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Calculations of Structures and Reaction Energy Profiles of As_2O_3 and As_4O_6 Species by Quantum Chemical Methods

Gabriel Costa A. da Hora, Ricardo L. Longo, and João Bosco P. da Silva*

Principal component analysis was used in the selection of the B3PW91/6-311+G(3df) method for calculations of As_2O_3 molecular species. This multivariate analysis compared experimental properties (structure and ionization energy) of As_4O_6 molecule with several computational methods (Hartree–Fock, second-order Møller–Plesset perturbation theory, and density functional theory) and basis sets. At the selected level of theory, we were able to calculate nine structures of As_2O_3 with three of them being stable ones (no negative force constants) in the following stability order: D3H (0.0), DIAMOND OUT (32.77 kJ mol⁻¹), and GAUCHE (43.81 kJ mol⁻¹). Several intramolecular conversions were

studied with the GAUCHE → DIAMOND OUT transformation being barrierless, whereas the DIAMOND OUT structure is converted into the D3H isomer through a Gibbs free-energy barrier of 40.83 kJ mol⁻¹. Starting from the GAUCHE structure of As_2O_3 and its enantiomeric form, it was possible to obtain directly (barrierless) the As_4O_6 species in a spontaneous process ($\Delta_r G = -399.92$ kJ mol⁻¹ at 298 K and 1 atm) in gas phase. Thus, the As_4O_6 species is probably the precursor of arsenic hydroxide through hydrolysis reactions. © 2012 Wiley Periodicals, Inc.

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Introduction

In recent years, the chemistry of arsenic-containing compounds has gained attention in chemistry as well as in biology because of two important findings, namely, the discovery of a bacterium that uses arsenic instead of phosphorus in life processes^[1] and the identification of the first known marine natural product containing multiple arsenic atoms, Arsenicin A, $\text{As}_4(\text{CH}_2)_3\text{O}_3$.^[2] In fact, Arsenicin A is isoelectronic to As_4O_6 , which may be found in two crystalline forms of arsenic oxide: arsenolite (cubic) and claudetite (monoclinic).^[3]

In addition, As_4O_6 has implications in semiconductor chemistry. It is the source for As_2O_3 , which X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray measurements have pointed out as the product of electrochemical treatment of GaAs with HX (X = F, Cl, and Br) electrolytes.^[4–6] However, by far the most cited aspect in the current literature on As_2O_3 is related to its medical applications. It is used in the treatment of patients with acute promyelocytic leukemia^[7–9] and in tumor growth inhibition in the orthotopic metastasis model of androgen-independent prostate cancer.^[10] Despite of their importance, there are only a few theoretical/computational studies on As_4O_6 ^[11,12] and As_2O_3 .^[13]

In this work, we present the first detailed conformational and structural analysis of As_2O_3 molecule.

We first performed a systematic analysis of different levels of calculation and basis sets for predicting geometrical and spectroscopic parameters of As_4O_6 . The predicted values were compared with experimental values using the chemometric multivariate technique principal component analysis (PCA).^[14] The most accurate method obtained from the PCA analysis was used to study the conversion processes between the energy-minimum structures of As_2O_3 and to determine the

respective transition states. Finally, a mechanism for converting the low energy structures of As_2O_3 toward the formation of As_4O_6 at T_d symmetry was proposed.

Calculations and Procedures

Electronic structure calculations of the isolated As_4O_6 molecule were performed with Hartree–Fock,^[15] second-order Møller–Plesset perturbation theory (MP2),^[16] and density functional theory (DFT) methods using the B3LYP^[17] and B3PW91^[18] hybrid functionals with different basis sets containing or not diffuse and polarization functions, 6-31G,^[19] 6-31G(d),^[20] 6-31+G(d),^[21] 6-311G,^[22] and 6-311+G(3df).^[23] All calculations were performed with the Gaussian03 program^[24] using its default criteria. Harmonic frequencies were obtained to ascertain the nature of the stationary points in the potential energy surface. To compare with the XPS data, the vertical ionization energy was evaluated in accordance with the time scale of the experimental measurements. The QST2 and QST3 methods^[25] were used for searching saddle points. The transition state was properly characterized and intrinsic reaction coordinate (IRC) calculations^[26] were performed to provide the corresponding structures of the reactant and the product. The details of PCA procedure may be found elsewhere.^[27,28] Four predicted parameters, namely, As–O bond length, As–O–As and O–As–O bond angles and the ionization energy were used in the PCA analysis. The information was organized in a 58 × 04 data matrix corresponding to the 58

