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An ab initio study and natural bond orbital (NBO) of the effective factors on the isomerization of halo carbonyl phospha-keten and their analoga containing As atom

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Abstract: The conformational behavior and structural stability of halo carbonyl phosphaketen derivatives (FC(O)PCO) and their analoga containing As atom (FC(O)AsCO), [F-P(**1**), Cl-P(**2**), Br-P(**3**), F-As(**4**), Cl-As(**5**), Br-As(**6**)] were investigated by means of G3MP2, CCSD, MP2 and B3LYP methods set on all atoms and natural bond orbital (NBO) interpretation. Calculations were done using 6-311+G** basis set. All methods showed that the Z-conformations of compounds **1**, **2**, **3**, **4**, **5** and **6** are more stable than their corresponding E conformations, but the stability of the Z conformations, when compared with the corresponding E conformations, increases from compound **1** to compound **3** and also from compound **4** to compound **6.** The behaviors of compounds **1-6** have been reasonably explained by their generalized anomeric effects (GAE), the electrostatic model associated with the dipole–dipole interactions (EM-DDI), resonance energy and the attractive electrostatic interactions (AEI).The correlations between the generalized anomeric effects (GAE), dipole–dipole interactions, donor and acceptor orbital energies and occupancies, structural parameters and conformational behavior of compounds **1–6** have been investigated.

Keywords: Halo carbonyl phospha-keten, Hyper-conjugative generalized, Natural bond orbital, Anomeric effects, Dipole moment changes.

Introduction

In 1989 the conformational properties chlorocarbonyl isocyanate and the geometric parameters have been studied by Mack et al. He used gas electron diffraction (GED) a mixture of *Trans* and cis isomers in a ratio of ca. 3: 1 ($\Delta G=0.7$ kcal mol^{-1}). Calculations with different basis set (4-31G*, 6-31G* and D95*) and at various levels of theory (HF, MP2 and MP4SDTQ) predict the cis form to be more stable, whereas experiments demonstrate the *Trans* isomer to be more stable [1].

In 1991 ab initio calculations at the MP2/6-31G(2d), MP2/6-31G(d) level of theory predict that the trans conformation of chlorocarbonyl isocyanate is 0.73 kcal/mol lower in energy than the cis isomer [2]. Joans and Frenking showed good agreement in experimentally obtained by gas-phase infrared and electron-diffraction experiments [2]. In the same year, Nguyen and co-workers investigated the conformational analysis of chlorocarbony isocyanate. Their results show that ab initio molecular orbital (MO) calculations are more reliable in predicting the trans conformer being the more stable, in agreement with experiment and this is a positive answer to the question of Mack et al, “How reliable are ab initio calculations?” The failure of the calculations by Mack to reproduce the cis-

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trans separation gap might be due to the geometrical parameters employed in their work. Nguyen employed the MP2/6-31G (d, p) optimized geometries, which show the cis conformers are predicted to have slightly higher stabilities than the trans conformers [3]. Afterward Hans- Georg Mack and Heinz Oberhammer' reported the geometric structure of acetyl isocyanatehas been determined based on electron diffraction intensities and rotational constants. In accordance with previous vibrational studies, only the cis conformation is observed. Ab initio quantum-mechanical calculations predict the preference of the cis form by 3.8 kcal mol^{-1}, (HF/6-31G*) and 2.4 kcal mol^{-1}, (MP2/6-31G*) [4].

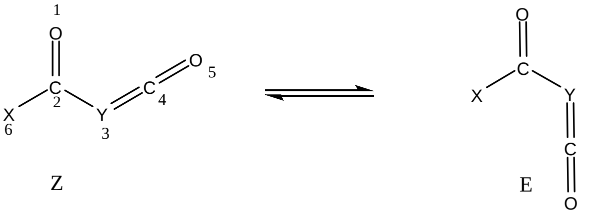
Sullivan and co-workers show that the fundamental Kaman frequencies and Raman intensities which have been determined experimentally are compared to those obtained from ab initio Hartree-Fock gradient calculations utilizing the 6-31G* basis set. These results are compared to some previous results on this molecule [5].

