correlation functional of Lee, Yang and Parr [34] has been employed for all computations. An NBO analysis was then performed for the axial and equatorial conformations of compounds **1-3** by the NBO 5.1 program [35]. NBO analyses such as orbital population, stabilization energies for the charge transfers have been also carried out at the B3LYP Methods using NBO 5.1 program [35, 36] implemented in GAUSSIAN 09 package.

RESULTS AND DISCUSSION

Conformational Preferences

The chair conformations of compounds **1-3** are more stable than their related twist-boat ones according to the B3LYP method. The relative zero-point energies, corrected electronic energies (ΔE_0), Gibbs free energy (ΔG), enthalpy (ΔH) and entropy differences (ΔS) at 25ºC and 1atm pressure between the axial and equato-

Table 1. Calculated total energies (E_0) and zero-point energies (ZPE) (in hartree) for equatorial and axial conformations of compounds **1-3**.

Compound	Conformer	B3LYP /6-311+G**// B3LYP /6-311+G**				B3LYP /6-31G**// B3LYP /6-31G**			
		ZPE	E_{el}	E_0	$\Delta E_{0(eq\text{-}ax)}$	ZPE	E_{el}	E_0	$\Delta E_{0(eq\text{-}ax)}$
1(O/S)	eq	0.1903	-1126.4901	-1126.2998	3.96	0.1915	-1126.3425	-1126.1510	3.83
	ax	0.1905	-1126.4970	-1126.3061		0.1918	-1126.3489	-1126.1571	
2(S/S)	eq	0.1842	-1772.4309	-1772.2467	2.14	0.1856	-1772.2773	-1772.0916	1.86
	ax	0.1845	-1772.4346	-1772.2501		0.1858	-1772.2804	-1772.0946	
3(Se/S)	eq	0.1819	-5779.1050	-5778.9232	0.98	0.1832	-5774.6834	-5774.5002	1.03
	ax	0.1822	-5779.1070	-5778.9248		0.1833	-5774.6852	-5774.5018	

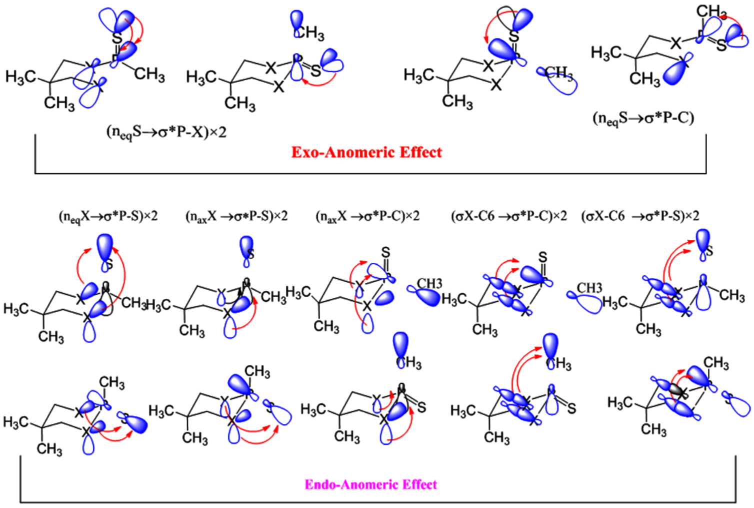


Fig. 1. Schematic representation of the electronic delocalization between donor/acceptor orbitals in the axial and equatorial conformations of compounds **1–3**.

rial of compounds **1-3**, as calculated at the B3LYP/6-311+G** and B3LYP/6-31G** levels of theory, are collected in Table 1. All of the methods used in this work (with fully geometry optimization) showed that in these compounds the values of calculated Gibbs free energies in axial conformations are lower than the equatorial conformations. Also, the $\Delta S_{(eq-ax)}$ values are relatively small, so the calculated $\Delta G_{(eq-ax)}$ parameters are close to the ΔE_{0eq-ax} values. (Table 1).