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combinations of theory/basis sets and the four parameters. The data matrix was autoscaled, that is, each element on a column was subtracted from the average value on that column and then each new mean centered element was scaled to unit variance on that column. The score values relative to the experimental point were obtained by substituting the autoscaled experimental values in the corresponding PC's equations. The PCA procedure was performed with the chemometrics package Ein*Sight 3.0.^[29]

Results and Discussions

Principal component analysis

Figure 1 shows the score plot of the first principal component (PC1) versus the second principal component (PC2) obtained for different methods used in the calculations of geometric (As—O bond length, As—O—As and O—As—O bond angles) and spectroscopic (ionization energy) parameters. Notice that the sum of the PC1 + PC2 represents 94.9% of the total variance.

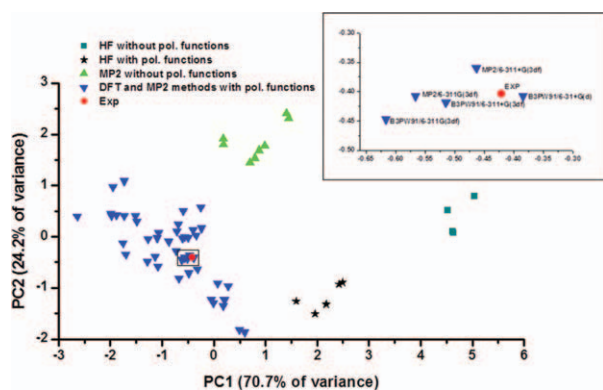


Figure 1. First (PC1) versus second (PC2) principal components score plot for the calculated values of geometric parameters and ionization energy. Experimental point was projected onto the score plot obtained from the calculated values. The inset is a magnification of the region around the experimental point and includes the labels of the calculation methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 1 shows that the correlated methods (MP2 and DFT) with polarization functions are the most appropriate for describing the experimental structure and ionization energy of As_2O_3 . The insert in Figure 1, which amplified the region around the experimental point, shows that increasing the number of polarization functions (3df) and including a diffuse function improves the performance of the MP2 method. However, this improvement comes with a high computational cost. So, considering that the DFT functional B3PW91 performs as well as the MP2 method at a much lower computational demand, we decided to adopt the B3PW91/6-311+G(3df) method as the best relation cost/accuracy for calculating structures, energies, and electronic and spectroscopic properties of As_2O_3 .

As_2O_3 isomers

Figure 2 depicts the B3PW91/6-311+G(3df) calculated structures of nine candidates for As_2O_3 isomers with their corre-

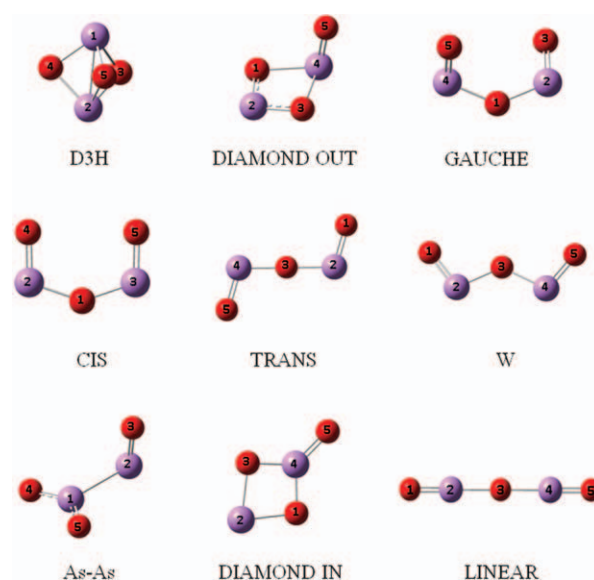


Figure 2. Calculated structures of the As_2O_3 molecule using the B3PW91/6-311+G(3df) method. Arsenic atoms in purple and oxygen atoms in red. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sponding denominations. These structures were characterized by their harmonic vibrational frequencies as well as their relative energies, which are presented in Table 1. The D3H isomer is the global minimum and was used as a reference for the relative energies. Only the lowest vibrational frequencies are presented to ascertain the nature of the calculated structure (minimum or saddle point).

