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## A Computational Study on the Configurational Behaviors of Dihalodiazenes and their Analogues Containing P and As Atoms

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In this research, we report the results of DFT calculations using xc-hybrid functional, B3LYP and employ NBO interpretation to investigate the stereoelectronic effects. Electrostatic and steric impacts on the conformational properties of 1,2-difluorodiazene (1), 1,2-dichlorodiazene (2) and 1,2-dibromodiazene (3) are also studied. Factors determining the thermodynamically stable molecular structure of 1,2-dihalodiazenes and their analogues containing P and As atom are discussed, and the energetic effects of intra-molecular hyperconjugations and steric repulsion in each molecular system are theoretically estimated using NBO theory. The Energy components calculated help us to justify the conformational behaviour of our target compounds. One of the interesting features extracted from NBO analysis is that dissociation energies are controlled by the stabilization energies associated with electron delocalizations in these compounds. The main parameter considered in this study is the Gibbs free energy estimated for *cis* and *trans* configurations of compounds and for the *cis*-to-*trans* conversion through rotation and inversion mechanisms.

**Keywords:** Hybrid density functional theory, Stereoelectronic effect, NBO

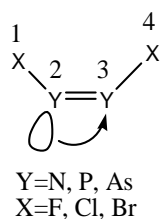
### INTRODUCTION

*N=N double bond* is highly considered in general organic chemistry, and molecules containing this kind of di-nitrogen bond are of considerable interest in this field. As an example, we can refer to the diarylazo compounds, using as dyes and pH indicators [1-2], diethyl azodicarboxylate (DEAD), reacting with phosphine in Mitsunobu reaction [3-7]. Furthermore, azobisisobutyronitrile (AIBN) is used as a radical initiator, which is decomposed into nitrogen and two cyanoisopropyl radicals by heating or light-irradiation.

Most of molecules possessing *N=N* bond are known to be stable under normal conditions and employed for many purposes. Accordingly, identification of the electronic structure and the factors governing their geometries have

gained lots of attention in recent decades. Among dihalodiazenes, 1,2-difluorodiazene (1) is known to be much more stable than 1,2-dichlorodiazene (2) [8], conversely, nothing has been reported on the stability of 1,2-dibromodiazene (3) in the experimental and theoretical literature [9]. There is no a comprehensive information about the relative stability of compounds containing nitrogen atom with coplanar lone pair (LP) on an adjacent heteroatom. This deficiency has been also documented by investigations on the general aspect of tautomerism especially in heterocyclic systems with two adjacent nitrogens and/or further heteroatoms [10-11]. The energetic relationship between different isomers of substituted diazenes, *cis* and *trans*, has been increasingly interested to understand the first step of Mitsunobu reaction [12-14]. Additionally, evaluating the *cis* effect observed for the reactive azenes is required [15], which cannot be efficiently modeled by semi empirical methods, so our first priority is

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Scheme 1. Numbering used for compounds 1-6

