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Molecular and electronic structure of AsH_nX_{3-n} (X = F, Cl)

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Abstract

The structure and properties of unknown halides AsH_2F, $AsHF_2$, AsH_2Cl and $AsHCl_2$ have been studied using *ab initio* calculations and extended basis sets. The results are discussed with reference to the experimental data available for arsenous trihalides and methyl derivatives of the title compounds.

Introduction

Arsenous trifluoride and trichloride are important reagents in preparative organic chemistry and their properties have been well established for a long time [1]. Related mono- and dihalides are however completely unknown. It has been suggested previously that mixed arsenous trihalides cannot be easily isolated as pure substances because of the rapidly established equilibria where they exist as components in the mixture. A similar argument can possibly be applied to arsinous halides and arsonous dihalides. In order to detect their presence in such mixtures it becomes useful to have a set of their molecular parameters (albeit approximate). This 'scanning' for possible new compounds uses theoretical analysis [2] to supplement and guide an increasingly sophisticated range of detection methods for such species [3].

Details of calculation

The *ab initio* MO method implemented in Gaussian 86 and MICROMOL VI packages [4] has been used to obtain molecular properties. The calculations were performed at the HF/6-31G** level with the recently introduced 641(d) basis set [5] describing the arsenic atom. All molecular geometries were fully optimized. In order to account (at least qualitatively) for the correlation energy the 92% rule [6] was used to correct orbital eigenvalues. All the converged structures corresponded to genuine minima on the potential surfaces as indicated by the lack of negative eigenvalues of the Hessian matrix. The symmetry plane (C_s point group) was assumed to be *xz*.

Results and discussion

The corrected orbital energies, electric moments, molecular geometries, enthalpies of formation, vibrational frequencies and atomic charges are presented in Tables 1–4 and Fig. 1 for AsH_2F, $AsHF_2$, AsH_2Cl and $AsHCl_2$.

Although it is possible to calculate enthalpies of formation using high level *ab initio* calculations with inclusion of electron correlation we decided to obtain them by summation of relevant bond enthalpies (Table 1). Bond enthalpies were derived from experimental ΔH_f° values for AsH_3 and AsX_3 (X = F, Cl) [7].

The dipole moments presented in Table 1 were obtained by vector addition of bond moments and *ab initio* geometries. Bond moments were in turn calculated from known geometries and dipole moments of AsH_3 and AsX_3 [8, 9]. This approach often provides more accurate dipole moment values than the *ab initio* method.

Qualitative assignments of normal modes of vibration (Table 2) were made on the basis of comparision with experimental IR spectra [10, 11] of AsH_3, AsF_3 and $AsCl_3$, respectively.

The corrected orbital eigenvalues for the title molecules were compared with ionization energies for AsH_3 and AsX_3 measured by photoelectron spectroscopy [12, 13] (Fig. 1) in order to establish possible trends within the electronic structures of the arsenic halides. Since the reliability of our data cannot be directly established by comparison with experiment we have tried to compare our corrected eigenvalues with photoelectron spectra of molecules which are very similar to ours, i.e. their methyl derivatives [14]. The methyl group induced only a small reduction

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TABLE 1. Total *ab initio* energies (E_T), equilibrium molecular geometries (r, ϑ), dipole and quadrupole moments and standard enthalpies of formation (298.15 K)[a,b]

Molecule	E_T (a.u.)	r, ϑ (pm) (°)	μ (D)	θ (10^{-40} Cm^2)	$\Delta H_f°$ (kJ mol^{-1})
AsH_2F	−2332.594	r(AsF) = 172.71 r(AsH) = 150.15 <HAsH = 93.1 <HAsF = 96.1	1.86	−6.580 (θ_{xx}) 7.795 (θ_{yy}) 5.719 (θ_{zz})	−217.6
$AsHF_2$	−2431.478	r(AsF) = 170.64 r(AsH) = 150.19 <HAsF = 94.9 <FAsF = 96.1	2.46	−1.705 (θ_{xx}) −8.818 (θ_{yy}) −2.262 (θ_{zz})	−501.7
AsH_2Cl	−2692.656	r(AsCl) = 219.91 r(AsH) = 149.64 <HAsCl = 95.0 <HAsH = 92.7	1.48	−7.640 (θ_{xx}) 6.099 (θ_{yy}) 4.240 (θ_{zz})	−42.9
$AsHCl_2$	−3151.584	r(AsCl) = 218.31 r(AsH) = 149.39 <HAsCl = 93.9 <ClAsCl = 99.7	1.89	0.478 (θ_{xx}) −13.977 (θ_{yy}) 1.425 (θ_{zz})	−152.2

[a] Three independent components of quadrupole moment tensor are given. [b] 1 a.u. ≈ 4.35975×10^{-18} J.