Table 1. Relative energy (ΔE), relative energy including zero-point energy (ΔE_0), and lowest harmonic vibrational frequency evaluated at the B3PW91/6-311+G(3df) level for the isomers of As_2O_3 .

Isomer ^[a]	ΔE (kJ mol ⁻¹)	ΔE_0 (kJ mol ⁻¹)	ν_1 (cm ⁻¹)
D3H	0 ^[b]	0 ^[c]	365.3
DIAMOND OUT	35.39	32.77	123.4
GAUCHE	47.87	43.81	48.7
CIS	58.71	54.12	70.6i
TRANS	63.81	57.82	89.2i
W	65.69	61.24	22.4i
As—As	252.98	247.70	14.8i
DIAMOND IN	328.86	325.99	418.9i
LINEAR	486.88	474.12	595.7i

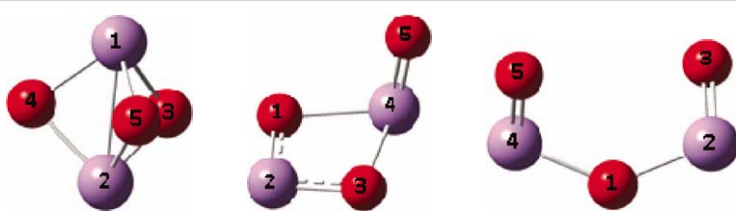
[a] See isomer structures in Figure 2. [b] Total energy of D3H = -4697.4067258 E_h . [c] Total energy + ZPE correction of D3H = -4697.395942 E_h , 1 Hartree (E_h) = 2625.497 kJ mol⁻¹.

At the selected level of calculation, only the D3H, DIAMOND OUT, and GAUCHE isomers correspond to minimum structures, whereas the CIS, TRANS, W, As—As, DIAMOND IN, and LINEAR isomers are first-order saddle points on the potential energy surface (only one imaginary frequency).

Table 2 presents selected geometric parameters and the electric dipole moment of the three stable isomers (D3H, DIAMOND OUT, and GAUCHE) of As_2O_3 .

The stability of the D3H isomer is related to its larger number of As—O bonds (six) in addition to a single As—As bond,

Table 2. Electric dipole moments and geometric parameters of the As_2O_3 isomers D3H, DIAMOND OUT, and GAUCHE obtained with the B3PW91/6-311+G(3df) method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

			
Parameter ^[a]			
Isomer (point group)	D3H (D_{3h})	DIAMOND OUT (C_2)	GAUCHE (C_2)
μ (D)	0	4.43	3.50
$d_{\text{As-O}}$ (Å)	1.836	1.688; 2.087; 1.606	1.610; 1.794
$d_{\text{As-As}}$ (Å)	2.375	2.807	3.301
$\theta_{\text{As-O-As}}$ (°)	80.6	95.5	133.8
$\theta_{\text{O-As-O}}$ (°)	82.7	95.4; 102.7	106.3
$\theta_{\text{O-O-O}}$ (°)	60.0	64.5	87.3
$\varphi_{\text{As-O-As-O}}$ (°)	41.8	± 101.4	-39.9
$\varphi_{\text{As-O-O-O}}$ (°)	59.5	-146.3	-121.4

[a] μ , electric dipole moment; d , bond length; θ , bond angle; φ , dihedral angle.