In 1993, Hans-Georg Mack reported the geometric structures and conformational compositions of fluorocarbonyl isocyanate and fluorocarbonyl azide by gas electron diffraction, vibrational spectroscopy. Fluoro carbonyl isocyanate and fluoro carbonyl azide, corresponding ab initio calculations are not stable and cannot be studied in the gas phase. The experiments illustrate the predominance of the cis conformation. The energy differences predicted by ab initio calculations depend on the level of the theory applied. Whereas HF/6-31G* and MP2/6-31G* approximations overestimates the energy differences between the two rotamers, MP2/6-3lG*//HF/6-31G* and MP4SDTQ/6-3lG*//HF/6-31G* calculations reproduce the experimental values within their error limits 6].Variable temperature infrared spectroscopy of chlorocarbonyl isocyanate and the effect of polarizable substituents on the conformations of carbonyl isocyanates and isothiocyanates were studied by Dieter Klapstein. The highest ability of the transoid conformation forchloro carbonyl isocyanate and bromo carbonyl isocyanate as well as for chloro carbonyl isothiocyanateis and bromo carbonyl isothiocyanateis attributed to the high polarizabilities of the halogen atoms and explained as an electrostatic interaction between the heavy halides and the isocyanato carbon atom in the transoid conformation. The limitations of ab initio calculations in predicting the relative stabilities and infrared frequencies of these molecules are discussed [7]. A series of carbonyl isothiocyanates and acetyl isothiocyanate have been examined by infrared and Raman spectroscopies. The IR data reveal the presence of more than one conformational isomer for all carbonyl isothiocyanates but not for acetyl isothiocyanate. The relative stabilities of the cisoid and transoid isomers have been deduced by variable temperature spectroscopy and semi empirical MO calculations. The conformational conclusions are very similar to those found for the corresponding carbonyl isocyanates [8].

In 2012, D. Nori Shargh showed that there are intriguing through space electron delocalizations (the charge transfer from the lone pairs of the halogen atoms into the anti bonding orbitals of the carbonyl groups of the isocyanate fragments) which are responsible for the increase of the stability of the trans-conformations, compared to their corresponding cis conformations ongoing from fluorocarbonyl isocyanate (1) to bromocarbonyl isocyanate (3) [9].

After that, in 2016, we showed that the cis-conformations of halocarbonyl isocyanates are more stable than their correspondingtrans-conformations. Effectively, the trans-conformation stability compared with its cis-conformation increases on going from compound **1** to **3** and from compound **4** to **6**. It is worth noting that the HC-GAE is in favor of the cis-conformations of compounds **1** and **4** but its effects on the conformational preferences of the trans-forms increase from compound **1** to **3** and from compound **4** to **6**. This fact is in the line with the published experimental data concerning the conformational preferences in compounds **1–3**. The hyper conjugative interactions are the main ones responsible for the generalized anomeric effects in the acyclic planaranomers. Importantly, the deletions of bond $LPN_3 \rightarrow 6^*_{C2-X6}$ hyperconjugative interactions from the Fock matrices of the cis and trans-conformations lead to the increase of the cis conformations' stability compared with their corresponding trans-conformations [10].

In this work, we examined the impacts of the hyper conjugative generalized anomeric effects, the electrostatic model associated with the dipole-dipole interactions and the attractive electrostatic interactions between the natural atomic charges on the conformational properties of halocarbonyl phospha-keten [halogen= F(**1**), Cl(**2**), Br(**3**)] and their analoga containing As atom[halogen= F(**4**), Cl(**5**), Br(**6**)] (Scheme **1**). The obtained Gibbs free energy, enthalpy and entropy differences (i.e., ΔG, ΔH and ΔS) for the cis and trans-conformations and Ts structures of compounds **1-3** and **4-6** are given in Table **1**. The cis-conformation stability compared with its trans-conformation increase going from compound **1** to **3** and from compound **4** to **6**.



Scheme 1: Schematic representations of compound **1-6** [**1**: X=F,Y=P, **2**: X=Cl,Y=P, **3**: X=Br,Y=P, **4**: X=F,Y=As, **5**: X=Cl,Y=As, **6**: X=Br,Y=As]

Results and discussion

Conformational preference:

The calculated Gibbs free energy, enthalpy, and entropy differences (i.e. ΔG, ΔH, and ΔS) for the cis- and trans-conformations and the transition state of compounds **1–3** and **4–6** calculated at CCSD/6–311+G**, MP2/6–311+G**, B3LYP/6–311+G** and G3MP2 levels of theory, given in Table **1**, So that the most stable stat -cis-conformation- is set to zero and $(\Delta G, \Delta H, \text{and } \Delta S)_{trans}$ is reported from the difference between the trans- and cis-conformation and $(\Delta G, \Delta H, \text{and } \Delta S)_{TS}$ the difference between the transition state and the cis-conformation.

