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Dedicated to Professor Ionel Haiduc
on the occasion of his 65th birthday

ELECTRONIC STRUCTURE OF HYPERVALENT ORGANOARSENIC BROMO DERIVATIVES. AN AB INITIO RHF AND DFT-B3LYP INVESTIGATION OF $H_{5-X}AsBr_X$ SYSTEMS

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ABSTRACT. B3LYP/LACVP* and HF/LACVP* molecular orbital calculations predict trigonal bipyramidal structure for all $H_{5-x}AsBr_x$ (x = 0-5) species and square pyramidal structures for the transition states during the Berry pseudorotation processes. In case of $HAsBr_4$ and H_2AsBr_3 the B3LYP calculations predict lower energies for the isomers with one and respectively two hydrogen atoms in axial positions, in variance with the electronegativity and apicophilicity rules. The homoleptic AsH_5 and $AsBr_5$ are unstable relative to reductive elimination of H_2 or Br_2; H_4AsBr decomposes to AsH_3 and HBr while elimination of Br_2 from H_2AsBr_3 and H_3AsBr_2 is endothermic.

Keywords: arsorane, mixed bromoarsoranes, density functional calculations on stabilities of.

Introduction

Hypervalency is a subject of rather great audience in the last years [1, 2] and in particular, pentacoordinated XY_5 systems have been intensively studied. In this line, hypervalent compounds of phosphorus and arsenic with first to third row substituents have been the subjects of considerable attention in numerous experimental and theoretical approaches. Relatively less is known about arsenic (V) bromine derivatives [3-10] and this paper is devoted to the investigation of electronic structure and energetics of various bromo-substituted arsorane $H_{5-x}AsBr_x$ systems. To have the complete series treated at the same level, the parent AsH_5 molecule has been also considered. The main points addressed here are: a) the geometry of these molecules; b) the geometry and energy of the transition states relating different trigonal bipyramidal (TBP) structures and c) the thermodynamic stability of $H_{5-x}AsBr_x$ toward decomposition to arsenic(III) derivatives.

Computational details

Ab initio molecular orbital calculations have been carried out at the hybrid DFT B3LYP level that uses the Becke's 3-parameter exchange functional [11] with LYP (Lee-Wang-Parr) [12] correlation functionals including both local and nonlocal terms. The LACVP* Los Alamos basis functions used throughout these calculations include also the Hay-Wadt pseudopotentials [13] for the heavy elements. The DFT calculations have been paralleled by pure HF/LACVP* calculations.

Full geometry optimizations on all TBP based isomers of $H_{5-x}AsBr_x$ and their transition states leading to axial-equatorial ligand exchanges have been carried out until the default convergence criteria from Spartan were achieved (energy convergence criterion = 10^{-6} hartrees; maximum gradient = $4.5x10^{-4}$ hartrees/bohr and maximum displacement criterion = $1.8x10^{-3}$ Å). The nature of all optima has been checked by frequency calculations. All calculations have been done by using the Spartan'02 package [14] run under Windows on a 550 MHz PC.

Results and Discussion

a. Possible structures of $H_{5-x}AsBr_x$

The total energies together with the zero point energies (ZPE) and the ZPE corrected energies of all possible TBP $H_{5-x}AsBr_x$ systems are given in Table 1 and Figure 1 shows the geometry of these species.

Table 1

Energy data on the $H_{5-x}AsBr_x$ TBP systems. The number of axial (ax) and equatorial (eq) bromine atoms are indicated in the first column.