compared with the other DIAMOND OUT (2 As—O bonds + 2 As—O partial double bonds + 1 As—O double bonds) and GAUCHE (2 As—O bonds + 2 As—O double bonds) structures. The value of the gas-phase As—As bond distance in the D3H isomer (2.375 Å) is in reasonable agreement (−2.3 to −3.5%) with typical solid phase As—As bond distances (2.43–2.46 Å) reported in the literature.^[30–32] Because of its symmetry, the D3H isomer has a null electric dipole moment, whereas the DIAMOND OUT isomer exhibits a large (4.43 D) dipole moment due to the As4—O5 polarized fragment that make an angle of -32.3° off the diamond plane. The dipole moment of the GAUCHE isomer is also large (3.50 D) and points toward the O1 atom as the contributions of the As4—O5 and As2—O3 fragments cancel each other due to their opposite orientation in the As4—O1—As2 plane. Recently, Shrivastava and co-workers^[13] have also performed DFT calculations on the linear and bipyramidal (D3H) structures of As_2O_3 and found that both are minima on the potential energy surface, that is, both isomers have only real vibrational frequencies. However, we calculated the LINEAR isomer to be a saddle point with a very large imaginary frequency (see Table 1). This discrepancy is probably due to the small basis sets without polarization functions as well as the lack of nonlocal contributions for exchange and correlation in the functional (local density approximation (LDA)) used in the calculations of many As_xO_y species.^[13] Also, the LDA method overestimates all the distances in the bipyramidal (D3H) structure of As_2O_3 ^[13]: $d_{\text{As-O}} = 1.927$ Å (+5.0%), $d_{\text{O-O}} = 2.496$ Å (+2.9%), and $d_{\text{As-As}} = 2.559$ Å (+7.7%) compared to the B3PW91/6-311+G(3df) calculated values (Table 2): $d_{\text{As-O}} = 1.836$ Å, $d_{\text{O-O}} = 2.425$ Å, and $d_{\text{As-As}} = 2.375$ Å. The value of the As—As distance was obtained from the reported LDA $d_{\text{As-O}}$ and $d_{\text{O-O}}$ distances using the D_{3h} symmetry constraints. Notice that this distance is quite dependent on the nonlocal corrections (LDA compared to B3PW91) and the quality of the basis sets (double-zeta compared to triple-zeta with polarization and diffuse functions).

Conversion processes

We have analyzed the possibility of conversion reaction between the minimum structures of As_2O_3 , that is, $\text{D3H} \leftrightarrow \text{DIAMOND OUT}$ and $\text{DIAMOND OUT} \leftrightarrow \text{GAUCHE}$. In addition, we have investigated if some of the isomers showing only one imaginary vibrational frequency in Table 2 (CIS, W, As—As e DIAMOND IN) could be transition states for interconversions of stable As_2O_3 isomers.

D3H → DIAMOND OUT

The QST2 approach^[25] with the B3PW91/6-311+G(3df) method has identified a possible structure for the transition

state between the stable D3H and DIAMOND OUT structures of As_2O_3 showing only one imaginary frequency at $208.3i \text{ cm}^{-1}$ associated with the angular deformation of the atoms As—As—O(5). The IRC calculations have confirmed that this saddle point indeed connects the D3H reactant to the DIAMOND OUT product. Figure 3a shows the reaction energy profile, whereas in Figure 3b, the transition state structure is presented.

DIAMOND OUT → GAUCHE

The QST2 approach did not succeed in yielding a transition state between the stable DIAMOND OUT and GAUCHE structures of As_2O_3 . So, the QST3 algorithm was tried using the CIS, W, As—As, and DIAMOND IN structures as tentative structures; however, it was also unable to provide a transition state structure. Finally, a two-dimensional reaction coordinate approach involving the movement of the As1 atom toward the O3 atom and As1 atom moving away from O4 atom was used. Again, no transition state structure was obtained because this process

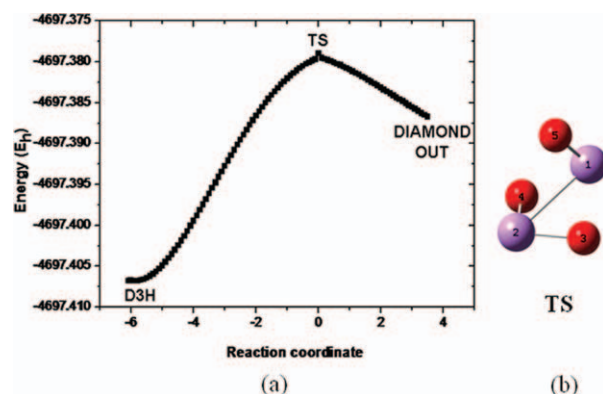


Figure 3. Intramolecular reaction between the As_2O_3 D3H and DIAMOND OUT structures. a) IRC plot and b) transition state structure. Arsenic atoms in purple and oxygen atoms in red. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