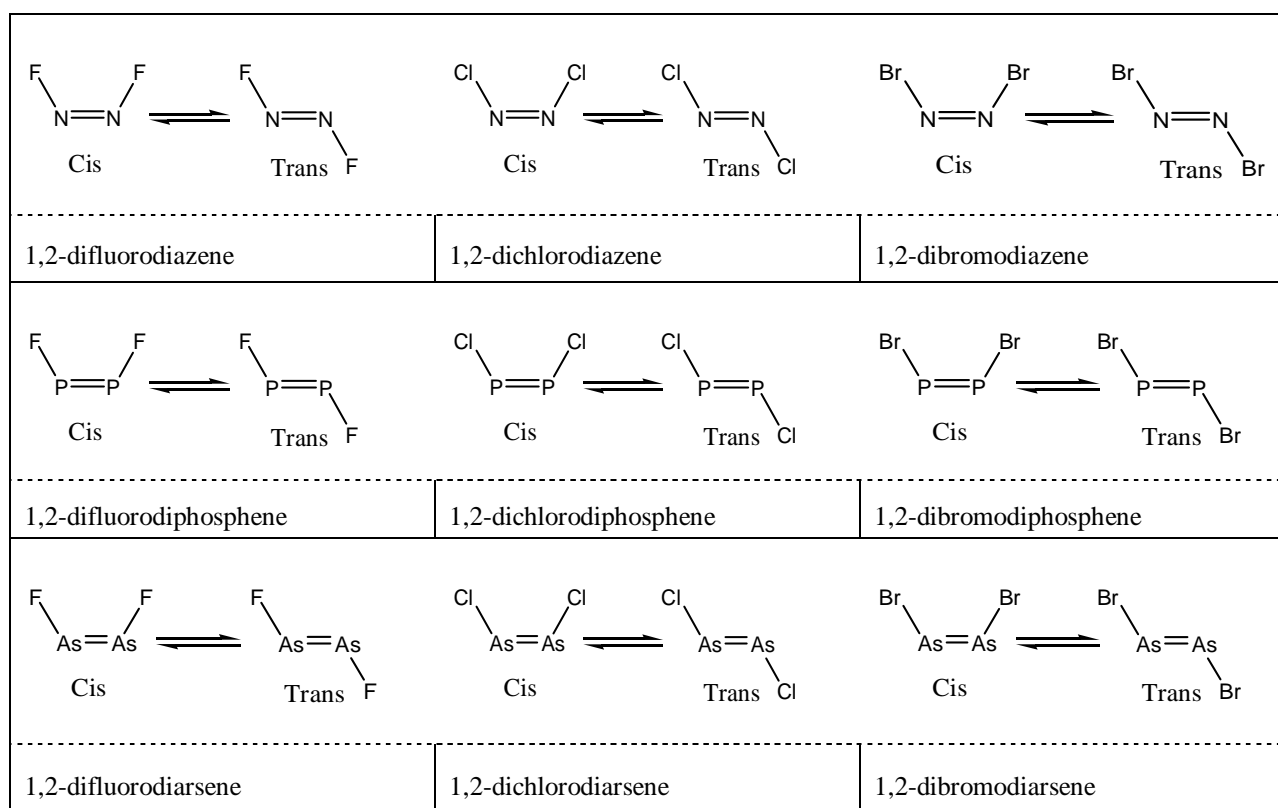
to simulate the phosphorylation step.

In this paper, the Gibbs free energy is examined as a proximate factor influencing the stability of *cis* and *trans* isomers of dihalodiazenes. In this regard, high-level density functional theory (DFT) combined with natural bond orbital (NBO) calculations are used to analyze dihalodiazenes and their analogues containing P and As atoms (See Scheme 1).

## THEORETICAL BACKGROUND

### Computational Details

Calculations of the electronic structures and thermodynamic parameters have been performed at the framework of DFT level embedded in the Gaussian 03 program [16]. This procedure was carried out using B3LYP exchange-correlation functional [17-19], within the hybrid generalized gradient approximation (hybrid-GGA) [18-19], and the Def2-TZVPP basis set [20]. Accordingly, the optimization procedure was performed on the initial estimated structures for compounds 1-9 at B3LYP/Def2-TZVPP level of theory, without imposing symmetry constraints. The most stable molecular geometry with the lowest energy state was located by comparing total energies. Frequency calculation has performed to ensure the nature of stationary points for compounds 1-9; for minimum state



Scheme 2. Schematic representation for the various conformations of dihalodiazenes and their analogs containing P and As atom

structures, only real frequency values are accepted [21-22]. We also employed NBO analysis [23] to evaluate the correlation between the electronic properties and energy components. NBO makes this interpretation more comprehensible through transforming the delocalized molecular orbitals into localized equivalents.

### Theoretical Framework

The non-Lewis delocalization shown within donor-acceptor charge transfers can be estimated from off-diagonal elements of the Fock matrix in the NBO basis. The bonding and antibonding orbital occupancies in the global and local minimum structures of dihydroxymethane, and also the stabilization energies associated with electron delocalizations are calculated using NBO analysis [24-25]. The second-order stabilization energies in the charge transfer list are proportional to  $S^2/\Delta E$ ; where  $S$  is the orbital overlap and  $\Delta E$  is the energy differences between two interacting orbitals [26]. The second-order perturbation ( $E_2$ ) for  $i \rightarrow j$  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,  $\varepsilon_i$ ,  $\varepsilon_j$  are diagonal elements (orbital energies), and  $F(i,j)$  is off-diagonal elements of the NBO Fock matrix. Obviously, there is a direct relationship between  $F(i,j)$  and orbital overlap ( $S$ ). Our recent works have shown that the NBO analysis is a reasonable approach to investigate the stereoelectronic effects on the reactivity and dynamic behaviors of chemical compounds [27-29].