Molecule	Lowest Frequency (cm^{-1})	Total energy (a.u.)	Zero point energy (a.u.)	Zero point corrected energy (a.u)	Method
$AsBr_5$	52.23	-70.6969240	0.0051680	-70.6917560	HF
	43.22	-72.0529615	0.0044923	-72.0484692	B3LYP
$HAsBr_4$	56.51	-58.3260179	0.0142930	-58.3117249	HF
1ax_3eq	49.93	-59.4651879	0.0127950	-59.4523929	B3LYP
$HAsBr_4$	56.40	-58.3270696	0.0136093	-58.3134603	HF
2ax_2eq	43.14	-59.4636066	0.0121034	-59.4515032	B3LYP
H_2AsBr_3	101.07	-45.9564312	0.0220650	-45.9343662	HF
2ax_1eq	87.69	-46.8735778	0.0197526	-46.8538252	B3LYP
H_2AsBr_3	54.04	-45.9530974	0.0215199	-45.9315775	HF
3eq	51.47	-46.8743380	0.0196761	-46.8546619	B3LYP
H_2AsBr_3	-*	-	-	-	HF
1ax_2eq	-	-	-	-	B3LYP
H_3AsBr_2	123.87	-33.5845574	0.0301987	-33.5543587	HF
3ax	104.90	-34.2840806	0.0272489	-34.2568317	B3LYP
H_3AsBr_2	130.75	-33.5596029	0.0302242	-33.5293787	HF
1ax_1eq	121.57	-34.2652664	0.0274752	-34.2377912	B3LYP
H_4AsBr	167.22	-21.1789109	0.0376838	-21.1412271	HF
1ax	183.98	-21.6664610	0.0341508	-21.6323102	B3LYP
H_4AsBr	268.97i	-21.1613565	0.0367580	-21.1245985	HF
1eq	195.52i	-21.6572840	0.0338225	-21.6234615	B3LYP
H_5As	568.30	-8.7522733	0.0423085	-8.7099648	HF
	454.47	-9.0336284	0.0388950	-8.9947334	B3LYP

*Isomer not identified during the optimization.

Similar data for the square pyramid (SP) structures are collected in Table 2 and Figure 2. Table 3 contains the barriers to Berry pseudorotation involving the TBP-SP-TBP pathways.

Table 2

Transition state to Berry pseudorotation energies of $H_{5-x}AsBr_x$ systems.

Molecule	Imaginary Frequency cm^{-1}	Total energy (a.u.)	Zero point energy (a.u.)	Corrected total energy (a.u.)	Method
AsBr5	39.87I 28.60I	-70.6906822 -72.0489773	0.0050947 0.0044270	-70.6855875 -72.0445503	HF B3LYP
$HAsBr_4$ 4_basal	43.01I 25.23I	-58.3178037 -59.4588934	0.0139424 0.0124890	-58.3038613 -59.4464044	HF B3LYP
$HAsBr_4$ 1_apical_3basal	57.64I 47.73I	-58.3215771 -59.4608190	0.0137527 0.0121974	-58.3078244 -59.4486216	HF B3LYP
H_2AsBr_3 1_apical_2basal_ opposed	55.46I 54.49I	-45.9513952 -46.8713502	0.0216825 0.0195789	-45.9297127 -46.8517713	HF B3LYP
H_2AsBr_3 3basal	43.33I -	-45.9430053 -	0.0224363 -	-45.920569 -	HF B3LYP
H_2AsBr_3 1apical_2basal_ vicinal	136.65i 102.19i	-45.9352653 -46.8584609	0.0218148 0.0119829	-45.9134505 -46.846478	HF B3LYP
H_3AsBr_2 2basal_vicinal	273.33i 170.75i	-33.5546274 -34.2633451	0.0298991 0.0272713	-33.5247283 -34.2360738	HF B3LYP
H_3AsBr_2 1apical_1basal	228.51i 259.53i	-33.5497591 -34.2556442	0.0292154 0.0265063	-33.5205437 -34.2291379	HF B3LYP
H_4AsBr 1basal	266.86i 194.66i	-21.1613628 -21.6572838	0.0367468 0.0338225	-21.1246160 -21.6234613	HF B3LYP
H_4AsBr 1apical	793.85i 842.93i	-21.1358041 -21.6273963	0.0349397 0.0321094	-21.1008644 -21.5952869	HF B3LYP
H_5As	408.41i 269.09i	-8.7483906 -9.0314574	0.0416870 0.0384169	-8.7067036 -8.9930405	HF B3LYP

