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Energetical and structural investigation for equatorial/axial conversion of different substituents on piperidine and phosphorinane: A theoretical study

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ABSTRACT

Equatorial/axial conversion in piperidine and phosphorinane with different substituents were investigated with great details. Three possible routes, i.e. heteroatom inversion and two ring inversion type were considered. Ring conversion can occur via two pathways one starts with ring flattening from the heteroatom site (nitrogen in piperidine and phosphorous in phosphorinane) and the other initiates by ring flattening in the C4 position, facing the nitrogen/ phosphorous site. Density functional theory calculations are applied at B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) level. The feasibility of equatorial/axial conversion for the substituted piperidine rings was found to be in the order of H>CH_3>Cl~OH~F, whereas for phosphorinane it turns out to be as F>OH>Cl~ H~CH_3. In the piperidine derivatives hydrogen and methyl substituents the atom inversion route is dominant process while the other substituents (Cl, F, OH) one of the two possible ring inversion is favored. For the phosphorinane, however, ring inversion is the favored route for all substituents.

Keywords: Equatorial/axial equilibrium; Piperidine; Phosphorinane; Ring inversion; DFT

INTRODUCTION

Several structural studies have been performed on piperidine present in biosystems [1-3]. It is present in alkaloids [4], analgesic drugs [5], and anti-diabetes drugs [6] Phosphorinane systems are famous among the biomolecules as well [7,8].

Various methods have been used to analyze structural energy profiles [9-19]. Computaitonal investigation on small mimics of the biomolecules have greatly been used to both determine the energy surface and intermediate structures [9-11], and to refer the consequences on the macromolecule in order to get a improve information of the biological character of the system. Most of the computational research however have been widely concentrated on the relative equatorial/axial stabilities with different

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substituents [13,20-29] and anomeric effects [19].

In this research, we present a widely investigation of different routes and related energy profiles for both piperidine and phosphorinane derivatives with various substituents such as hydrogen, methyl, chlorine, hydroxyl and fluorine. We have used DFT calculations to elaborate relative equatorial/axial stabilities in these systems. It has been appeared that while piperidine is much dependant on substituents to prefer between ring inversion and nitrogen inversion pathways, phosphorinane relies on ring inversion mechanism.

COMPUTATIONAL DETAILS

At different theoretical studies it has been shown that density functional methods specially the hybrid density functional methods, in particular B3LYP, yield geometrical results that are comparable to those obtained by perturbational methods like MP2 for example [19,25-29].

However in some investigation it has been reported that methods based on DFT such as B3LYP underestimate the barrier of reaction yet these are mostly concerned with processes involving breaking and formation of chemical bonds [30,31]. Considering these points, all optimized geometries and their harmonic vibrational frequency were obtained at B3LYP level [32-34], without any symmetrical constraining by using a restricted formalism. The final energies were reported at B3LYP [32-34].

All structural, vibrational frequencies and energetical insight of piperdine were obtained by using the 6-31G(d) basis set for all atoms. [35,36] IRC calculations have been performed to check the smooth connection of the all obtained transition states structures to the minima.

Thermodynamical corrections assuming ideal gas and rigid rotor approximation resulting from a standard statistical method have been calculated [37]. All computations have been performed using Gaussian 09 suite of programs [38].

RESULT AND DISCUSSION

To search for the minima and related transition states for connect the minima in the potential energy surface ten cyclic derivatives categorized in two main groups, i.e. group of piperidines and group of phosphorinane, have been studied (Fig. 1). The relative energy values and Full analysis of the preferred routes from equatorial to axial conformers will be presented in the following.

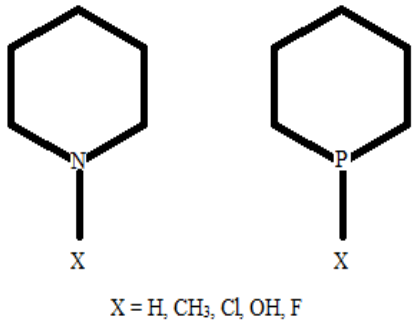


Fig. 1. Piperidine, phosphorinane and their derivatives considered in this work.

