

The effect of the Coulombic potential energies in the origin of the axial-conformation preference in the 3-haloarsinan cations

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Abstract: In the past few decades, the origin of the axial-conformation preference in 3-haloarsinan cations (charge-dipole orientation effect), has been brought into question [halogen=F (**1**), Cl (**2**), Br (**3**)]. In order to explore the source of the axial-conformation preferences in compounds **1-3**, with G3MP2, LC- ω PBE and B3LYP technique and interpretations of natural bond orbital (NBO) we assessed the effect of the Coulombic electrostatic interactions, the hyperconjugative interactions, the electrostatic model associated with dipole-dipole interactions and the steric effects associated with the Pauli exchange type repulsions on the conformational properties of compounds **1-3**. Natural Coulombic potential energies associated with attraction and repulsion between atoms that are adjacent or nonadjacent is in favor of the axial conformations of compounds **1-3**. Between the *axial*- and equatorial-conformations the natural Coulombic potential energy distinction diminished from compound **1** to compound **3**, this is justify their difference in corresponding total energy. From compound **1** to compound **3** through-space hyperconjugative interactions increase between the donor lone pairs of halogen atoms (LP₃X) and the acceptor antibonding of H-As bonds [σ_{H-As}^*], LP₃X \rightarrow σ_{H-As}^* . Although, the electrostatic model correlated with the diversity of the total amount of dipole moments fails to account for rationalizing the conformational behaviors of compounds **1-3**, the exploration of the dipole moments of the corresponding C-X and H-As bonds revealed that the variations of their four-center dipole-dipole interactions correlate well with their parallel conformational behaviors. The steric effects associated with the Pauli exchange type repulsions are in favor of the equatorial-conformations of compound **1-3**.

Keywords: 3-haloarsinan cation, Charge-dipole interactions, Hyperconjugative interactions, Density functional calculation, Molecular modeling.

Introduction

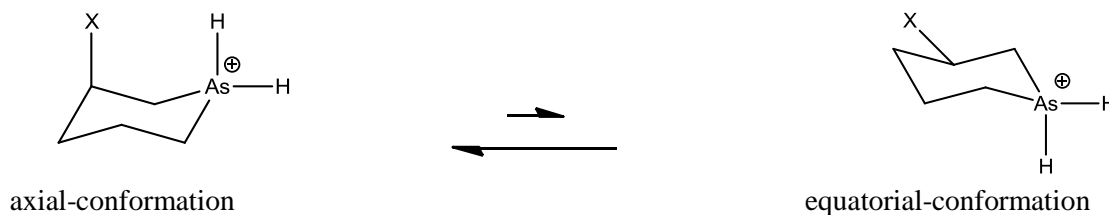
It has been catch-all term that due to steric hindrance in the axial conformations of the mono-halocyclohexane derivatives, in the six-membered ring chairs halogen atoms opt the equatorial conformation. Meanwhile, when their C-2 atoms have been substituted with O, N, S and etc, brings about the preference of their corresponding axial-conformations. The reason behind this fact is anomeric effect [1-17].

Although, there are some published data in the literature concerning the origin of the axial-conformation preferences in As-protonated 3-haloarsinan [18-25], to the best of our knowledge, there are no published quantitative data about 3-haloarsinan and the roles and contributions of the hyperconjugative interactions, the steric effects, the Coulombic electrostatic interactions associated with the attractive or repulsive interactions between adjacent or nonadjacent atoms, the electrostatic model associated with the dipole-dipole interactions and the

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conformational behaviors of As-protonated 3-fluoroarsinan (1), 3-chlorarsinan(2) and 3-bromarsinan (3). In this work, the importance of the factors that previously mentioned on the conformational behaviors of compounds 1-3 were assessed by means of the G3MP2,22 the long-range-corrected version of the

Perdew-Burke-Ernzerhof (PBE) exchange functional (LC- ω PBE),23 and hybrid density functional (B3LYP)24 based methods with the 6-311++G** basis set25-28 on all atoms, and natural bond orbital (NBO) analysis (Scheme 1).