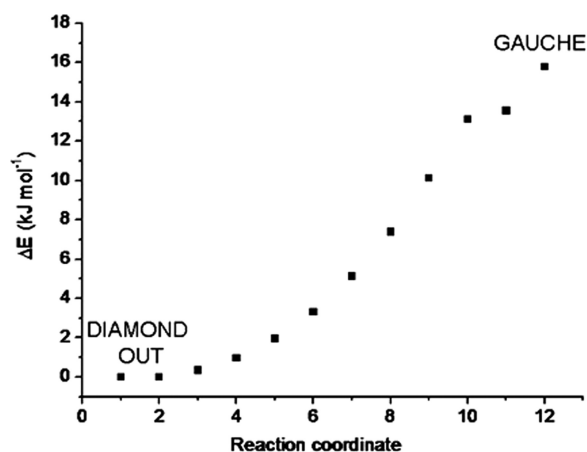


Figure 4. B3PW91/6-311+G(3df) calculations of the energy profile in a reaction coordinate connecting the minima structures of As_2O_3 DIAMOND OUT and GAUCHE.

occurred without passing through a barrier as can be seen in Figure 4. So, this is an indication that the DIAMOND OUT and GAUCHE interconversion is barrierless.

D3H \rightarrow GAUCHE

The QST2 and QST3 approaches with the B3PW91/6-311+G(3df) method were used without success to provide a transition structure between the stable D3H and GAUCHE structures of As_2O_3 . Therefore, such intramolecular reaction is predicted to occur directly at this level of calculation.

In Table 3, the B3PW91/6-311+G(3df) calculated enthalpy, Gibbs free energy, and Gibbs free energy of activation for these three intramolecular transformations are presented.

Notice that these reactions are endergonic, so that none of these transformations are spontaneous. These results can be

Table 3. B3PW91/6-311+G(3df) calculated reaction enthalpy ($\Delta_r H$), Gibbs free energy ($\Delta_r G$), and Gibbs activation free energy ($\Delta^\ddagger G$) for the intramolecular conversions between As_2O_3 minimum structures.			
Reaction	$\Delta_r H$	$\Delta_r G$	$\Delta^\ddagger G$
D3H \rightarrow DIAMOND OUT	35.40	23.28	64.11
DIAMOND OUT \rightarrow GAUCHE	12.48	4.82	–
D3H \rightarrow GAUCHE	47.70	28.11	–
All values in kJ mol^{-1} at 298 K and 1 atm.			

rationalized by the number of As–As and As–O bonds that are broken when the D3H isomer is transformed into either DIAMOND OUT or GAUCHE structures. Also, if the GAUCHE structure is formed during some physical or chemical process, it can go directly to the stable D3H structure or via a DIAMOND OUT structure pathway, which has a sizeable energy barrier to convert into the D3H form. Therefore, the role of the DIAMOND OUT stable structure in As_2O_3 reactions needs to be explored in more details, particularly in (aqueous) solution, where its large dipole moment (see Table 1) could be of special importance. In fact, this is the subject of ongoing research in our group and will be reported elsewhere.

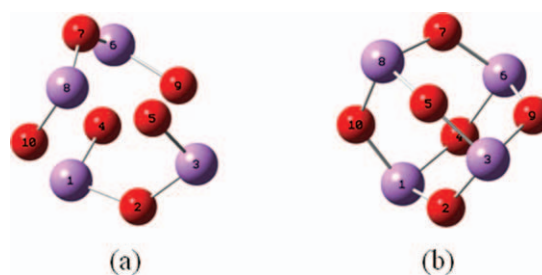


Figure 5. $2\text{As}_2\text{O}_3 \rightarrow \text{As}_4\text{O}_6$: (a) the GAUCHE isomer and his enantiomer form (reactants) and (b) As_4O_6 in the T_d point group (product). Structures calculated at the B3PW91/6-311+G(3df) level. Arsenic atoms in purple and oxygen atoms in red. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Intermolecular reaction: $2\text{As}_2\text{O}_3(\text{GAUCHE}) \rightarrow \text{As}_4\text{O}_6$

After studying the As_2O_3 isomers and their intramolecular reactions, a natural question that arises is related to the role of these As_2O_3 species in the As_4O_6 formation/decomposition. To answer this question, we decided to investigate the intermolecular reaction $2\text{As}_2\text{O}_3(\text{GAUCHE}) \rightarrow \text{As}_4\text{O}_6$.

Using the GAUCHE structure and its enantiomer as reactants in a B3PW91/6-311+G(3df) optimization process, we obtained the As_4O_6 species in the T_d point group as depicted in Figure 5.