Change in Gibbs free energy determines whether the cis-conformation is more stable ($\Delta G=0$) or the trans-conformation is less stable ($\Delta G>0$). The Gibbs free energy content from compound **1** to **3** and **4** to **6** increases in the trans-conformation. All methods showed that the cis-conformations of compounds **1-3** and **4-6** are more stable than their corresponding trans-conformations. The energy difference between the cis- and trans-conformations of compound **4** is greater than that in compound **1** as calculated at all levels of theory used in this work [6]. The cis-conformation stability compared with its trans-conformation increases going from compound **1** to **3** and from compound **4** to **6** (Table **1**). While this effect can only be described as error compensation, the CCSD method certainly deserves attention in accurate calculations of inappropriate interactions. Surprisingly, compared with the experimental data, the CCSD/6–311+G** level gives an incorrect result for the energy differences between the cis- and trans-conformations of compound **6** (Table **1**).

ΔG_{E-Z}) of compounds **1-3**, **4-6** (Tables **1** and **2**). The stabilization energies associated with $LPY_3\rightarrow\sigma^*_{C2-X6}$ electron delocalizations increase from the trans-conformations of compound **1** to compound **3** are 3.35, 5.65 and 6.63 kcalmol^{-1}, respectively. This trend is also for compounds **4-6** which are 2.29, 4.27 and 5.09 k cal mol^{-1}, respectively. Whereas the stabilization energies associated with $LPY_3\rightarrow\sigma^*_{C2-X6}$ electron delocalizations cannot observe for the cis-conformations. Therefore, the stabilization energies associated with $LPY_3\rightarrow\sigma^*_{C2-X6}$ electron delocalization's cannot observe for the cis-conformations. Therefore, the stabilization energies associated with $LPY_3\rightarrow\sigma^*_{C2-X6}$ electron delocalizations cannot explain the increase of Z corresponding E conformations. There are not the same trends between the stabilization energies associated with $LPY_3\rightarrow\sigma^*_{C2X6}$ electron delocalizations for the trans-conformations of compounds 1-6 and the Gibbs free energy difference values between the E and Z conformations (E_2 and ΔG_{E-Z}) of compounds **1-3**, **4-6** (Tables **1** and **2**).

The total HC-GAE is calculated by the differences between the HC-GAE values of the trans- and cis-conformations [16, 17]:

$$\text{HC-GAE}_{total}=\text{HC-GAE}_{trans}-\text{HC-GAE}_{cis} \qquad (2)$$

The calculated total HC-GAE values associated with $LPY_3\rightarrow 6^*_{C2-O1}$, $LPY_3\rightarrow 6^*_{C2-X6}$, $LP_1O_1\rightarrow 6^*_{C2-Y3}$, $LP_2O_1\rightarrow 6^*_{C2-Y3}$, $LP_1X_6\rightarrow 6^*_{C2-O1}$, $LP_2X_6\rightarrow 6^*_{C2-O1}$, $LP_3X_6\rightarrow\pi^*_{C2-O1}$, $LP_2X_6\rightarrow\pi^*_{C4-O5}$, $LP_1X_6\rightarrow 6^*_{C2-Y3}$ and $LP_2X_6\rightarrow 6^*_{C2-Y3}$ electron delocalizatios.

The calculated HC-GAE differences, $\Delta(GAE_{trans}-GAE_{cis})$, increase from compound **1** to **3** but decrease from compound **4** to **6**. Since the calculated Gibbs-free energy differences between the trans- and cis-conformations, $\Delta(G_{trans}-G_{cis})$, increases from compound 1-3 and from compound **4- 6**. Therefore, the calculated HC-GAE differences between the cis- and trans conformations fails to determining impact on the conformational preferences in compounds **1-3** and **4-6**.

Table 1: G3MP2, CCSD/6-311+G**, MP2/6-311+G**and B3LYP/6-311+G** calculated thermodynamic parameters [ΔH, ΔG (in hartree) and ΔS (in cal $mol^{-1}K^{-1}$)] at 298 K for the cis- and trans-conformations of compounds **1-6**. The cis→$[TS]^{\neq}$→ trans inter conversion processes were only investigated for compounds **1-3**.