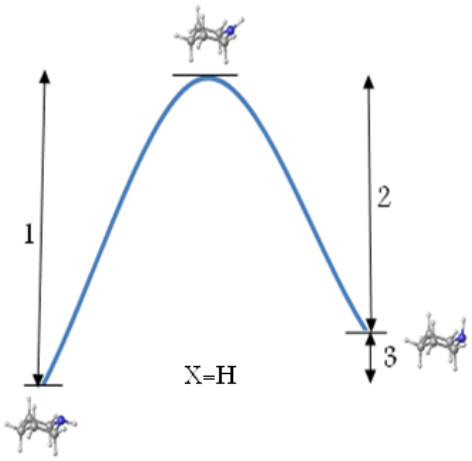
One step pathway

Herein, a simple nitrogen (phosporous) inversion is considered. Criteria for determine the most favored route will be determined according to the energy demand of the related pathway.

Piperidines

As shown in Fig. 2, equatorial structure is converted to the axial structure via a planar transition state. Note that the above conversion is a one step process. In all derivatives of piperidine the equatorial conformer is more stable than the axial one. For founding transition state in this pathway, one could lifted a point that for

all the derivatives the pyramidal nitrogen is flattened. Energy difference between Eq-Ax (3 in Fig. 2) is the lowest when the substituent is hydrogen and the highest when it is hydroxyl group.



		ΔE_0	ΔG	ΔH			ΔE_0	ΔG	ΔH
X=H	1	3.59	3.56	3.57	X=OH	1	15.15	15.23	14.92
	2	2.91	2.92	2.86		2	9.04	8.98	8.92
	3	0.68	0.64	0.71		3	6.11	6.25	6.00
X= CH_3	1	7.36	7.12	7.30	X=F	1	18.16	17.66	18.18
	2	3.48	3.24	3.40		2	16.64	16.11	16.66
	3	3.88	3.88	3.89		3	1.52	1.55	1.52
X=Cl	1	11.85	11.91	11.6					
	2	9.84	9.84	9.69					
	3	2.01	2.07	1.98					

Fig. 2. Equatorial/axial conversion through atom inversion pathway for H, CH3, Cl, OH, F substituents. Energies unit is kcal/mol. levels of theory: A = B3LYP/6-311+G(d,p)//B3LYP/6-31G(d).

As can be seen in Fig. 2 in this pathway when the substituent is hydrogen, transition barrier is low, about 3.6 kcal/mol then the conversion is easily accessible. With move to more electronegative substituent the energy barrier of this route is increase. Change of substituent to hydroxyl and fluorine will increase the destabilizing coulomb repulsion between lone pairs of substituent and nitrogen in the transition state. Schematic picture and structural parameters in Eq(1), Ts(2) and Ax(3) conformer of each derivatives in atom inversion of piperidine is shown in Fig. 3 and Table 1.

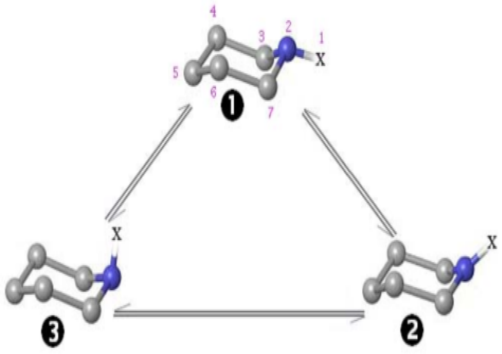


Fig. 3. Shematic picture of Equatorial/axial conversion through atom inversion pathway for X, substituents (X= H, CH_3, Cl, OH, F). 1, 2 and 3 represent Eq, TS and Ax conformers, respectively.

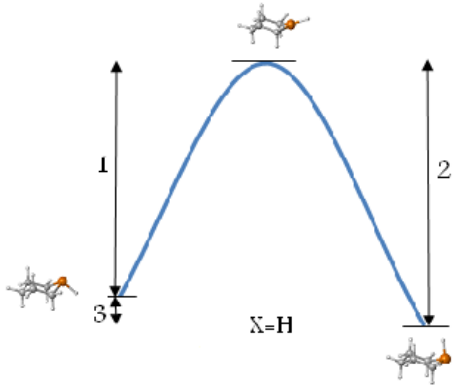
Table 1. Structural parameters of present conformers in atom inversion pathway of piperidine derivatives. Distances reported at A° and unit of angles is degree