## RESULTS AND DISCUSSION

### Thermodynamic Parameters

In this research, selected DFT method was used to evaluate the Gibbs free energy for both *cis* and *trans* configurations of all compounds 1 to 9, and their conversion to each other through rotation (1) and inversion (2) mechanisms.

The DFT results at B3LYP/Def2-TZVPP level [30], including the Gibbs free energy differences,  $\Delta G$ , enthalpy

and entropy differences,  $\Delta H$  and  $\Delta S$ , for the dihalodiazenes and their analogs containing P and As atoms are listed in Tables 1, 2 and 3. The noticeable feature is that the *cis* configuration of compounds 1 to 3 is more stable than their *trans* counterparts, by 1.93, 4.57 and 5.16 kcal mol<sup>-1</sup>, respectively. While, the amount of the Gibbs free energy to convert *cis* to *trans* form in compound 1 through mechanism (1) is 65.94 kcal mol<sup>-1</sup>, this value drops to 59.85 kcal mol<sup>-1</sup> for the same compound through mechanism (2). The corresponding quantity for compound 2 through mechanism (1) is equal to 32.62 kcal mol<sup>-1</sup>, and for mechanism (2) is equivalent to 31.65 kcal mol<sup>-1</sup>; these values are decreased to 20.57 and 18.62 kcal mol<sup>-1</sup> for compound 3, respectively. So, the Gibbs free energy differences between the mechanisms 1 and 2 are 6.09 kcal mol<sup>-1</sup>, 1.37 kcal mol<sup>-1</sup>, and 1.95 kcal mol<sup>-1</sup> for compounds 1, 2 and 3, respectively. It can be concluded that conversion of *cis* into *trans* conformation is performed *via* the mechanism which needs less energy, mechanism (2), for compounds 1 to 3. This conclusion can be easily recognized from the energy diagram of mechanisms (1) and (2) for the compounds 1, shown in Scheme 3. To sum up, it is expected that the conversion of *cis* to *trans* counterpart in these compounds is carried out *via* inversion mechanism. The stability of *cis* conformer and its conversion into *trans* form by inversion mechanism are observed in all cases, 1 to 9.

The same conclusion can be drawn for 1,2-dihalodiphosphene and 1,2-dihalodiarsene, Tables 2 and 3. Another significant feature worth mentioning is that the Gibbs free energy changes are in the line of *cis* stability, which is inconsistent with increasing the size of halogen atom from F to Br; so, other factors affecting the stability of *cis* orientation.

### Dipole Moments

Dipole moment can provide information on stability of the various conformations of chemical compounds [31]. Generally, conformation with the larger dipole moment, in the gas phase, has the larger electrostatic energy, which leads to an increase in the total energy. On this basis, we have performed molecular dipole moment calculation using DFT to gain insight into the stability of our systems.

Obtained results show that the dipole moment is not a determining factor in configuration properties of the

**Table 1.** Calculated Enthalpy, Gibbs Free Energy, and Entropy (H, G, S) for Dihalodiazenes and their Differences at B3LYP/Def2-TZVPP Level [ $\Delta H$ ,  $\Delta G$  (in hartree) and  $\Delta S$  (in cal mol<sup>-1</sup> K<sup>-1</sup>)]