Table 4. B3PW91/6-311+G(3df) electronic energy, enthalpy, Gibbs energy, and their corresponding variations for the reaction: $2\text{As}_2\text{O}_3(\text{GAUCHE}) \rightarrow \text{As}_4\text{O}_6(T_d)$ at 298 K and 1 atm.			
Total energy (E_h)		$\Delta_r E^{[a]}$	
$2\text{As}_2\text{O}_3$ GAUCHE	$\text{As}_4\text{O}_6 T_d$	E_h	kJ mol^{-1}
$2 \times (-4697.3885582)$	-9394.9684019	-0.1912855	-502.22
Enthalpy (E_h)		$\Delta_r H$	
$2 \text{As}_2\text{O}_3$ GAUCHE	$\text{As}_4\text{O}_6 T_d$	E_h	kJ mol^{-1}
$2 \times (-4697.371900)$	-9394.933008	-0.189208	-496.77
Gibbs energy (E_h)		$\Delta_r G$	
$2 \text{As}_2\text{O}_3$ GAUCHE	$\text{As}_4\text{O}_6 T_d$	E_h	kJ mol^{-1}
$2 \times (-4697.413398)$	-9394.979117	-0.152321	-399.92
[a] 1 Hartree (E_h) = 2625.497 kJ mol^{-1} .			

In Table 4, the energetic quantities involved in the $2\text{As}_2\text{O}_3(\text{GAUCHE}) \rightarrow \text{As}_4\text{O}_6(T_d)$ reaction are presented.

From Table 4, it can be observed that the $2\text{As}_2\text{O}_3(\text{GAUCHE}) \rightarrow \text{As}_4\text{O}_6$ reaction is highly exothermic ($-496.77 \text{ kJ mol}^{-1}$) due to the formation of four As–O chemical bonds and has a strong negative variation of the entropy ($-303.47 \text{ JK}^{-1} \text{ mol}^{-1}$) due to the loss of translational degrees of freedom. Despite this entropic contribution, this process is still highly exergonic ($-399.92 \text{ kJ mol}^{-1}$) at 298 K and 1 atm indicating that it is highly spontaneous. The QST2 and QST3 approaches as well as the reaction coordinate calculations were used in an attempt to locate a transition state, but in all cases, the optimization processes led directly to the As_4O_6 species in the T_d point group from the As_2O_3 GAUCHE and its enantiomer. So, this dimerization reaction is barrierless and highly spontaneous. Notice that if we correct this dimerization reaction by

starting from the most stable D3H isomer of As_2O_3 , we still obtain an exergonic ($-343.70 \text{ kJ mol}^{-1}$) process.

Conclusion

PCA has enabled us to ascertain the main features, namely, electron correlation and basis functions, of the electronic structure calculations to properly describe the structure and ionization energy of As_4O_6 molecule. Comparisons with experimental properties through this multivariate analysis allowed us to select the B3PW91/6-311+G(3df) method for calculations of arsenic oxide molecular species. At this level of theory, we were able to calculate nine structures of As_2O_3 with three structures being stable ones (no negative force constants) in the following stability order: D3H > DIAMOND OUT > GAUCHE. This stability order is correlated with the number of As—O and As—As bonds; however, it might be altered in polar solvents due to the large dipole moments of the DIAMOND OUT and GAUCHE species compared with the apolar D3H one. Several intramolecular conversions were studied with the GAUCHE \rightarrow DIAMOND OUT transformation being barrierless, whereas the DIAMOND OUT structure is converted into the D3H isomer through a Gibbs free-energy barrier of $40.83 \text{ kJ mol}^{-1}$. Starting from the GAUCHE structure of As_2O_3 and its enantiomeric form, it was possible to obtain directly (barrierless) the As_4O_6 species with a T_d symmetry. Thus, the As_4O_6 species is probably the precursor of arsenic hydroxide through hydrolysis reactions in aqueous media. The structures and conversion processes studied in this work have improved our comprehension of the roles of the As_2O_3 and As_4O_6 species in generating active products in aqueous solution relevant in cancer research and environmental chemistry.

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Keywords: As_2O_3 • As_4O_6 • isomers • ionization energy • molecular structure • chemometrics • PCA • DFT

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