Scheme1. Schematic representation of the axial- and equatorial conformations of compounds 1-3

Result and Discussion

Conformational persistence

Gibbs free energy ,Enthalpy and entropy and differences that exist between the axial- and equatorial-conformations of compounds **1-3**, as calculated at the G3MP2, LC- ω PBE/6-311++G**, B3LYP/6-311++G** levels of theory, are summarized (Tables 1-6). Based on the previous study the axial conformations of fluoro, chloro, and bromocyclohexanes have smaller stability than their corresponding equatorial conformations (owing to the presence of 1,3-diaxial repulsions in their axial conformations), apart from that the axial conformations of compounds **1-3** are the most stable than their corresponding equatorial conformations. We evaluated total steric exchange energies (TSEE) of the axial and equatorial conformations of compounds **1-3**. According to the results obtained, total steric exchange energies (TSEE) are in favor of the equatorial conformations of compounds **1-3**, and $\Delta(TSEE_{ax}-TSEE_{eq})$ parameters become smaller from compound **1** to compound **3**. Since the strong axial-conformation preferences decline from compound **1** to compound **3**, there are no correlations between their conformational behaviors and their corresponding $\Delta(TSEE_{ax}-TSEE_{eq})$ parameters (Tables 1-4). The calculated entropies of the equatorial- conformations of compounds **1-3** are bigger than those in their corresponding axial- conformations and the entropy differences between the equatorial- and axial-conformations increased slightly from compound **1** to compound **3**.

Assessing the associate between the natural Coulombic energies (NCE) and the axial conformation persistence in compounds 1-3

The attractive and repulsive electrostatic interactions among atoms that are adjacent and nonadjacent in a molecule can be ascribe to the Coulombic electrostatic interactions. Therefore, a simple electrostatic descriptor can be formulated in terms of the effective net atomic charges (q_A) and associated Coulombic potential energy function (V_{NCE}):

$$V_{NCE} = \sum_{A < B}'' \frac{q_A q_B}{|R_A - R_B|} \quad (2)$$

Equation (2) expresses repulsive electrostatic interactions or the Natural Coulombic Energy (NCE) as a qualitative measure of total atom-atom attractive. Given two different isomeric geometries and associated natural atomic charges, we would be able to assess the natural Coulombic potential energy distinction (ΔV_{NCE}) that might be effectively ascribes to their corresponding electrostatic type forces. We considered the effect of the attractive or repulsive electrostatic between the natural atomic charges of the adjacent and nonadjacent atoms on the conformational preferences of compounds **1-3** (Table 4). Based on obtaining result, the natural Coulombic potential energy differences between the *axial*- and equatorial conformations of compounds **1-3** [$\Delta E^{(es)}(L+NL) = V_{NCE}(ax) - V_{NCE}(eq)$] are in favor of the axial-conformations and $\Delta E^{(es)}$

parameter (without assessing their negative signs) **3** (Table 5).
declined dramatically from compound **1** to compound

Table 1: G3MP2 calculated thermodynamic functions and parameters [H , G (in hartree) and S (in $\text{cal mol}^{-1}\text{K}^{-1}$)] for the axial and equatorial conformations of compounds **1-3**.

	G3MP2					
	H	S	G	ΔH^a	ΔS^a	ΔG^a
1-ax	-550.947309	99.608	-550.985012	0.00	0.000	0.00
1-eq	-550.939285	98.296	-550.977289	0.009924(7.04) ^a	0.888	0.008723(6.85) ^a
2-ax	-910.948226	99.755	-810.987051	0.00	0.000	0.00
2-eq	-910.941226	99.892	-810.980401	0.008900(4.39) ^a	0.937	0.00865(4.17) ^a
3-ax	-4824.023404	99.987	-4824.063533	0.00	0.000	0.00
3-eq	-4824.016863	99.998	-4824.057361	0.008541(4.10) ^a	0.977	0.008172(3.87) ^a

Table 2: LC- ω PBE/6-311++G** calculated thermodynamic functions and parameters [H , G (in hartree) and S (in $\text{cal mol}^{-1}\text{K}^{-1}$)] for the axial and equatorial conformations of compounds **1-3**.

	LC- ω PBE/6-311++G**					
	H	S	G	ΔH^a	ΔS^a	ΔG^a
1-ax	-551.237685	98.331	-551.274903	0.00	0.000	0.00
1-eq	-551.228892	98.942	-451.266399	0.009893(7.52) ^a	0.811	0.008504(7.34) ^a
2-ax	-911.506266	98.353	-911.544444	0.00	0.000	0.00
2-eq	-911.499679	99.195	-911.538258	0.008587(5.13) ^a	0.998	0.008186(4.88) ^a
3-ax	-4825.185238	98.978	-3925.224663	0.00	0.000	0.00

3- <i>eq</i>	-4825.178974	99.892	-3925.218834	0.008264(4.93) ^a	0.998	0.007829(4.66) ^a
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Table 3: B3LYP/6-311++G** calculated thermodynamic functions and parameters [H , G (in hartree) and S (in cal mol⁻¹K⁻¹)] for the axial and equatorial conformations of compounds **1-3**.