There is so far no experimental evidence for the existence of AsH_5, this system has been however the subject of a few theoretical (ab initio) investigations [6, 15, 16]. In accordance with simple VSEPR theory, all these calculations along with those reported here predict that the TBP structure is a minimum on the potential energy surface. The other possible geometry-square pyramid proofs to be a transition state (saddle point) separated by 1.06 kcal/mol (B3LYP) or 2.05 kcal/mol (HF) from the TBP state. These barriers are close to that reported by Trinquier by ab initio valence only SCF+CI calculation: 2.5 kcal/mol) [6] and Moc (2.1 kcal/mol MP4/ECP; 2.2 kcal/mol MP2/AE) [15].

Table 3.

Barriers to Berry pseudorotation in $H_{5-x}AsBr_x$ systems.(kcal/mol)

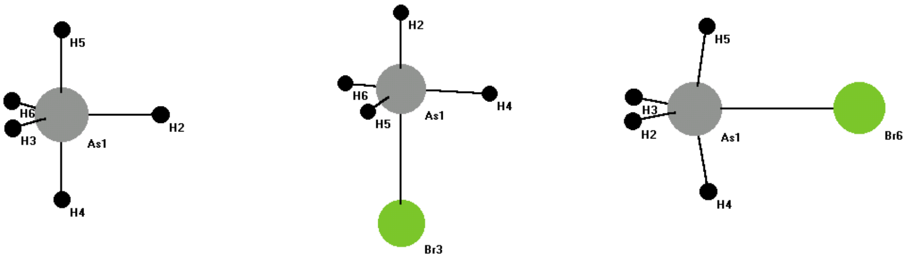
Molecule	Isomer	Transition state description	Barrier	Method
AsBr5			3.87 2.46	HF B3LYP
$HAsBr_4$	2ax_2eq	4_basal	6.02 3.42	HF B3LYP
	1ax_3eq	1_apical_3_basal	2.45 2.37	HF B3LYP
H_2AsBr_3	2ax_1eq	1_apical_2_basal_vicinal	2.92 1.29	HF B3LYP
	2ax_1eq	3_basal	8.63 -	HF B3LYP
H_3AsBr_2	1ax_1eq	2_basal_vicinal	2.92 1.08	HF B3LYP
	1ax_1eq	1_apical_1_basal	5.54 5.43	HF B3LYP
H_4AsBr	1ax	1_basal	10.42 5.55	HF B3LYP
	1eq	1_apical	14.89 17.68	HF B3LYP
H_5As			2.05 1.06	HF B3LYP

To the best of our knowledge, the trigonal bypiramidal isomers of $H_{5-x}AsBr_x$ (x = 1-4) have not been studied by any theoretical methods and no experimental data on these systems are known.

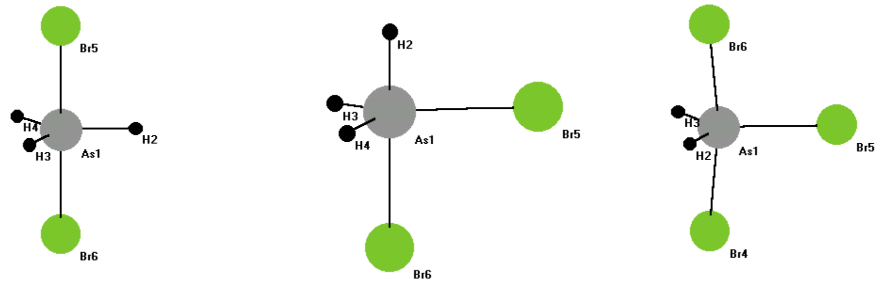
The hydrogen bond and correlation effect on the binding energies in $H_3As…HBr$ ensemble and in other $H_3E…HX$ complexes was investigated by Hincliffe [17] and Alabart [18].