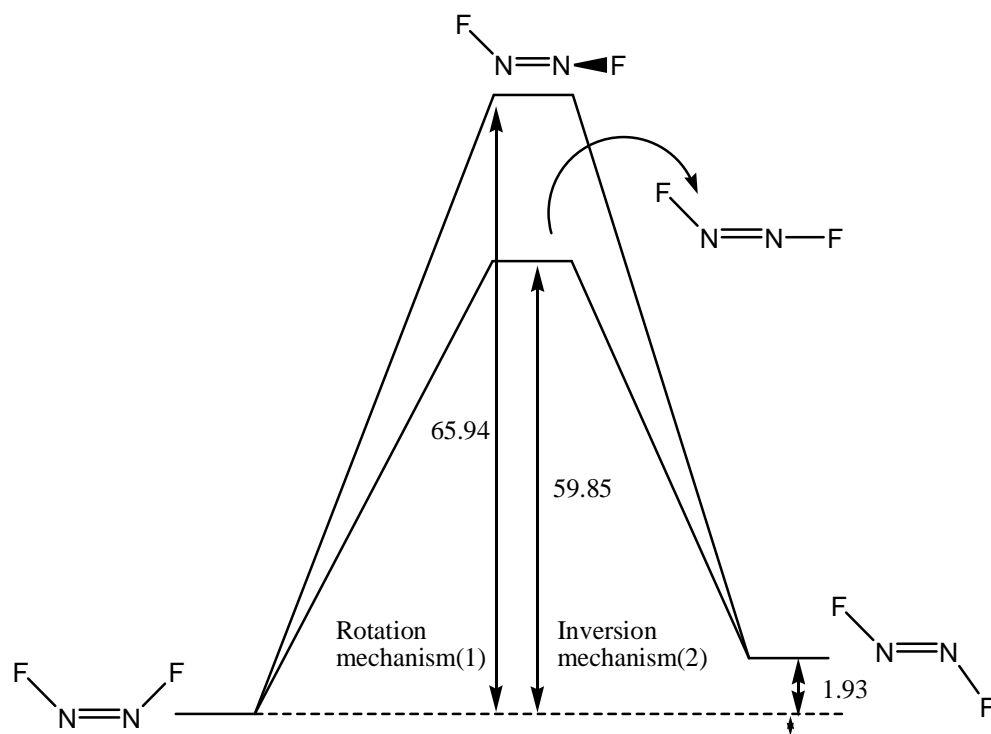
	H (hartree)	S (cal mol <sup>-1</sup> K <sup>-1</sup> )	G (hartree)	$\Delta H$ (hartree)	$\Delta S$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G$ (hartree)
Geometries						
N <sub>2</sub> -F <sub>2</sub> - <i>Trans</i>	-309.137913	62.484	-309.167601	0.002941 (1.84)	0.0000	0.003074 (1.93)
N <sub>2</sub> -F <sub>2</sub> - <i>Cis</i>	-309.140854	62.762	-309.170675	0.0000 (0.000)	0.2780	0.0000 (0.000)
N <sub>2</sub> -F <sub>2</sub> -TS-1	-309.034657	65.114	-309.065594	0.10619 (66.64)	2.6300	0.105081 (65.94)
N <sub>2</sub> -F <sub>2</sub> -TSD	-309.044039	65.802	-309.075303	0.096815 (60.75)	3.3180	0.095372 (59.85)
N <sub>2</sub> -Cl <sub>2</sub> - <i>Trans</i>	-1029.883328	68.752	-1029.915994	0.007044 (4.420)	0.0000	0.007213 (4.57)
N <sub>2</sub> -Cl <sub>2</sub> - <i>Cis</i>	-1029.890372	69.106	-1029.923207	0.0000 (0.000)	0.3540	0.0000 (0.000)
N <sub>2</sub> -Cl <sub>2</sub> -TS-1	-1029.835644	74.887	-1029.871225	0.054728 (34.34)	6.1350	0.051982 (32.62)
N <sub>2</sub> -Cl <sub>2</sub> -TSD	-1029.834915	70.946	-1029.868624	0.050676 (31.80)	2.1940	0.04980 (31.25)
N <sub>2</sub> -Br <sub>2</sub> - <i>Trans</i>	-5257.813569	75.777	-5257.849573	0.008193 (5.14)	0.0000	0.008225 (5.16)
N <sub>2</sub> -Br <sub>2</sub> - <i>Cis</i>	-5257.821762	75.844	-5257.857798	0.0000 (0.000)	0.0670	0.0000 (0.000)
N <sub>2</sub> -Br <sub>2</sub> -TS-1	-5257.789631	81.180	-5257.828203	0.032131 (20.16)	5.4030	0.032780 (20.57)
N <sub>2</sub> -Br <sub>2</sub> -TSD	-5257.790005	80.230	-5257.828124	0.031757 (19.98)	4.4530	0.029674 (18.62)

**Table 2.** Calculated Enthalpy, Gibbs Free Energy, and Entropy (H, G, S) for Dihalodiphosphene and their Differences at B3LYP/Def2-TZVPP Level [ $\Delta H$ ,  $\Delta G$  (in hartree) and  $\Delta S$  (in cal mol<sup>-1</sup> K<sup>-1</sup>)]