	B3LYP/6-311++G**					
	H	S	G	ΔH^a	ΔS^a	ΔG^a
1- <i>ax</i>	-551.447593	98.843	-551.485054	0.00	0.000	0.00
1- <i>eq</i>	-551.439751	99.346	-551.477451	0.009842(5.92) ^a	0.703	0.009603(5.77) ^a
2- <i>ax</i>	-911.803039	99.072	-911.841559	0.00	0.000	0.00
2- <i>eq</i>	-911.797387	99.853	-911.836278	0.007652(5.55) ^a	0.881	0.007281(5.31) ^a
3- <i>ax</i>	-4825.724623	98.930	-4825.764454	0.00	0.000	0.00
3- <i>eq</i>	-4825.719303	99.980	-4825.759537	0.00732(4.34) ^a	0.989	0.006917(4.09) ^a

Table 4: NBO-B3LYP/6-311++G**.-Calculated Total Steric Exchange Energies (TSEE, in kcal mol⁻¹) for the Equatorial and Axial Conformations of Compounds 1-3

	NBO-B3LYP/6-311++G**					
	1		2		3	
	<i>ax</i>	<i>eq</i>	<i>ax</i>	<i>eq</i>	<i>ax</i>	<i>eq</i>
TSEE	510.48	494.32	530.71	523.46	537.61	529.78
$\Delta TSEE$	32.16	0.00	9.25	0.00	9.74	0.00

Table 5: B3LYP/6-311++G** calculated natural Coulombic potential energy (V_{NCE}) and its Lewis [$E(L)$] and non-Lewis [$E(NL)$] components (in a.u.) and also their corresponding differences for the *axial*- and equatorial-conformations of compounds **1-3**

	NBO- B3LYP/6-311++G**					
	1		2		3	
	<i>ax</i>	<i>eq</i>	<i>ax</i>	<i>eq</i>	<i>ax</i>	<i>eq</i>

$E^{(es)}(L)$	-0.60435	-0.59341	-0.56185	-0.54828	-0.56954	-0.55619
$\Delta E^{(es)}(L)$	-0.03094(-6.86) ^a	0.00000	-0.03357(-9.52) ^a	0.00000	-0.03335(-9.38) ^a	0.00000
$E^{(es)}(NL)$	0.03801	0.04026	0.00503	0.00089	0.00450	-0.00109
$\Delta E^{(es)}(NL)$	-0.00425(-1.41) ^a	0.00000	0.00434(1.47) ^a	0.00000	0.00542(2.15) ^a	0.00000
V_{NCE}	-0.58634	-0.57315	-0.55882	-0.54759	-0.56704	-0.55712
$\Delta E^{(es)}$	-0.03319(-8.28) ^a	0.00000	-0.03123(-7.05) ^a	0.00000	0.01099(-6.22) ^a	0.00000

Values are in kcal mol⁻¹. $\Delta E^{(es)} = V_{NCE}(C_{2h}) - V_{NCE}(D_{2h})$

Table 6. NBO- B3LYP/6-311++G** calculated molecular dipole moment contributions in terms of natural bond orbital contributions (μ , in Debye) for the equatorial and axial conformations of compounds **1-3**.

	NBO- B3LYP/6-311++G**					
	1		2		3	
	<i>ax</i>	<i>eq</i>	<i>ax</i>	<i>eq</i>	<i>ax</i>	<i>eq</i>
$\mu(\text{total})$	7.10	8.91	8.07	9.95	9.77	15.31
	0.00	3.81	0.00	3.98	0.00	4.54
$\mu(\text{P-H}_{\text{ax}})$	0.80		0.80		0.79	
$\mu(\text{C-X})$	3.08		0.97		0.70	
$\mu(\text{LP}_1\text{X})$	3.27		4.91		4.86	
$\mu(\text{LP}_2\text{X})$	0.47		0.78		0.83	
$\mu(\text{LP}_3\text{X})$	0.39		0.48		0.38	

This fact shows that Coulombic electrostatic interactions fairly explain the plunge of the axial-conformation preferences going from compound **1** to compound **3**. The resonance improve electrostatic effect (non-Lewis component of Coulombic potential energy, $[E^{(es)}(NL)]$, is in favor of the axial-conformation of compound **1** in stark contrast it is oppositely in favor of the equatorial-conformations of compounds **2** and **3**. However, the Lewis components $[E^{(es)}(L)]$ on the magnitudes of the natural Coulombic potential energies have determining contributions. Although, $\Delta[E^{(es)}(L)_{(ax)} - E^{(es)}(L)_{(eq)}]$ parameter is in favor of the