	G3MP2			CCSD/6-311+G**			MP2/6-311+G**			B3LYP/6-311+G**		
	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a
Geometries												
1-*cis*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.04	0.07
1-*trans*	0.26	0.12	0.22	0.30	0.15	0.26	0.24	0.15	0.20	0.00	0.00	0.00
1- **1**-*cis*→[*TS*]‡→**1**-	18.0	-	19.3	21.9	-	23.2	17.1	-	18.0	15.7	-	16.6
2-*cis*	0.71	0.25	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-*trans*	0.00	0.00	0.00	1.23	0.26	1.15	0.91	0.08	0.88	0.96	-	1.00
2-*trans* **2**-*cis*→[*TS*]‡→**2**-	10.4	-	11.2	14.8	-	16.1	10.4	-	11.5	8.42	-	9.47
3-*cis*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-*trans*	1.09	0.27	1.02	1.38	0.27	1.30	0.98	0.07	0.96	1.18	-	1.25
3-*trans* **3**-*cis*→[*TS*]‡→**3**-	8.44	0.40	8.33	11.3	-	12.7	6.78	-	7.96	5.71	-	6.92
4-*cis*	0.00	0.00 0	0.00	0.00	0.00 0	0.00	0.00	0.00 0	0.00	0.00	0.00 0	0.00
4-*trans*	0.40	0.10 3	0.37	0.44	0.11 3	0.40	0.05	- 0.15 4	0.09	0.38	0.08 3	0.35
4- **4**-*cis*→[*TS*]‡→**4**-	17.6	-	19.0	21.3	-	22.6	15.3	-	16.4	17.1	-	18.1
5-*cis*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5-*trans*	0.94	0.10	0.91	1.19	0.25	1.18	0.91	-	0.93	1.17	-	1.24
5-*trans* **5***cis*→[*TS*]‡→**5**-	9.87	-	10.6	13.9	-	15.3	10.3	-	11.4	8.19	-	9.32
6-*cis*	0.00	0.00	0.00	0.00	0.00	0.00	0.45	-	0.50	0.47	0.05	0.49
6-*trans*	1.25	0.00	1.25	1.47	-	1.51	1.16	-	1.23	1.55	-	1.71
6-*trans* →[*TS*]‡→**6**- *trans′* **6***cis*→[*TS*]‡→**6**-	7.79	- 3.20 9	8.74	10.4 7	- 4.96 5	11.9 5	6.80	- 4.24 4	8.07	5.58	- 4.59 6	6.95

Orbital occupancies:

The nonbonding orbital occupancies of the Y atoms (LPY3, Y=P, As) in the cis- and trans-conformations of compounds **4-6** is greater than those in compounds **1-3**. As we mentioned above, this fact can be justified by the stronger the $LPO_5 \rightarrow \pi^*_{C4=Y3}$ electron delocalizations in compounds **4-6** compared to the $LPO_5 \rightarrow \pi^*_{C4=Y3}$ hyper-conjugations in compounds **1-3** (Table **2**). It is worth noting that there are significant differences between the $\sigma^*_{C2\text{-}X6}$ anti-bonding orbital occupancies of the cis-conformations of compounds **1-3** and **4-6**. The occupancies of the $\sigma^*_{C2\text{-}X6}$ anti-bonding orbitals increase drastically from the trans-conformations of compound **1** to **3** and also from compound **4** to **6**. This fact can be justified by the increase of the $LPY_3 \rightarrow \sigma^*_{C2\text{-}X6}$ hyper-conjugative interactions ongoing the trans-conformations of compound **1-3** and also from compound **4-6**. The stronger $LPY_3 \rightarrow \sigma^*_{C2\text{-}X6}$ hyper-conjugative interactions deploy more electrons from the donor orbitals (LPN_3) and increase the electronic occupancies of the acceptor orbitals ($\sigma^*_{C2\text{-}X6}$) (Table **2**).

Table 2: NBO-B3LYP/6-311+G** 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 (ε, in a.u.), orbital occupancies (e), natural atomic charges (NAC), dipole moments (μ, in Debye) for the cis- and trans-conformations of compounds **1-6**.