Optimisations of TBP H_4AsBr, starting from two classes of initial geometries (axial bromine or equatorial bromine) show that bromine prefers the axial position (in agreement with the greater apicophilicity of bromine [19]. The alternative structure with the bromine in the equatorial position is in fact a transition state characterised by one imaginary frequency (see Table 1).

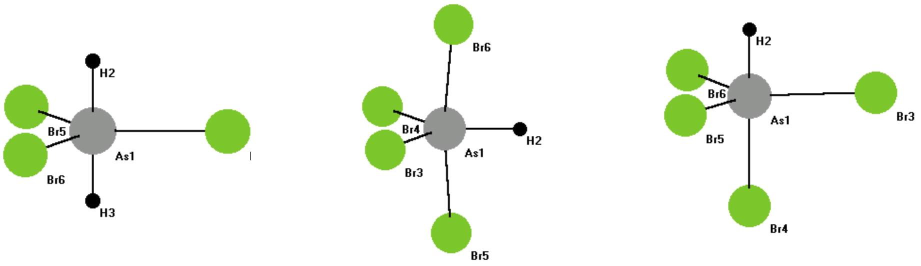
For H_3AsBr_2 two relative arrangement of bromine atoms are possible within a TBP structure: a) with axial and equatorial bromine (1ax1eq in Figure 1) and b) with the Br atoms in axial positions (2ax in Figure 1). At both level of calculations, the (1ax1eq) isomer is found at higher energy (B3LYP: +11.94 kcal/mol, HF: +15.67 kcal/mol). There are two known examples of TBP R_3AsBr_2 systems with bromine in axial positions R = Ph [4, 9]) and R = neo-pentyl [10]. It is interesting to note that R_3AsBr_2 does not adopt always a TBP type structure.



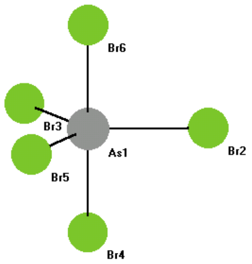
AsH_5 H_4AsBr (ax) H_4AsBr (eq)



H_3AsBr_2 (2ax) H_3AsBr_2 (1ax1eq) H_2AsBr_3 (2ax1eq)

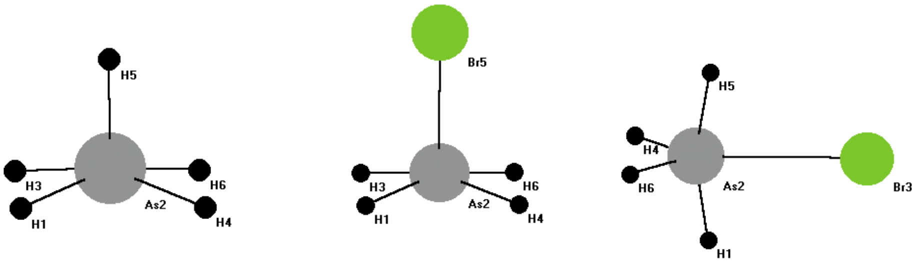


H_2AsBr_3 (3eq) $HAsBr_4$ (2ax2eq) $HAsBr_4$ (1ax3eq)