	H (hartree)	S (cal mol <sup>-1</sup> K <sup>-1</sup> )	G (hartree)	$\Delta H$ (hartree)	$\Delta S$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G$ (hartree)
Geometries						
P <sub>2</sub> -F <sub>2</sub> - <i>Trans</i>	-882.137913	67.344	-882.167601	0.003527 (2.21)	0.000	0.004374 (2.74)
P <sub>2</sub> -F <sub>2</sub> - <i>Cis</i>	-882.14144	67.752	-882.171975	0.0000 (0.00)	0.408	0.0000 (0.00)
P <sub>2</sub> -F <sub>2</sub> -TS-1	-882.021207	73.124	-882.048594	0.120233 (75.45)	5.780	0.123381 (77.42)
P <sub>2</sub> -F <sub>2</sub> -TSD	-882.034129	73.812	-882.063303	0.107311 (67.33)	6.468	0.11 (68.19)
P <sub>2</sub> -Cl <sub>2</sub> - <i>Trans</i>	-1603.87831	74.344	-1603.87821	0.012054 (7.56)	0.000	0.012154 (7.63)
P <sub>2</sub> -Cl <sub>2</sub> - <i>Cis</i>	-1603.89037	74.742	-1603.89037	0.0000 (0.00)	0.398	0.0000 (0.00)
P <sub>2</sub> -Cl <sub>2</sub> -TS-1	-1603.83436	78.126	-1603.83216	0.0560076 (35.14)	3.782	0.0582076 (36.52)
P <sub>2</sub> -Cl <sub>2</sub> -TSD	-1603.83865	78.815	-1603.83765	0.051717 (32.45)	4.471	0.052717 (33.08)
P <sub>2</sub> -Br <sub>2</sub> - <i>Trans</i>	-5831.80569	82.344	-5831.8147	0.017172 (10.77)	0.000	0.018163 (11.40)
P <sub>2</sub> -Br <sub>2</sub> - <i>Cis</i>	-5831.82286	82.731	-5831.83286	0.0000 (0.00)	0.387	0.0000 (0.00)
P <sub>2</sub> -Br <sub>2</sub> -TS-1	-5831.77362	88.118	-5831.78093	0.064241 (30.89)	5.774	0.069325 (43.58)
P <sub>2</sub> -Br <sub>2</sub> -TSD	-5831.77962	88.730	-5831.78271	0.063233 (27.12)	6.386	0.066146 (31.46)

**Table 3.** Calculated Enthalpy, Gibbs Free Energy, and Entropy (H, G, S) for Dihalodiarsene and their Differences at B3LYP/Def2-TZVPP Level [ $\Delta H$ ,  $\Delta G$  (in hartree) and  $\Delta S$  (in  $\text{cal mol}^{-1} \text{K}^{-1}$ )]

	H (hartree)	S ( $\text{cal mol}^{-1} \text{K}^{-1}$ )	G (hartree)	$\Delta H$ (hartree)	$\Delta S$ ( $\text{cal mol}^{-1} \text{K}^{-1}$ )	$\Delta G$ (hartree)
Geometries						
<i>As<sub>2</sub>-F<sub>2</sub>-Trans</i>	-4671.14763	93.344	-4671.13210	0.00911 (5.72)	0.000	0.009174 (5.75)
<i>As<sub>2</sub>-F<sub>2</sub>-Cis</i>	-4671.15674	93.752	-4671.14125	0.0000 (0.00)	0.408	0.0000 (0.00)
<i>As<sub>2</sub>-F<sub>2</sub>-TS-1</i>	-4671.02107	96.124	-4671.00109	0.13567 (85.13)	2.780	0.140181 (87.96)
<i>As<sub>2</sub>-F<sub>2</sub>-TSD</i>	-4671.03511	97.812	-4671.01790	0.12163 (76.32)	4.468	0.123372 (77.42)
<i>As<sub>2</sub>-Cl<sub>2</sub>-Trans</i>	-5392.87430	98.344	-5392.87251	0.017104 (10.73)	0.000	0.017854 (11.20)4
<i>As<sub>2</sub>-Cl<sub>2</sub>-Cis</i>	-5392.89141	98.742	-5392.89037	0.0000 (0.00)	0.398	0.0000 (0.00)
<i>As<sub>2</sub>-Cl<sub>2</sub>-TS-1</i>	-5392.82436	101.936	-5392.82116	0.067048 (42.07)	3.592	0.0692076 (43.43)
<i>As<sub>2</sub>-Cl<sub>2</sub>-TSD</i>	-5392.82965	104.815 103.815	-5392.82815	0.061757 (38.75)	6.471	0.062217 (39.04)
<i>As<sub>2</sub>-Br<sub>2</sub>-Trans</i>	-9741.78799	107.344	-9741.80644	0.023972 (15.04)	0.000	0.026416 (16.58)
<i>As<sub>2</sub>-Br<sub>2</sub>-Cis</i>	-9741.81196	107.791	-9741.83286	0.0000 (0.00)	0.447	0.0000 (0.00)
<i>As<sub>2</sub>-Br<sub>2</sub>-TS-1</i>	-9741.75511	111.998	-9741.77481	0.056843 (35.67)	4.654	0.058044 (36.42)
<i>As<sub>2</sub>-Br<sub>2</sub>-TSD</i>	-9741.76153	115.930	-9741.78099	0.050423 (31.64)	8.586	0.051866 (32.55)