	1		**2**		**3**		**4**		**5**		**6**	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
$LPY_3 \rightarrow \sigma^*_{C2\text{-}O1}$	4.88	-	6.04	-	6.45	-	4.03	-	5.46	-	5.96	-
$LPY_3 \rightarrow \sigma^*_{C2\text{-}X6}$	-	3.35	-	5.65	-	6.63	-	2.29	-	4.27	-	5.09
$LP_1O_1 \rightarrow \sigma^*_{C2\text{-}Y3}$	3.24	2.67	3.53	2.52	3.62	2.50	2.87	2.61	3.24	2.50	3.30	2.46
$LP_2O_1 \rightarrow \sigma^*_{C2\text{-}Y3}$	21.17	18.58	19.85	17.84	18.19	16.97	21.21	20.27	21.34	19.4	19.46	18.47
$LP_1X_6 \rightarrow \sigma^*_{C2\text{-}O1}$	0.64	-	0.85	0.59	0.8	0.53	0.6	-	0.75	0.59	0.74	0.52
$LP_2X_6 \rightarrow \sigma^*_{C2\text{-}O1}$	7.93	8.04	6.17	5.85	4.95	4.55	7.25	7.91	5.99	5.85	4.77	4.58
$LP_3X_6 \rightarrow \pi^*_{C2\text{-}O1}$	26.09	25.67	16.96	16.65	12.78	12.46	22.78	25.69	16.22	16.47	12.1	12.22
$LP_2X_6 \rightarrow \pi^*_{C4\text{-}O5}$	-	2.03	-	3.21	-	3.72	-	1.50	-	2.61	-	3.16
$LP_1X_6 \rightarrow \sigma^*_{C2\text{-}Y3}$	1.02	1.16	1.79	2.05	1.7	1.91	0.97	1.05	1.87	1.99	1.76	1.89
$LP_2X_6 \rightarrow \sigma^*_{C2\text{-}Y3}$	3.41	5.71	1.02	2.66	1.92	1.49	3.54	5.84	0.83	2.58	2.38	1.33
GAE	68.38	67.21	56.21	57.02	50.41	50.76	62.58	67.16	55.70	56.26	50.47	49.72
$GAE_{trans\text{-}cis}$	-1.17		0.81		0.35		4.58		0.56		-0.75	
e												
LP_1Y_3	1.9114	1.9063	1.9121	1.8940	1.9116	1.8870	1.9359	1.9371	1.9406	1.9277	1.9398	1.9219
$\sigma^*_{C2\text{-}X6}$	0.1619	0.1692	0.2013	0.2121	0.2347	0.2503	0.1756	0.1676	0.2118	0.2131	0.2498	0.2536
ε												
LPY_3	-	-	-	-	-	-	-	-	-	-	-	-
$\sigma^*_{C2\text{-}X6}$	0.1828	0.1779	0.0373	0.0325	-	-	0.1413	0.1821	0.0339	0.0349	-	-

$\Delta[\varepsilon(\sigma^*_{C2-X6})$-	0.7283	0.7929	0.5885	0.5770	0.5362	0.5234	0.7226	0.8050	0.6739	0.6678	0.6244	0.6152
F_{ij}												
$LPY_3 \rightarrow \sigma^*_{C2-X6}$	-	0.045	-	0.052	-	0.054	-	0.039	-	0.049	-	0.052
μ	2.485	2.437	2.355	2.299	2.381	2.288	2.634	2.712	2.722	2.608	2.793	2.648
$\Delta(\mu_{trans}$-$\mu_{cis})$	-0.048		-0.057		-0.093		0.079		-0.113		-0.145	
NAC												
X_6	-	-	-	-	-	-	-	-	-	-	-	-
C_4	0.4027	0.3816	0.4048	0.3743	0.4035	0.3751	0.3680	0.3921	0.4108	0.3857	0.4097	0.3865
$\Delta[NAC(X_6)_{trans}$-	0.0023		0.0004		0.0002		0.0080		0.0120		0.0140	
$\Delta[NAC(X_6)_{tra}$	-	0.7514	-	0.4431	-	0.	-	0.7657	-	0.4635	-	0.4422

Dipole moments:

Due to the larger polarizabilities in the conformations with the larger dipole moments, it has been accepted that there are preferences for the conformations with the smallest resultant dipole moments in the gas phase or in the nonpolar media;[18] accordingly, the conformations with the larger dipole moment may have the larger electrostatic energy. The calculated dipole moments for the cis- and trans-conformations of compounds **1-3** and **4-6** are given in Table **2**. The energy difference between the different conformations of a molecule can be explained by the electrostatic, electronic and steric descriptors. In this regard, using the dipole moments obtained, a "Δ" parameter is found as $\Delta(\mu_{trans}-\mu_{cis})$. $\Delta(\mu_{trans}-\mu_{cis})$ parameters for compounds **1-3**and **4-6** possess positive values. Based on the results obtained, $\Delta(\mu_{trans}-\mu_{cis})$ parameter decreases significantly from compound **1** to compound **3**. This trend is also observed for compound **4-6**. The EM-DDI had a determinant impact on the conformational preferences in compounds **1-3** and **4-6**, their cis conformations could be found as their predominant conformations. Since the cis conformations stabilities compared to their corresponding trans-conformations increase from compound **1** to **3** and also from compound **4** to **6**, accordingly, the rationalization of the conformational preference solely in terms of the EM-DDI succeeds in accounting for compounds **1-3** and **4-6** (Tables **1**, **2**).