		1(Eq)	2(TS)	3(Ax)
X=H	N_2-H_1	1.01	1.00	1.02
	C_7- N_2-H_1	110.53	120.62	109.80
X=F	N_2-F_1	1.45	1.41	1.46
	C_7- N_2-F_1	104.17	114.37	103.74
X=Cl	N_2-Cl_1	1.79	1.72	1.82
	C_7- N_2-Cl_1	108.45	119.53	109.04
X=OH	N_2-OH_1	1.45	1.40	1.46
	C_7- N_2-OH_1	106.58	118.89	106.82
X=CH3	N_2-$CH3_1$	1.45	1.44	1.46
	C_7- N_2-$CH3_1$	111.86	123.03	114.09

Phosphorinane

By replacing the nitrogen with phosphorous one would expect a different behavior due to both larger steric bulk of the phosphorous atom relative to nitrogen. Most interesting point is that the axial substituents are the unstable conformers relative to equatorial one except when the substituent is methyl (Fig. 4). But for a more convenient comparison the equatorial/axial conversion in all

derivatives will be considered from equatorial to axial form.



		ΔE_0	ΔG	ΔH			ΔE_0	ΔG	ΔH
X=H	1	36.29	36.25	36.24	X=OH	1	55.50	55.65	55.11
	2	37.97	37.98	37.91		2	56.03	56.14	55.66
	3	1.69	1.72	1.67		3	0.54	0.49	0.55
$X=CH_3$	1	41.13	40.36	41.10	X=F	1	61.96	61.88	61.77
	2	40.49	39.75	40.44		2	63.05	62.88	62.91
	3	-0.6	-0.61	-0.66		3	1.09	0.99	1.13
X=Cl	1	55.49	55.44	55.49					
	2	56.27	56.13	56.27					
	3	0.79	0.69	0.79					

Fig. 4. Equatorial/axial conversion through atom inversion pathway for H, CH_3, Cl, OH, F substituents. Energies unit is kcal/mol. levels of theory: A = B3LYP/6-311+G(d,p)//B3LYP/6-31G(d).

As can be shown in Fig. 4 in this route when the substituent is hydrogen, transition barrier is low, about 36 kcal/mol then the conversion is easily accessible relative to other in this route. Similarly to piperidine with move to more electronegative substituent the energy barrier of this route is increase. It seems that the steric effect of phosphorous cause to the barriers be larger than from similar case in piperidine (see Fig 2 and 4). Similarly Change of substituent to hydroxyl and fluorine will increase the destabilizing coulomb repulsion between lone pairs of substituent and nitrogen in the transition state. Schematic picture and structural parameters in Eq(1), Ts(2) and Ax(3) conformer of each derivatives in atom inversion of phosphorinane is shown in Fig. 5 and Table 2.

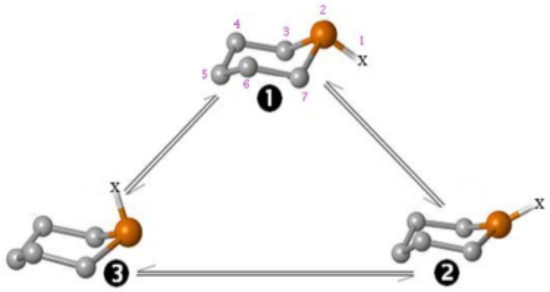


Fig. 5. Shematic picture of Equatorial/axial conversion through atom inversion pathway for X, substituents (X= H, CH_3, Cl, OH, F). 1, 2 and 3 represent Eq, TS and Ax conformers, respectively.