Scheme 3. Energy diagram for  $N_2F_2$  at the B3LYP/Def2-TZVPP level of theory

**Table 4.** Calculated Dipole Moment of Dihalodiazenes and their Analogs Containing P and As Atoms at B3LYP/Def2-TZVPP Level

μ (Debye)	$N_2-F_2-Trans$	0.0000	$\Delta\mu =$	$P_2-F_2-Trans$	0.0000	$\Delta\mu =$	$As_2-F_2-Trans$	0.0000	$\Delta\mu =$
	$N_2-F_2-Cis$	0.1235	0.1235	$P_2-F_2-Cis$	1.3483	1.3483	$As_2-F_2-Cis$	3.0415	3.0415
	$N_2-Cl_2-Trans$	0.0000	$\Delta\mu =$	$P_2-Cl_2-Trans$	0.0000	$\Delta\mu =$	$As_2-Cl_2-Trans$	0.0000	$\Delta\mu =$
	$N_2-Cl_2-Cis$	0.5853	0.5853	$P_2-Cl_2-Cis$	0.7203	0.7203	$As_2-Cl_2-Cis$	2.1208	2.1208
	$N_2-Br_2-Trans$	0.0000	$\Delta\mu =$	$P_2-Br_2-Trans$	0.0000	$\Delta\mu =$	$As_2-Br_2-Trans$	0.0000	$\Delta\mu =$
	$N_2-Br_2-Cis$	0.4213	0.4213	$P_2-Br_2-Cis$	0.4786	0.4786	$As_2-Br_2-Cis$	1.1280	1.128

**Table 5.** Stabilization Energies ( $E2$ , in kcal mol<sup>-1</sup>), Estimated From the NBO Perturbation Theory and Generalized Anomeric Effect ( $GAE$ , in kcal mol<sup>-1</sup>)

E2	N <sub>2</sub> F <sub>2</sub>		N <sub>2</sub> Cl <sub>2</sub>		N <sub>2</sub> Br <sub>2</sub>	
	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>
donor → acceptor						
LP <sub>1X1</sub> → σ* <sub>N3-X4</sub>	-	-	0.62	-	0.57	-
LP <sub>2X1</sub> → σ* <sub>N3-X4</sub>	1.95	-	1.23	-	0.69	-
LP <sub>3X1</sub> → σ* <sub>N3-X4</sub>	-	-	-	-	-	-
LP <sub>1X1</sub> → σ* <sub>N2=N3</sub>	-	-	-	1.69	-	2.30
LP <sub>2X1</sub> → σ* <sub>N2=N3</sub>	-	-	3.19	3.02	2.34	0.78
LP <sub>3X1</sub> → σ* <sub>N2=N3</sub>	16.02	17.93	-	-	-	-
LP <sub>1X1</sub> → π* <sub>N2=N3</sub>	-	-	-	-	-	-
LP <sub>2X1</sub> → π* <sub>N2=N3</sub>	3.26	5.42	-	-	-	-
LP <sub>3X1</sub> → π* <sub>N2=N3</sub>	-	-	11.09	12.84	5.97	7.83
σ <sub>N2-F1</sub> → σ* <sub>N3-X4</sub>	6.38	2.31	15.19	4.65	27.37	13.36
LP <sub>N2</sub> → σ* <sub>N3-X4</sub>	3.05	16.77	0.72	22.81	-	22.83
Σ	28.71	42.43	30.19	45.01	35.68	44.8
<i>GAE</i>	-13.72			-14.28		-9.12