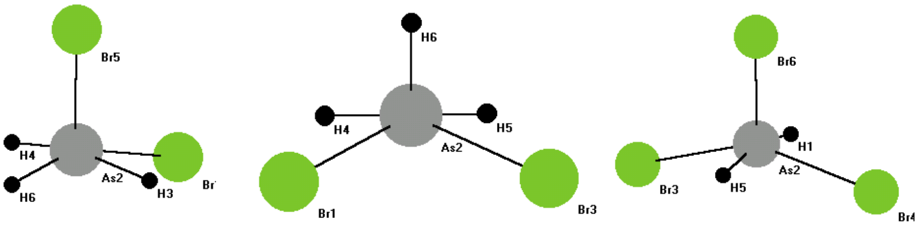


$AsBr_5$

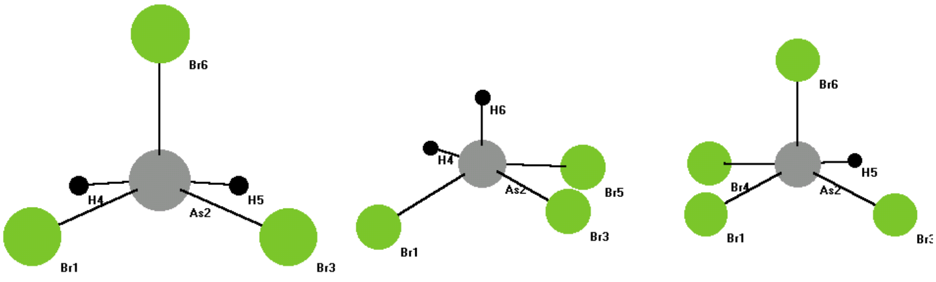
Figure 1. The HF/LACVP* and B3LYP/LACVP* calculated structures of $H_{5-x}AsBr_x$



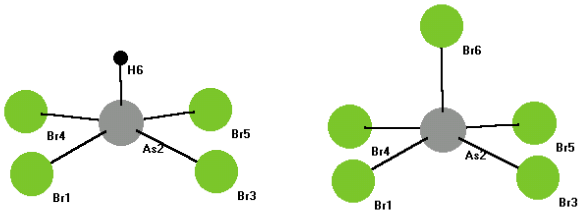
AsH_5 H_4AsBr (1a) H_4AsBr (1b)



H_3AsBr_2 (1b1a) H_3AsBr_2 (2bv) H_2AsBr_3 (2bo1a)



H_2AsBr_3 (2bv1a) H_2AsBr_3 (3b) $HAsBr_4$ (3b1a)



$HAsBr_4$ (4b) $AsBr_5$

Figure 2. Transition state structures for the Berry pseudorotations of $H_{5-x}AsBr_x$ systems

Thus, the crystal structure of Me_3AsBr_2 is based on an ER_3-X-X tetrahedral arrangement around the arsenic atom [4], which can be also interpreted as an arsonium $ER_3X^+X^-$ salt [5]. This flexibility toward different types of arrangements around the arsenic atoms might be related to the small barrier to pseudorotation for the 1ax1eq isomer (B3LYP 1.08 kcal/mol, HF 2.92 kcal/mol).

H_2AsBr_3 might have the bromine atoms in three different arrangements: all equatorial (3eq in Figure 1), two in equatorial positions (1ax2eq not included in Figure 1) and two in axial positions (2ax1eq in Figure 1). All attempts to optimise the structure of 1ax2eq ended either with 3eq or with 2ax1eq (depending on the exact starting geometry), so we could not locate at this level of calculations a genuine 1ax2eq isomer.

At the B3LYP level 2ax1eq is higher by 0.52 kcal/mol while at the HF, the order is reversed (3eq higher by 1.74 kcal/mol). Since the barrier to pseudorotation converting the 2ax1eq isomer to the 3eq isomer is relatively small (B3LYP1.29 kcal/mol; HF 2.92 kcal/mol, see Table 3) this species is rather flexible.

There is only one known representative of the R_2AsBr_3 class (R = Ph) and this has a TBP structure with two bromine atoms in axial positions [8].

For $HAsBr_4$ the B3LYP results again predict that the isomer with two axial bromine atoms (2ax2eq) is higher in energy by 0.57 kcal/mol (B3LYP) than the 1ax3eq isomer. Such discrepancies between the prediction based on electronegativity rules or apicophilicity of the substituents have been discussed earlier [20]. Thus, higher-level calculations are required, in order to confirm this deviation from the order predicted by the apicophilicity of bromine.