Table 2. structural parameters of present conformers in atom inversion pathway of phosphorinane derivatives. Distances reported at A° and unit of angles is degree

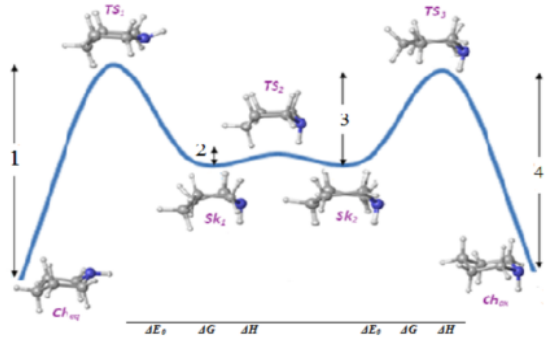
		1	2	3
X=H	P_2-H_1	1.43	1.39	1.43
	C_7-P_2-H_1	98.35	123.73	96.67
X=F	P_2-F_1	1.63	1.62	1.64
	C_7- P_2-F_1	99.87	119.70	98.45
X=Cl	P_2-Cl_1	2.1	2.05	2.12
	C_7- P_2-Cl_1	100.44	121.09	100.42
X=OH	P_2-OH_1	1.68	1.66	1.69
	C_7- P_2-	99.92	121.67	99.49
X=CH3	P_2-$CH3_1$	1.86	1.84	1.87
	C_7- P_2-	100.67	123.83	101.42

Ring inversion pathways

Piperidine

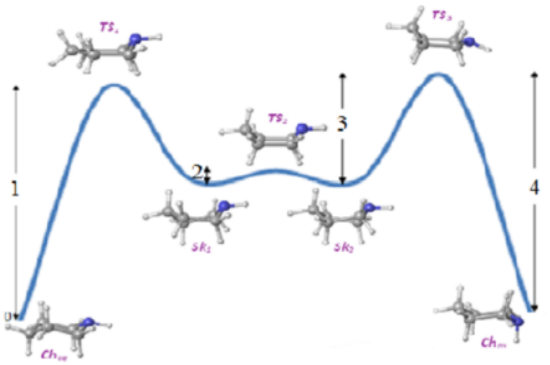
Ring inversion can occur via two pathways one starts with ring flattening from the heteroatom site (nitrogen in piperidine and phosphorous in phosphorinane) and the other initiates by ring flattening in the C4 position, facing the nitrogen site. The schematic representation of such conversions is shown in Figs. 6 and 7

along with energy barriers values at B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) level.



		ΔE_0	ΔG	ΔH			ΔE_0	ΔG	ΔH
X=H	1	10.81	10.27	10.88	X=OH	1	13.98	13.99	13.77
	2	0.49	1.14	0.01		2	0.71	1.22	0.26
	3	4.62	4.63	4.29		3	3.92	3.51	3.71
	4	10.49	10.02	10.37		4	9.76	9.09	9.68
X=CH_3	1	11.27	10.47	11.41	X=F	1	17.13	17.62	18.16
	2	1.27	1.90	0.79		2	0.54	1.01	0.12
	3	3.48	3.69	3.09		3	4.21	4.08	3.94
	4	9.62	9.37	9.45		4	9.77	9.41	9.64
X=Cl	1	14.11	13.50	14.11					
	2	0.85	1.42	0.39					
	3	2.99	3.12	2.65					
	4	9.47	9.22	9.33					

Fig. 6. The schematic representation of ring inversion that starts with ring flattening from the nitrogen site. Barrer energies are in kcal/mol at the B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) level.



		ΔE_0	ΔG	ΔH			ΔE_0	ΔG	ΔH
X=H	1	10.45	10.08	10.31	X=OH	1	10.43	9.82	10.35
	2	0.49	1.00	0.04		2	0.58	1.15	0.12
	3	4.32	4.17	4.19		3	6.65	6.78	6.29
	4	10.13	9.63	10.17		4	11.51	11.16	11.38
X=CH_3	1	10.51	9.96	10.38	X=F	1	10.30	9.74	10.19
	2	0.54	1.12	0.06		2	0.49	1.11	0.00
	3	5.00	4.60	4.94		3	6.80	7.79	5.93
	4	7.39	6.59	7.52		4	12.40	12.	11.74
X=Cl	1	10.54	9.93	10.44					
	2	0.47	1.09	0.01					
	3	7.34	7.49	7.08					
	4	12.18	11.80	12.18					

Fig. 7. The schematic representation of ring inversion which initiates by ring flattening in the C4 position, facing the nitrogen site. Energies are in kcal/mol at the B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) level.