According to the results of the methods, the axial chair conformation of compounds **1-3** are more stable than their corresponding equatorial conformations and it could be the reason of the axial conformation preferences of compounds **1-3**. There is a good accommodation between these consequences and experimental documents which have published in the literature for compound **1** [23]. It is observed that from compound **1** to compound **3** the preference of the axial conformations relative to their corresponding equatorial conformations is decreasing. The stabilization energies associated with electronic delocalization and their influences on the conformational properties of compounds **1-3** were quantitatively investigated by the Natural Bond Orbital (NBO) analysis (Table 2). The stabilization energy, E2, associated with the donor–acceptor electronic delocalization is proportional to $S^2/\Delta E$, where S is the overlap integral of the two interacting orbitals and ΔE is the energy difference between the donor and acceptor orbitals [9,30,37-40]. Detailed descriptions of the NBO calculations are available in the literature [9, 30, 37-40]. Also, the stabilization energies associated with $n_{eq}X\rightarrow\sigma^*P\text{-}S$, $n_{ax}X\rightarrow\sigma^*P\text{-}S$, $n_{ax}X\rightarrow\sigma^*P\text{-}C$, $\sigma X\text{-}C6\rightarrow\sigma^*P\text{-}C$, $\sigma X\text{-}C6\rightarrow\sigma^*P\text{-}S$ (Endo-GAE) and $n_{eq}S\rightarrow\sigma^*P\text{-}X$, $n_{eq}S\rightarrow\sigma^*P\text{-}C$ (Exo-GAE) electronic delocalization were calculated (see Fig. 1).

Electronic structures of model compounds were studied using NBO analysis [35-41]. The importance of the stabilization generated by a two-electron/two-orbital hyperconjugative interaction is based on four factors: the energy gap, the acceptor ability of the empty orbital, the donor ability of the filled orbital, and the spatial overlap between the donor and acceptor orbitals that is settled by molecular geometry.

The NBO analysis of bonding®antibonding (donor→acceptor) interactions at the B3LYP/6–311+G** level of theory showed that the most stabilization energies (Resonances energies) (E^2) are associated with $n_{ax}X\rightarrow\sigma^*P\text{-}S$ electron delocalization for the axial conformations of compounds **1-3**. The values of resonances energies associated with $n_{ax}X\rightarrow\sigma^*P\text{-}S$ electron delocalization for the axial conformations of compounds **1-3** are 12.48, 9.86 and 8.12 (kcal.mol^{-1}), respectively. This stereoelectronic orbital interaction for the axial forms is more effective to indicate the axial conformations preference of compounds **1-3** (Table 2). The Generalized Anomeric Effects (GAE) values that calculated for compounds **1-3** are 5.56, 3.4 and 2.9 (kcal.mol^{-1}) respectively. The results showed the GAE value decreases from compound **1** to compound **3** (Table 2).

Table 2. Calculated stabilization energies (E2, in kcal mol^{-1}), GAE (Generalized Anomeric Effects, in kcal mol^{-1}) values and Fock matrix elements (Fij, in a.u.), for the equatorial and axial conformations of compounds **1-3**, based on the geometries optimized at the B3LYP/6-311+G** level.