According to the present calculations and in agreement with previous reported results [3] $AsBr_5$ adopts a TBP structure while the SP structure is a transition state during the Berry pseudorotation process. The barrier to pseudorotation is estimated to 2.46kcal/mol (B3LYP).

b. Thermodynamic considerations. Table 4 lists the calculated enthalpies of the decomposition reactions of all $H_{5-x}AsBr_x$.

Table 4.

Calculated Enthalpies of Decomposition Reactions of $H_{5-x}AsBr_x$

Molecule	ΔH (Kcal/mol)	
AsBr5 = $AsBr_3$+Br_3	-15.15 -8.65	HF B3LYP
$HAsBr_4$ = $AsBr_3$ + HBr 1ax_3eq	-32.62 -26.75	HF B3LYP
$HAsBr_4$ = AsBr3 + HBr 2ax_2eq	-31.53 -27.30	HF B3LYP
$HAsBr_4$ = $HAsBr_2$ + Br_2 1ax_3eq	-3.46 3.84	HF B3LYP

Molecule	ΔH (Kcal/mol)	
$HAsBr_4 = HAsBr_2 + Br_2$ 2ax_2eq	-2.38 3.28	HF B3LYP
$H_2AsBr_3 = AsBr_3 + H_2$ 2ax_1eq	-22.68 -32.09	HF B3LYP
$H_2AsBr_3 = AsBr_3 + H_2$ 3eq	-24.43 -31.56	HF B3LYP
$H_2AsBr_3 = HAsBr_2 + HBr$ 2ax_1eq	-19.28 -15.80	HF B3LYP
$H_2AsBr_3 = HAsBr_2 + HBr$ 3eq	-21.03 -15.08	HF B3LYP
$H_2AsBr_3 = H_2AsBr + Br_2$ 2ax_1eq	10.08 12.71	HF B3LYP
$H_2AsBr_3 = H_2AsBr + Br_2$ 3eq	8.32 13.24	HF B3LYP
$H_3AsBr_2 = HAsBr_2 + H_2$ 2ax	-10.98 -20.16	HF B3LYP
$H_3AsBr_2 = HAsBr_2 + H_2$ 1ax_1eq	-26.65 -32.11	HF B3LYP
$H_3AsBr_2 = H_2AsBr + HBr$ 2ax	-7.37 -5.96	HF B3LYP
$H_3AsBr_2 = H_2AsBr + HBr$ 1ax_1eq	-23.04 -17.90	HF B3LYP
$H_3AsBr_2 = H_3As + Br_2$ 2ax	21.48 19.61	HF B3LYP
$H_3AsBr_2 = H_3As + Br_2$ 1ax_1eq	5.81 7.65	HF B3LYP
$H_4AsBr = H_3As + HBr$ ax	-16.76 -16.33	HF B3LYP
$H_4AsBr = H_2AsBr + H_2$ ax	-19.88 -27.58	HF B3LYP
$H_5As = H_3As + H_2$	-40.64 -46.16 -58.6	HF B3LYP Ref. 6

$AsBr_5$ is thermodynamically unstable relative to $AsBr_3$ + Br_2 like is the chlorine analog [21]. The instability of AsH_5 relative to AsH_3 and H_2 is even more accentuated. Note also that the elimination of HBr or H_2 from $H_{5-x}AsBr_x$ (x = 1-4) is constantly highly exothermic while decomposition to Br_2 (x = 2-4) and the corresponding As(III) species is endothermic. These data suggest, that the simultaneous presence of hydrogen and bromine induces a relative stabilization of the As(V) derivatives compared to the homoleptic AsH_5 or $AsBr_5$. Thus, it might be speculated that even the existence of the above-cited R_2AsBr_3 and R_3AsBr_2 derivatives is a consequence of this kind of stabilization.

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