axial-conformations of compounds **1-3**, the natural Coulombic potential energy differences $[\Delta E^{(es)}]$ between the *axial*- and equatorial conformations of compounds **1-3** result from the combinations of their non-Lewis and Lewis components $[\Delta E^{(es)}(L+NL) = V_{NCE}(ax) - V_{NCE}(eq)]$. Because of it the diversity of the axial- conformation preferences in compounds 1-3 are able to control by their corresponding $\Delta E^{(es)}$ parameters. Between the axial halogen atoms and the axial hydrogen atoms of the H-As bonds the electrostatic interactions in the axial-

conformations of compounds **1-3** have noticeable impact on their corresponding $\Delta E^{(es)}$ parameters. The result from NBO-B3LYP/6-311++G** reveals that axial fluorine atom of the axial-conformation of compound **1** have (as it is expectable) negative natural charges while the chlorine atom consists smaller negative natural atomic charge (≈ 0) and the bromine atom of the axial conformation of compound **3** have positive natural atomic charges. Since the hydrogen atoms of the axial H-P bonds of compounds **1-3** possess positive natural atomic charges (≈ 0.70), accordingly, the strength of the attractive electrostatic interaction declined drastically from compound **1** to compound **2** but there is an repulsive electrostatic between the axial bromine atom and the axial hydrogen atom of the H-As bond in compound **3**.

Evaluating the effect of the hyperconjugative interactions on the axial-conformation preferences in compounds 1-3

There are between the lone pairs of the axial halogen atoms [LP₃X, X=F (**1**), Cl(**2**), Br(**3**)] and the antibonding orbital's of the axial H-As bonds [$LP_3X \rightarrow \sigma_{H-As}^*$] through-space hyperconjugative interactions. NBO-B3LYP/6311++G** results showed that the stabilization energies associated with the through-spaced $LP_3X \rightarrow \sigma_{H-As}^*$ negative hyperconjugative interactions slight increase from the axial conformations of compound **1** to compound **3**, which may brings about the increase of the axial-conformation stability compared to their corresponding equatorial conformations. However, the energy of resonance associated with the through space $LP_3X \rightarrow \sigma_{H-As}^*$ negative hyperconjugative interactions increased slightly from the axial conformations of compound **1** to compound **3**, their corresponding axial-conformation preferences decrease. Consequently, the through space $LP_3X \rightarrow \sigma_{H-As}^*$ negative hyperconjugative interactions has a critical impact on the axial-conformation preferences in compounds **1-3**.

Assessing the impact and contribution of the As-H...X-C dipole orientation effect on the conformational behaviors of compounds 1-3

As we mentioned above, the electrostatic model associated with dipole-dipole interactions cannot to account quantitatively for the rationalization of the

diversity of the axial-conformation preferences in compounds **1-3** (Table **6**). In order to evaluating the impact of the As-H...X-C dipole orientation impact on the conformational properties of compounds **1-3**, we explored the dipole moments of the natural bond orbital's of the axial-conformations of compounds **1-3**. According to the results that obtained, total dipole moments of the C-X [X=F(**1**), Cl(**2**), Br(**3**)] bonds result from the combinations of the natural bond orbital dipole moments of C-X bonds and the s-type nonbonding orbital's of the halogen (X) atoms, $\mu(C-X) + \mu(LP_1X)$. The As-type lone pairs of the halogen atoms (LP₂X and LP₃X) have no critical impact on the overall natural dipole moments of the C-X bonds. Strikingly, $\mu(C-X) + \mu(LP_1X)$ parameters and the natural bond order dipole moment of the H-As bonds [$\mu(H-As)$] are contrary to their instructive interactions leads to the As-H...X-C dipole orientation effects. $\mu(C-X) + \mu(LP_1X)$ parameter decline from the axial-conformations of compound **1** to compound **3**. Though, there is no significant change is obvious for $\mu(H-As)$. The variations of the As-H...X-C dipole orientation effects contributed well with the variations of the axial-conformation preferences in compounds **1-3**.