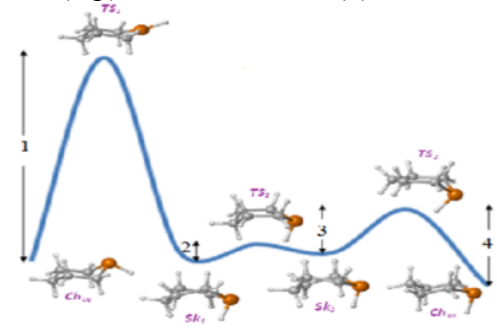
Ring inversion from the nitrogen site will first put the nitrogen atom in the plane of four adjacent carbons and the substituent will be also in this plane as one reaches the envelopes form in the transition state (TS1) and then as the ring will reach the first potential energy well, the $skew_1$ intermediate is formed. $Skew_1$ intermediate can go to another intermediate $skew_2$ by gaining less than 1 kcal/mol (at B3LYP level) by passing through a boat transition state (TS2). It is noticeable that skew conformers (skew1 and skew2) are mirror images of each other and have same energies. Now the substituent is in axial position and the $skew_2$ form can pass through a final transition state (TS3) to reach the chair conformer with the substituent on the axial position (Fig. 6).

Ring inversion from the C4 site have also four steps (Fig. 7). But the first step has rather nothing to do with the hetero atoms (nitrogen in piperidine and phosphorous in phosphorinane) and the substituent on it. Here again the first minimum is an envelope and then it goes to skew minima. By passing through the TS3 the substituent on nitrogen will reach an axial position and the chair conformer with axial substituent will be formed (Fig. 7). As can be seen in the Figs. 6 and 7 the rate determining step for both ring inversion pathways is the first step to attain an envelope structure. By comparison Figs. 6 and 7 it appears that ring inversion from the nitrogen site is energetically more demanding than the C4 site ring inversion. Because present of the nitrogen site ring flipping steric factors between hetero atom and substituent will be probable. As depicted in Fig. 6, by moving from hydrogen to fluorine the barrier height increase in the first step transition state (TS1) however this increase is slower than the one in nitrogen atom inversion process (see Fig. 2) . It is because here the nitrogen

is moving into the plane of the four carbon atoms in the envelope form. The two remaining steps are not the rate determining step. The second step is the conversion of mirror image skew intermediates, with the boat transition state (TS2) standing in between them. The final barrier is caused by another envelope to reach the final axial chair conformer and it barely exceeds 7.4 kcal/mol (Figs. 6 and 7). So far it has been deduced that for hydrogen and methyl the favored pathway is nitrogen atom inversion with barriers of 3.6 and 7.4 kcal/mol, respectively (Fig. 2). But for other substituents the preferred route is the C4 site ring inversion route with a rate determinig barrier of nearly 10.5 kcal/mol for all the three substituents (Fig. 7).

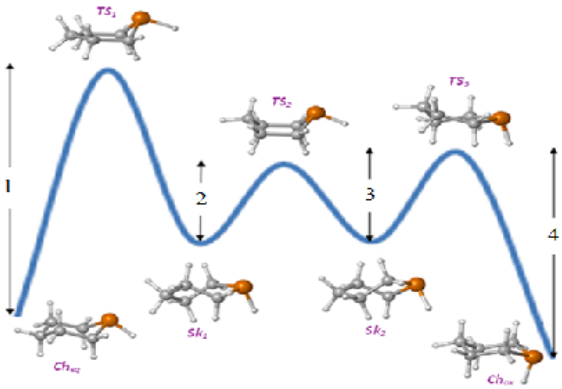
Phosphorinane

The schematic representation of two pathways of phosphorinane ring inversion is shown in Figs. 8 and 9 along with energy barriers values at B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) level.



		ΔE_0	ΔG	ΔH			ΔE_0	ΔG	ΔH
X=H	1	8.1	36.36	36.28	X=OH	1	7.02	6.91	6.77
	2	1.31	1.67	0.91		2	1.36	1.65	1.01
	3	7.02	6.88	6.74		3	6.77	5.97	6.54
	4	12.20	11.75	12.07		4	11.74	10.74	11.61
X=CH_3	1	8.21	8.22	7.91	X=F	1	5.96	6.12	5.63
	2	2.21	2.58	1.78		2	1.11	1.37	0.76
	3	7.00	6.96	6.74		3	3.29	3.30	2.96
	4	12.27	11.87	12.13		4	3.93	3.94	3.60
X=Cl	1	7.55	7.49	7.27					
	2	1.79	2.10	1.44					
	3	6.38	6.10	6.14					
	4	11.70	11.20	11.58					

Fig. 8. The schematic representation of ring inversion that starts with ring flattening from the nitrogen site. Barrier energies are in kcal/mol at the B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) level.