Structural parameters:

Representative structural parameters (bond lengths, bond angles and torsion angles) for the cis- and trans-conformations of compounds **1-3** and **4-6** as calculated at the CCSD(T), MP2, and B3LYP method with the 6-311+G** on all atoms are summarized in Figures **1, 2**. Although we do not expect to obtain exactly the experimental values by means of the theoretical techniques, it is possible to carry out theoretical calculations to obtain many properties and also structural parameters with an accuracy that is competitive with experiments [10]. It is worth noting that in the trans-conformations of compounds **1-3** and **4-6**, the X-C-Y bond angles are bigger than their corresponding cis conformations. $LPY_3 \rightarrow 6^*_{C2-O1}$ electron delocalizations which increase in the cis-conformations of compounds **1-3** and **4-6** compared to those in their corresponding trans-conformations justify the bigger X-C-Y bond angles in the trans-conformations than those in their corresponding cis-conformations (Figures **1**,**2**).

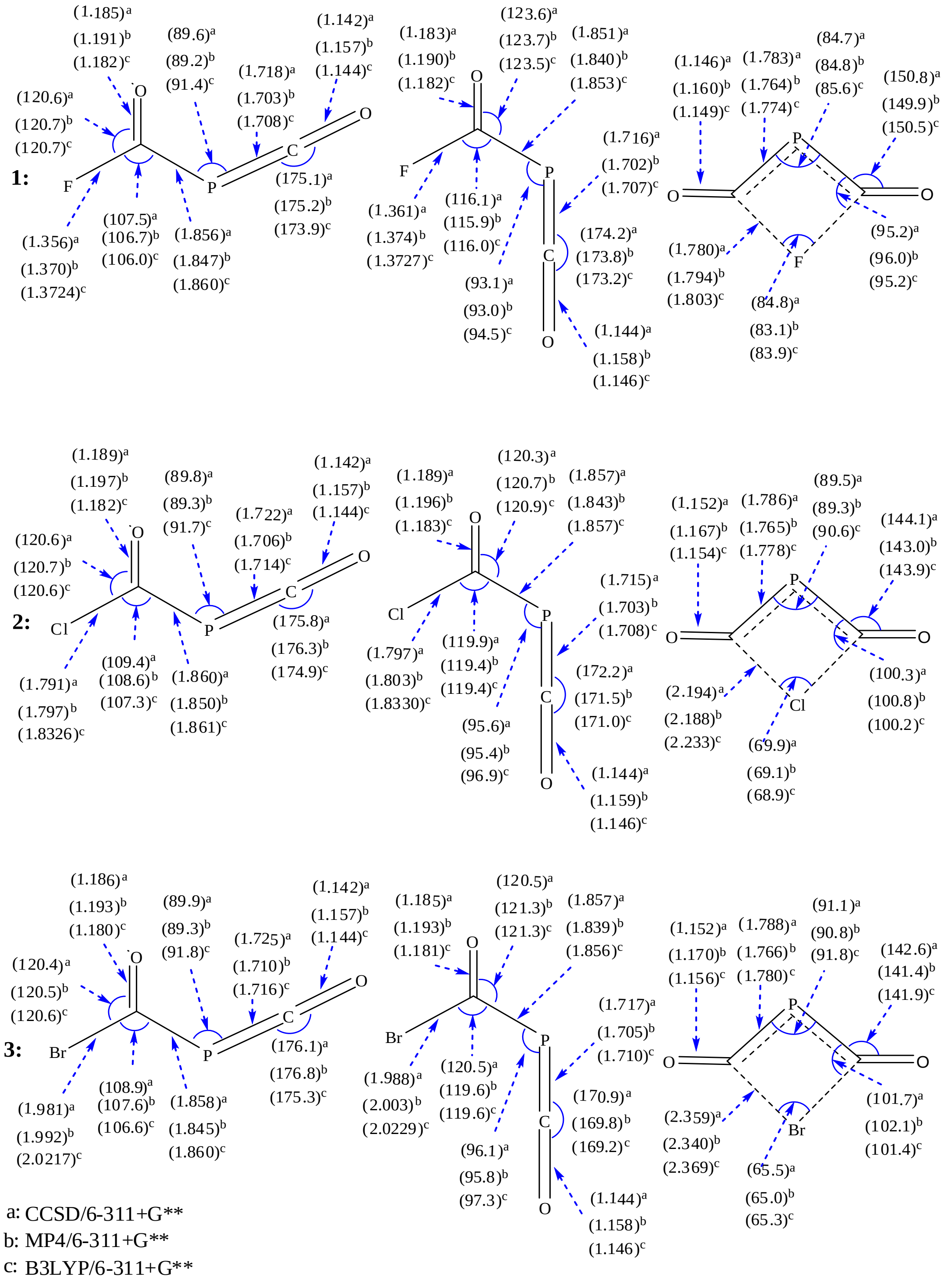


Figure 1: (a) CCSD/6–311G**, (b) MP2/6–311G** and (c) B3LYP/6–311G** calculated structural parameters of the cis-and trans-conformations of compounds **1–3**.

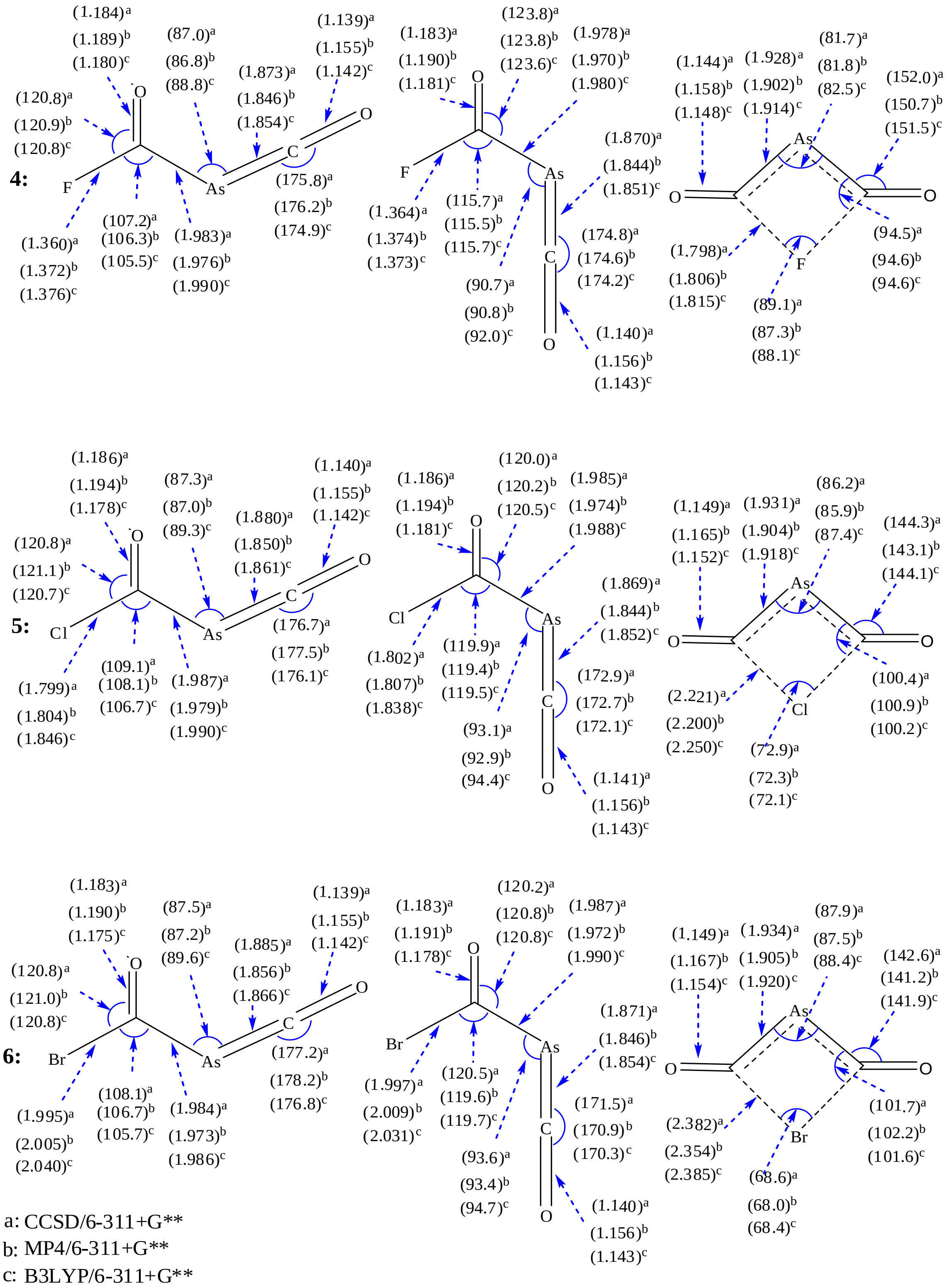


Figure 2: (a) CCSD/6–311G**, (b) MP2/6–311G** and (c) B3LYP/6–311G** calculated structural parameters of the cis- and trans-conformations of compounds **4**–**6**.