Exploring the structural properties of compounds 1-3

Selected structural parameters of the axial-conformations of compounds **1-3** as calculated at the B3LYP/6-311++G** level of theory are shown in **Table3**. Importantly, the As₁-C₂ bonds of the axial-conformations of compounds **1-3** are drastically contracted rather than their corresponding As₁-C₆ bonds. The inspections the impact and contributions of the attractive electrostatic interactions between two atoms that are adjacent and hyperconjugative interactions on the contractions of the P₁-C₂ bonds of the axial-conformations of compounds **1-3** compared to their corresponding As₁-C₆ bonds show that these two elements have no important impact on the contractions of As₁-C₂ bonds compared to the As₁-C₆ bonds. Accordingly, we may assume that the attractive interactions between two oppositely oriented dipole moments of the C-F and H-As bring about the contractions of the As₁-C₂ bonds. Interestingly, the contractions of the As₁-C₂ bonds compared to the As₁-C₆ bonds are also obvious in the equatorial-conformations of compounds **1-3**. The As-C₂ lengths of bond in the axial-conformations of compounds

1-3 are smaller than those in their corresponding equatorial-conformations. This fact could be explained with the greater attractive interactions between two oppositely (in plane) oriented dipole moments of the C-F and H-As bonds in the axial-conformations of compounds **1-3** compared to their corresponding nonplanar dipole in the equatorial-conformations. This phenomenon is a striking example which reveals the greater effect of the attractive dipole interactions on the structural parameters of chemical substances.

Conclusion

The composite of G₃MP₂ method, long range corrected hybrid-density functional theory (LC- ω PBE), B₃LYP and natural bond orbital investigation prepared a clear and logical image from structural, stereo electronic, bonding, natural electrostatic energies, dipole-dipole interaction and energetic points of views to consider the origin of the *axial*-conformation persistence in compounds **1-3**. Natural Coulombic potential energies correlated between adjacent or nonadjacent atoms with attractive or repulsive interactions are in favor of the axial conformations of compounds **1-3** and the natural Coulombic potential energy differences [$\Delta E^{(es)}$] between the *axial*- and equatorial-conformations and this is justifying their corresponding total energy differences. Interpretations from NBO-dipole moment provided reveals that the C-X...H-As charge-dipole orienting effect diminished from the axial-conformations of compound **1** to compound **3** which is in line with the diversity of their corresponding axial-conformation preferences. Seemingly, between the halogen atoms and the hydrogen atoms of the axial H-As bonds the attractive electrostatic interaction declined drastically from compound **1** to compound **3**, and this justify the conformational preferences of compounds **1-3**.

Experimental

Computational details

The conformational behaviors of the axial-conformations and equatorial-conformations of compounds **1-3** were considered at the G₃MP₂, B₃LYP and LC- ω PBE methods with the 6-311++G** basis set on all atoms and their corresponding electronic energies and thermodynamic functions were gained by the GAMESS US package of programs [29, 30]. Since there are least many-electron self-interaction faults in the kernel of the LC- ω PBE functional among variety of exchange- correlation functionals, the degree of electrons localizations and delocalizations could be

effectively predicted by this functional [31-33]. Natural bond orbital (NBO) interpretation were performed with the well-tested B₃LYP/6-311++G** level of hybrid density functional theory [34] for exploring the effect of the potential hyperconjugative interactions in particular, (the through-space $LP_3X \rightarrow \sigma_{H-As}^*$ negative hyperconjugative interactions) Pauli exchange type repulsions, natural Coulombic energies (NCE) [35] and electrostatic model associated with dipole-dipole interactions on the conformational and structural properties of compounds **1-3**. Moreover, in the axial-conformations, the natural bond orbital dipole moments of compounds 1-3 and their corresponding bonding and antibonding orbital occupancies and energies were considered with NBO-B₃LYP/6-311++G** analysis by means of the NBO 5.G program [36]. The stabilization energies (second order perturbational energies) ascribe to the hyperconjugative interactions (donor (*i*) acceptor (*j*) electron delocalization's) are inversely to the energy differences between the donor and acceptor orbitals and proportional directly to the magnitudes of the orbital overlap integrals [37, 38]:

Stabilization or resonance energy $\propto S_{ij}^2 / \Delta \epsilon_{ij}$

We could evaluate the stabilization or second order perturbative energy (E_2) associated with $i \rightarrow j$ electron delocalization, according to the following equation:

(1)

$$E_2 = q_i \frac{F_{ij}^2}{\epsilon_i - \epsilon_j}$$

Where ϵ_i and ϵ_j are diagonal elements (orbital energies), and $F_{(i,j)}$ is the offdiagonal natural bond orbital Fock matrix element and q_i is the *i*th donor orbital occupancy.

In order to evaluate the role of the hyperconjugative interactions on conformational properties of compounds **1-3**, we deleted all off-diagonal factors of all hyperconjugative interactions from the Fock matrices of their axial- and equatorial-conformations. After that, by re-diagonalization and comparing the current Fock matrices with their original forms, we estimated the contributions and effect of the hyperconjugative interactions on the conformational properties of compounds **1-3**. It may be worth to mention that the procedure mentioned above is an efficient approach and able to performed for evaluating the contributions of some specific hyperconjugative interactions on the conformational properties of chemical substances [39].

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