Compounds	1		2		3	
(E_2): Stabilization energies	ax	eq	ax	eq	ax	eq
$(n_{1X}\rightarrow\sigma^*_{P\text{-}S})\times2$	3.60	0.26	3.68	0.04	3.54	0.28
$(n_{2X}\rightarrow\sigma^*_{P\text{-}S})\times2$	12.48	0.30	9.86	0.30	8.12	0.34
$(n_{2X}\rightarrow\sigma^*_{P\text{-}C})\times2$	0.82	7.74	0.38	9.88	0.28	8.28
$(\sigma_{X\text{-}C6}\rightarrow\sigma^*_{P\text{-}C})\times2$	0.18	0.20	2.40	0.18	2.60	0.16
$(\sigma_{X\text{-}C6}\rightarrow\sigma^*_{P\text{-}S})\times2$	0.00	3.80	0.00	3.40	0.00	3.50
$\sum$ Endo – GAE[a]	17.08	12.3	16.32	13.8	14.54	12.56
$(n_{1S}\rightarrow\sigma^*_{P\text{-}X})\times2$	1.00	2.32	2.60	2.40	2.86	2.60
$(n_{1S}\rightarrow\sigma^*_{P\text{-}C8})$	1.72	0.67	1.53	1.19	1.54	1.21
$\sum$ Exo – GAE[b]	2.72	2.99	4.13	3.59	4.40	3.81
GAE	-4.51		-3.06		-2.57	
$F_{i,j}$						
$(n_{1X}\rightarrow\sigma^*_{P\text{-}S})$	0.034	0.009	0.035	0.003	0.036	0.010
$(n_{2X}\rightarrow\sigma^*_{P\text{-}S})$	0.051	0.008	0.039	0.007	0.035	0.007
$(n_{2X}\rightarrow\sigma^*_{P\text{-}C})$	0.015	0.046	0.008	0.041	0.007	0.036
$(\sigma_{X\text{-}C6}\rightarrow\sigma^*_{P\text{-}C})$	0.009	0.010	0.028	0.008	0.028	0.007
$(\sigma_{X\text{-}C6}\rightarrow\sigma^*_{P\text{-}S})$	0.002	0.040	0.001	0.032	0.000	0.031
$(n_{1S}\rightarrow\sigma^*_{P\text{-}X})$	0.022	0.034	0.029	0.028	0.030	0.029
$(n_{1S}\rightarrow\sigma^*_{P\text{-}C8})$	0.039	0.024	0.034	0.028	0.034	0.030

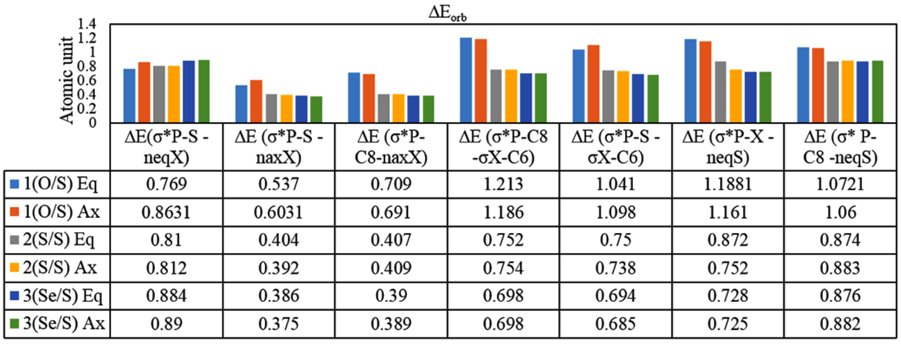
[a] Endo-Generalized Anomeric Effects values. [b] Exo-Generalized Anomeric Effects values.

Based on the results of the NBO analysis, the σX-C→σ*P-C electron delocalization is increasing in axial conformations from compound **1** to **3**, but these values are close to each other in equatorial conformations. In the equatorial conformations, stereoelectronic effects have an insignificant magnitude, but in the axial conformations, stability energy of electronic transitions is significant. In other words, the sum of the stabilization energy consequent from donor→acceptor electron delocalization for compounds **1** to **3** in axial conformations is higher than that of the corresponding equatorial conformations. Thus, the results of the NBO analysis and the results of the thermodynamic parameters are in agreement with each other. In other words, the conformational behavior of the compounds is affected by stereoelectronic interactions.