onclusions

The G3MP2, CCSD, MP2 and B3LYP calculations reported above and the natural bond orbital interpretations provided a reasonable picture from energetic, structural, bonding and stereo electronic points of view for compounds **1-3** and **4-6**. All methods used in this work showed that the cis-conformations of compounds **1-3** and **4-6** are more stable than their corresponding trans-conformations. Effectively, the cis-conformation stability compared to its trans-conformation increases ongoing from compound **1-3** and also from compound **4-6**. The dipole–dipole repulsion effects decrease from compound **1** to compound **3**, increases compound **4** to compound **6** but the total dipole moment changes ($\Delta\mu_{E-Z}$), decrease from compound **1-3** and **4-6**. There is a direct correlation between the calculated GAE and ($\Delta\mu_{E-Z}$) parameters. Accordingly, $\Delta\mu_{E-Z}$ succeeds in accounting for the increase of the cis-conformation stability from compound **1** to compound **3** and compound **4** to compound **6**. The GAE values calculated (ΔGAE_{E-Z}) increase from compound **1** to compound **3** but decreases compound **4** to compound **6**. Therefore, there are none of the same trends between the calculated GAE values and the Gibbs free energy difference values between the cis- and trans-conformations (ΔGAE_{E-Z} and ΔG_{E-Z}) of compounds **1-3**, **4-6**. Importantly, non bonded lone pairs of the P,As atoms and the anti-bonding orbitals ($LP_1Y_3 \rightarrow 6*_{C2-O1}$) that justify the increase of the cis-conformation stability from compound **1** to compound **3**, compound **4** to compound **6** when compared with their corresponding trans-conformations. In the trans-conformations, the hyper-conjugative interactions do not exist between them on bonded lone pairs of the P,As atoms (LPY_3) and the anti-bonding orbitals ($6*_{C2-O1}$). On the other hand, ($LP_1Y_3 \rightarrow 6*_{C2-X6}$) decreases of the E conformation stability from compounds **4**, **5**, **6** when compared with compounds **1**, **2**, **3**.

Computational method

Conformational details:

G3MP2, CCSD(T), MP2 and B3LYP functions with the 6-311+G** basis set of all atoms were performed to optimize the structural parameters and also to calculate the electronic energies and thermodynamic functions of the ground and transition state structures compounds **1-6** with the Gaussian09 package of programs [6, 11]. The NBO-B3LYP/6-311+G** interpretation was performed to investigate the bonding and anti-bonding orbital occupancies and energies of the cis- and trans-conformations of compounds **1-3** and **4-6** by use of the NBO 5.G program [9].

The stabilization energies (second order perturbation energies) associated with the hyperconjutative interactions associated with the donor(i)→acceptor(j) electron delocalizations are proportional inversely to the energy differences between the donor and acceptor orbitals and directly to the magnitudes of the orbital overlap integrals [12, 13].

Stabilization or resonance energy α ($S_{ij}^2/\Delta\varepsilon_{ij}$):

Accordingly, the stabilization or resonance energy (E_2) associated with i→j electron 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, εi and εj 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).[14,15]

The hyper-conjugative generalized anomeric effects (HC-GAEs) associated with $LPY_3 \rightarrow 6*_{C2-O1}$, $LPY_3 \rightarrow 6*_{C2-X6}$, $LP_1O_1 \rightarrow 6*_{C2-Y3}$, $LP_2O_1 \rightarrow 6*_{C2-Y3}$, $LP_1X_6 \rightarrow 6*_{C2-O1}$, $LP_2X_6 \rightarrow 6*_{C2-O1}$, $LP_3X_6 \rightarrow \pi*_{C2-O1}$, $LP_2X_6 \rightarrow \pi*_{C4-O5}$, $LP_1X_6 \rightarrow 6*_{C2-Y3}$ and $LP_2X_6 \rightarrow 6*_{C2-Y3}$, the attractive electrostatic interactions between two adjacent atoms (AEI), dipole-dipole interactions) and their influences on the structural and conformational properties of compounds **1-3** and **4-6** were quantitatively investigated by means of the natural bond orbital (NBO) interpretations(Table **2**) [10].

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