		ΔE_0	ΔG	ΔH			ΔE_0	ΔG	ΔH
X=H	1	11.51	11.45	11.28	X=OH	1	11.29	10.90	11.14
	2	3.75	4.22	3.36		2	3.15	3.68	2.77
	3	4.12	4.28	3.78		3	3.94	4.20	3.58
	4	9.34	9.23	9.11		4	8.26	8.18	8.01
X=CH_3	1	11.23	11.11	11.04	X=F	1	11.31	11.03	11.13
	2	2.79	3.22	2.43		2	3.69	4.32	3.28
	3	4.24	4.48	3.85		3	3.57	3.86	3.19
	4	7.90	7.95	7.59		4	8.05	7.89	7.82
X=Cl	1	11.27	11.04	11.09					
	2	3.53	3.95	3.18					
	3	4.39	4.51	4.05					
	4	8.94	8.80	8.70					

Fig. 9. The schematic representation of ring inversion which initiates by ring flattening in the C4 position, facing the nitrogen site. Energies are in kcal/mol at the B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) level.

Ring inversion from the phosphorous site will first put the phosphorous atom in the plane of four adjacent carbons like what shown in piperidine and the substituent will be also in this plane as one reaches the envelopes form in the transition state (TS1) and then as the ring will reach the first potential energy well, the $skew_1$ conformer is formed. $Skew_1$ can go to another intermediate $skew_2$ by gaining less than 3 kcal/mol (at B3LYP level) by passing through a boat transition state (TS2). Now the substituent is in axial position and the $skew_2$ form can pass through a final transition state (TS3) to reach the chair conformer with the substituent on the axial position (Fig. 8).
Inversion from the C4 site has also four steps (Fig. 9). But the first step has rather nothing to do with the hetero atoms (phosphorous) and the substituent on it.

Here again the first minimum is an envelope and then it goes to skew minima. By passing through the TS3 the substituent on phosphorous will reach an axial position and the chair conformer with axial substituent will be formed (Fig. 9). As can be seen in the Figs. 8 and 9 the rate determining step for both ring inversion pathways is the first step to attain an envelope structure. By comparison Figs. 8 and 9 it appears that ring inversion from the nitrogen site is feasible than the C4 site ring inversion. This result is in contrast to what obtain for piperidine. It can be suggests that the favorite route for all the substituents is the phosphorous site ring inversion. It seems that phosphorous hybridization will be slightly affected in this route and the substituent here in contrast to nitrogen containing homologues tends not to lie in the C-P-C plane but rather moves directly to the axial position. As shown in Fig. 8 with move to more electronegative substituent the rate determining energy barrier is slightly decrease.

CONCLUSIONS

Three possible routes for the conversion of equatorial/axial forms in piperidine and phosphorinane derivatives with substituents comprising hydrogen, methyl, chlorine, hydroxyl and fluorine were considered. These routes are including atom inversion of nitrogen or phosphorous and two ring inversion types, one starting from the heteroatom and the other from the C4 site (the carbon opposite to the heteroatom). The atom inversion pathways is a one step conversion while the ring invertion types are three step conversions with the first step being the rate determining step in all cases. In all the investigated substituents for the piperidine and phosphorinane rings the equatorial forms were found to be more stable, while in phosphorinane with only methyl substituent axial conformer is more stable than equatorial one.

For piperidine rings the following trend was found ($H>CH_3>Cl\sim OH\sim F$) while for the phosphorous bearing six-membered rings the order turns out to be ($F>OH>Cl>H\sim CH_3$) at B3LYP levels. Moreover, for the piperidine system hydrogen and methyl substituents preferred the atom inversion while the others favored C4 site ring inversion. In case of, however, phosphorous retards atom inversion in equatorial/axial equilibrium and phosphorous site ring inversion was found as the favored route for all substituents.

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