Orbital energies, overlap and Fock elements matrix

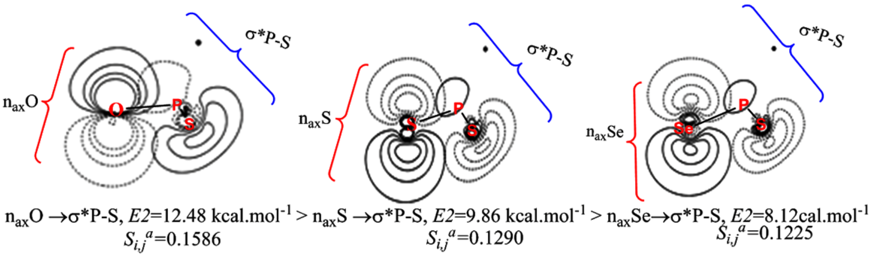
The stabilization energy associated with donor-acceptor electron delocalization decreases as the acceptor orbital energy decreases and the donor orbital energy increases [46-54]. According to the results of the NBO analysis for the axial conformations of compounds **1-3**, the energy difference between $n_{ax}X$ as donor orbital and σ*P-S as acceptor orbital [i.e. $\Delta(E_{\sigma^*P\text{-}S\ -\ naxX})$] decreases from compounds **1** to **3** (see Fig. 2).

Due to the electronegativity of oxygen, $n_{ax}O$ has much lower orbital energy than $n_{ax}S$ and $n_{ax}Se$. Accordingly, the energy difference between the donor $n_{ax}O$ bonding and the acceptor σ*P-S antibonding orbitals $[\Delta(E_{\sigma^*P\text{-}S}\text{-}n_{ax}O)]$ is greater than the energy difference between the naxS and naxSe nonbonding orbitals. Then, the naxSe nonbonding orbital could be a better electron donor to the σ*C-F antibonding orbitals compared to $n_{ax}S$ and $n_{ax}O$. This fact can also be explained by the profiles of the orbital amplitudes for the mixing of the doubly occupied $n_{ax}O$, $n_{ax}S$ and $n_{ax}Se$ nonbonding orbitals with the adjacent unoccu-



	ΔE(σ*P-S - neqX)	ΔE (σ*P-S - naxX)	ΔE (σ*P-C8-naxX)	ΔE (σ*P-C8 -σX-C6)	ΔE (σ*P-S - σX-C6)	ΔE (σ*P-X - neqS)	ΔE (σ* P-C8 -neqS)
🟦 1(O/S) Eq	0.769	0.537	0.709	1.213	1.041	1.1881	1.0721
🟥 1(O/S) Ax	0.8631	0.6031	0.691	1.186	1.098	1.161	1.06
■ 2(S/S) Eq	0.81	0.404	0.407	0.752	0.75	0.872	0.874
🟧 2(S/S) Ax	0.812	0.392	0.409	0.754	0.738	0.752	0.883
🟦 3(Se/S) Eq	0.884	0.386	0.39	0.698	0.694	0.728	0.876
🟩 3(Se/S) Ax	0.89	0.375	0.389	0.698	0.685	0.725	0.882

Fig. 2. NBO Calculated energy level differences of non-bonding and anti-bonding orbital energies, ΔE_{orb}, for the compounds **1-3** at B3LYP/6-311+G** level.



[a] Overlap matrix elements

Fig. 3. Comparison of profiles of the orbital amplitudes (electron densities) for $n_{ax}X \rightarrow \sigma^*P\text{-}S$ electron delocalization in the compounds **1** to **3**.

pied orbitals of σ*P-S in the axial conformations of compounds **1-3**. The overlap of main lobes of the O nonbonding orbital with the antibonding orbital of P-S bond is greater than the corresponding values for the overlaps between the $n_{ax}S$ and naxSe nonbonding orbitals (nonbonding orbitals) and σ*P-S. The Figs. 3 and 4 show that this trend is observed for mixing of the nonbonding $n_{ax}Se$, $n_{ax}S$ and $n_{ax}O$ orbitals with the antibonding orbitals of P-S.