compounds under study. For *cis* conformer, molecular dipole moment is enhanced from compounds 1 to 2, while a reduction in dipole is observed for compound 3 compared to that for compound 2. Accordingly, it is expected that the Gibbs free energy difference between *cis* and *trans* forms increases in favor of *trans* counterparts from compounds 1 to 2, and decreases from compounds 2 to 3, while this trend was not observed. Therefore, the Gibbs free energy difference in these compounds may be derived from a confrontation between the total anomeric effects and dipole moments (see Table 4).

### Anomeric Effect

It is generally accepted that the increment in anomeric

effect is associated with the increase in stability of the system under consideration [32-33]. In this research, factors impacting the structural and configuration properties of 1,2-difluorodiazene (1), 1,2-dichlorodiazene (2) and 1,2-dibromodiazene (3) have been analyzed by hybrid density functional and natural bond orbital (NBO) analyses. Findings show that, in spite of space repulsion in *cis* configuration, this conformer is more stable than *trans* counterpart of compounds 1 to 3. The Gibbs free energy differences between these two configurations ( $\Delta G_{\downarrow}(trans - cis)$ ) follow a rising trend from compounds 1 to 3, 4 to 6 and 7 to 9. The NBO results indicate that anomeric effect of electron transfer in *cis* form of compounds 1 to 3 is greater than that for *trans* form. In this regard, total anomeric effect



is increased from compounds 1 to 2 (-13.72 → -14.28), conversely, decreased from compounds 2 to 3 (-14.28 → -9.12). Therefore, it is expected that the presence of dipole moment in *cis* form makes this conformer more unstable than *trans* ones, contrary to what was observed based on the Gibbs free energy comparison, Table 5. This behavior is also observed for dihalodiphosphene and dihalodiarsene systems; for dihalodiphosphene, total anomeric effect is increased from compound 4 to 5 (-13.21 → -13.92) and decreased from compound 5 to 6 (-13.92 → -8.16). Additionally, for dihalodiarsene, this quantity exhibits an increasing change from compound 7 to 8 (-10.16 → -12.11), and a decreasing trend from compound 8 to 9 (-12.11 → -7.91).

## CONCLUSIONS

In this research, factors impacting the structural and configuration properties of 1,2-difluorodiazene (1), 1,2-dichlorodiazene (2) and 1,2-dibromodiazene (3) were analyzed by hybrid-GGA calculations at the framework of DFT and natural bond orbital (NBO) analysis. The obtained results suggest that in spite of space repulsion in *cis* configuration, this form is more stable than *trans* configuration in compounds under consideration. The Gibbs free energy difference, between *cis* and *trans* configurations ( $\Delta G_{\downarrow}(\text{trans-cis})$ ), is increased from compound 1 to 3, 4 to 6 and 7 to 9. While, it can be expected that the presence of a dipole moment in *cis* forms makes them more unstable than *trans* forms of compounds 1 to 3, which is not in agreement with our findings based on Gibbs free energy calculations. To sum up, the dipole moment is not a determining factor for conformational properties of the compounds 1 to 9, and the Gibbs free energy difference between *cis* and *trans* forms in these compounds may be derived from a confrontation between the total anomeric effects and dipole moments mechanisms. The results derived from NBO indicate that anomeric effects of electron transfer in *cis* forms in compounds 1 to 3 are greater than those for the corresponding *trans* ones. In this regard, total anomeric effects are increased from compound 1 to 2, and decreased from compound 2 to 3. The results of the Gibbs free energy for *cis* and *trans* conformations of compounds 1 to 9, and their conversion through rotation (1) and inversion (2) paths

indicate that the *cis* configuration is more stable than the *trans* configuration in the compounds 1 to 9. Also, the conversion of the *cis* configuration to the corresponding *trans* configuration is performed through mechanism (2) which needs less amount of energy. The same conclusion is drawn for dihalodiphosphene and dihalodiarsene systems.

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