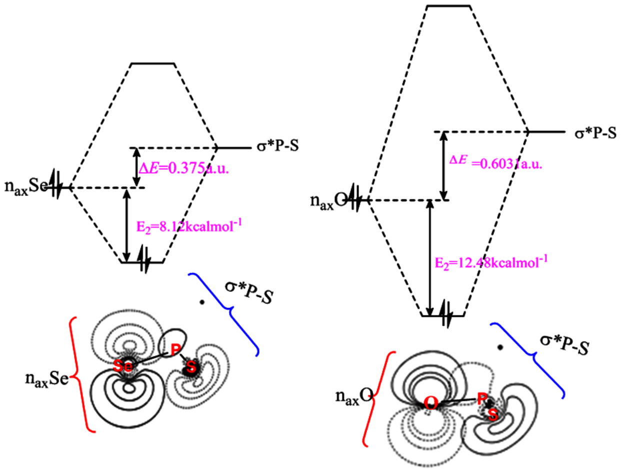
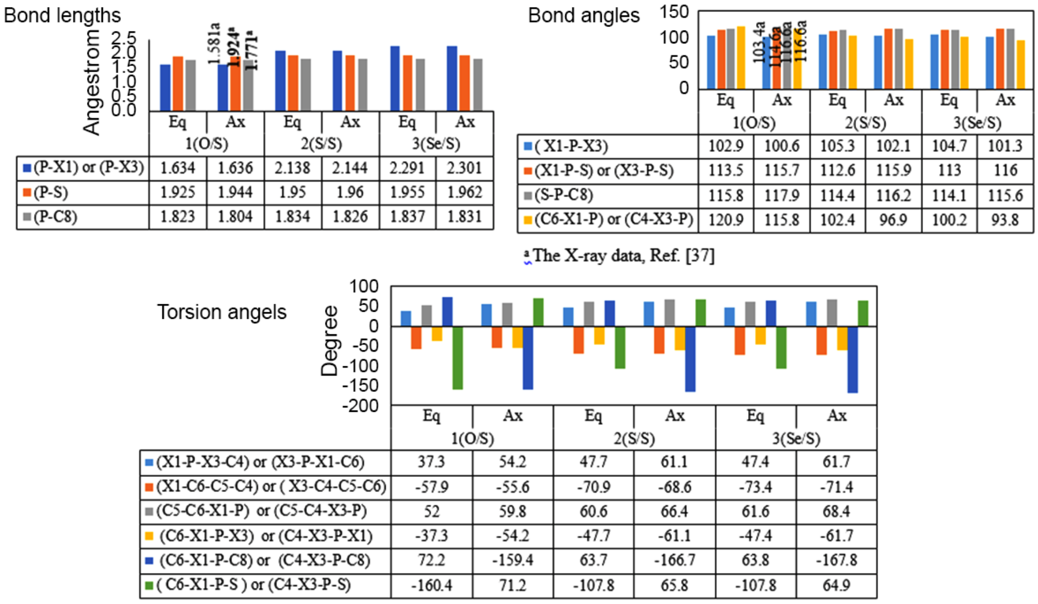


Fig. 4. Representation of the correlations between the second-order perturbation energies (resonance energies, E^2) and the energy gaps between the donor $n_{ax}O$ and $n_{ax}Se$ nonbonding.

The calculated Fij values for $n_{ax}X \rightarrow \sigma^*P\text{-}S$ electron delocalization for the axial conformations of compounds **1-3** are 0.051, 0.039, 0.035 respectively (see Table 2). Since the stabilization energy is proportional to both of the F^2ij and $1/\Delta(E_{acceptor\text{-}donor})$, it seems that in the axial conformations of compounds **1-3**, the Fij values could influence and control the order of the stabilization energy associated with $n_{ax}X \rightarrow \sigma^*_{P\text{-}S}$ electron delocalization. According to this study, the decrease in the Fij value contributes with reduction in the stabilization energy associated with $n_{ax}X \rightarrow \sigma^*P\text{-}S$ electron delocalization from compounds **1** to **3** (see Table 2). The indicative structural parameters for compounds 1 to 3 were calculated using B3LYP/6-311+G** level of theory and are shown in Fig. 5. Remarkably, the P-X and P-C bond lengths are increasing from compound **1** to compound **3**. The increase in P-X bond length of compounds **1** to **3** can be justified with the changes in the stability energy of the $n_{ax}X \rightarrow \sigma^*P\text{-}S$ and



	Eq	Ax	Eq	Ax	Eq	Ax
	1(O/S)		2(S/S)		3(Se/S)	
■ (P-X1) or (P-X3)	1.634	1.636	2.138	2.144	2.291	2.301
■ (P-S)	1.925	1.944	1.95	1.96	1.955	1.962
■ (P-C8)	1.823	1.804	1.834	1.826	1.837	1.831

	Eq	Ax	Eq	Ax	Eq	Ax
	1(O/S)		2(S/S)		3(Se/S)	
■ (X1-P-X3)	102.9	100.6	105.3	102.1	104.7	101.3
■ (X1-P-S) or (X3-P-S)	113.5	115.7	112.6	115.9	113	116
■ (S-P-C8)	115.8	117.9	114.4	116.2	114.1	115.6
■ (C6-X1-P) or (C4-X3-P)	120.9	115.8	102.4	96.9	100.2	93.8

[a] The X-ray data, Ref. [37]

	Eq	Ax	Eq	Ax	Eq	Ax
	1(O/S)		2(S/S)		3(Se/S)	
■ (X1-P-X3-C4) or (X3-P-X1-C6)	37.3	54.2	47.7	61.1	47.4	61.7
■ (X1-C6-C5-C4) or (X3-C4-C5-C6)	-57.9	-55.6	-70.9	-68.6	-73.4	-71.4
■ (C5-C6-X1-P) or (C5-C4-X3-P)	52	59.8	60.6	66.4	61.6	68.4
■ (C6-X1-P-X3) or (C4-X3-P-X1)	-37.3	-54.2	-47.7	-61.1	-47.4	-61.7
■ (C6-X1-P-C8) or (C4-X3-P-C8)	72.2	-159.4	63.7	-166.7	63.8	-167.8
■ (C6-X1-P-S) or (C4-X3-P-S)	-160.4	71.2	-107.8	65.8	-107.8	64.9

Fig. 5. B3LYP/6-311+G** Calculated structural parameters for the equatorial and axial conformations of compounds **1-3**.

n_{eq}S→σ*P-X electron delocalization in axial conformations and σX-C→σ*P-S electron delocalization in the equatorial conformations. Also, the variation of P-C bond length corresponds to the variation of the stability energy of n_{eq}S→σ*P-C electron delocalization in axial conformations (see Fig. 5).

Importantly, the results obtained from X-ray are in agreement with the results obtained in this study for compound **1** [23]. It is interesting to note that as the internal bonding angle of X_1-P-X_3 is smaller than the ideal tetrahedron angle, the phosphorus atom will have less inhibition than a linear phosphonate, then the electrophilic center will be more accessible (see Fig. 5). The value of bonding angle of X_1-P-X_3 is increasing from compound **1** to compound **2**, and it is decreasing from compound **2** to compound **3**. So that the bonding angle of O-P-O in **1**-ax has the lowest value. That is, the phosphorus atom in this compound is a good electrophilic center. In contrast, the phosphorus atom in compound **2**-eq is not a good electrophilic center. From compounds **1** to **3** the C_6-X-P angle is contracting and X_1-P-X_3-C_4 dihedral angle is expanding the ring. Therefore, these structural parameters variations in axial and equatorial conformations justify electrostatic and stereoelectronic interactions. The radius of the heteroatom inside the ring increase as O→S→Se, then the steric effect reduces from compound **1** to **3**. However, the thermodynamic parameters indicate that steric effects do not play a role in justifying the conformational behavior of compounds **1** to **3**, and they are dominated by stereoelectronic effects for justifying the conformational behavior.

CONCLUSION

The DFT, ab-initio and NBO analysis calculations has been used to the inquiry of the structural and conformational behaviors of titled compounds. According to the result of research, stereoelectronic effect in the axial conformations of compounds **1** to **3** is more effective than for corresponding equatorial conformations. These results are in accordance with the values of thermodynamic and structural parameters. The results of thermodynamic parameters show that steric effects have any role in justification of the conformational behavior of titled compounds and stereoelectronic effects are dominant on steric effects in justification of conformational behaviors. In other words, conformational preference is better explained in terms of AE rather than electrostatic and steric effects.

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