in ionization energy of several high lying orbitals so that corrected orbital energies of our molecules and ionization energies of their methyl derivatives may be directly compared (Table 3). Table 3 shows the maximum difference of <0.6 eV which is a strong indication that our corrected orbital energies are

TABLE 2. Normal modes of vibration in AsH_nX_{3-n}[a]

Molecule	Frequency (cm^{-1})	Symmetry	Mode type
AsH_2F	2180	a″	As–H asym. stretch
	2169	a′	As–H sym. stretch
	1032	a′	HAsH deform
	833	a′	HAsF sym. deform
	796	a″	HAsF asym. deform
	691	a′	As–F stretch
$AsHF_2$	2169	a′	As–H stretch
	855	a′	HAsF sym. deform
	816	a″	HAsF asym. deform
	726	a′	As–F sym. stretch
	715	a″	As–F asym. stretch
	268	a′	FAsF deform
AsH_2Cl	2214	a″	As–H asym. stretch
	2203	a′	As–H sym. stretch
	1065	a′	HAsH deform
	797	a′	HAsCl sym. deform
	794	a″	HAsCl asym. deform
	382	a′	As–Cl stretch
$AsHCl_2$	2228	a′	As–H stretch
	844	a″	HAsCl asym. deform
	794	a′	HAsCl sym. deform
	392	a′	As–Cl sym. stretch
	380	a″	As–Cl asym. stretch
	166	a′	ClAsCl deform

[a] Calculated frequencies were scaled by a factor of 0.8929 (ref. 15).

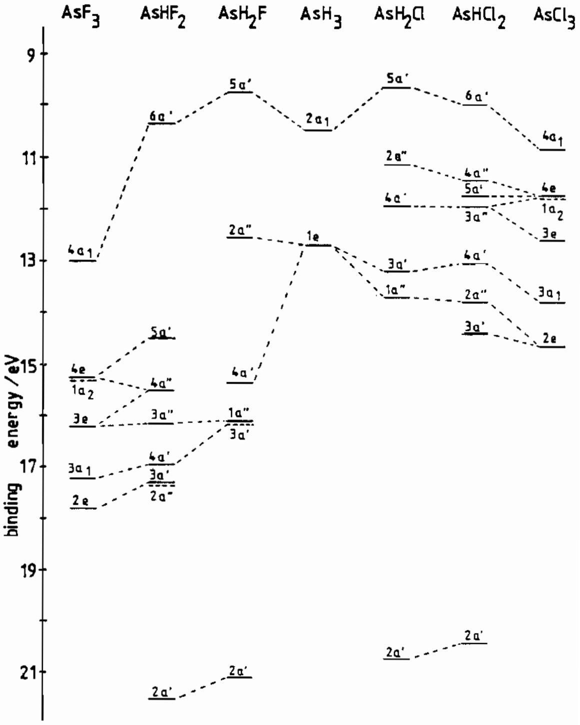

Fig. 1. Energy level diagram for AsH_nX_{3-n} (values for AsH_3, AsF_3 and $AsCl_3$ were obtained from photoelectron spectra).

TABLE 3. Comparison of electronic structures of CH_3AsCl_2, $AsHCl_2$, $(CH_3)_2AsCl$ and AsH_2Cl[a]

Molecule	IE_1 (eV)	IE_2 (eV)	IE_3 (eV)	$IE_{4,5}$ (eV)	IE_6 (eV)
CH_3AsCl_2	10.02	11.50	11.59	12.55	13.36
$AsHCl_2$	9.98	11.43	11.74	11.95	13.06
$(CH_3)_2AsCl$	9.45	10.74	11.49	12.08 12.47	13.43
AsH_2Cl	9.65	11.14	11.95	13.18	13.71

[a] IE_n (eV) represent corrected orbital energies or ionization energies.

TABLE 4. Mulliken population analysis[a]

	As			H		X (F, Cl)		
	s	p	d	s	p*	s	p	d*
AsH_2F								
g.o.p	8.59	14.51	9.25	1.04	0.02	3.86	5.56	0.11
n.a.c.		+0.65			+0.06		−0.53	
$AsHF_2$								
g.o.p.	8.61	13.99	9.29	1.07	0.02	3.86	5.55	0.11
n.a.c.		+1.12			−0.08		−0.52	
AsH_2Cl								
g.o.p.	8.55	14.82	9.33	1.00	0.02	5.95	11.29	0.03
n.a.c.		+0.30			−0.01		−0.27	
$AsHCl_2$								
g.o.p.	8.53	14.56	9.47	0.97	0.02	5.95	11.25	0.03
n.a.c.		+0.44			+0.01		−0.22	

[a] p*, d* represent polarization functions; g.o.p. = gross orbital population; n.a.c. = net atomic charge.

useful and can be used for analysis of photoelectron spectra of AsH_nX_{3-n} once they become available. The photoelectron spectra of $(CH_3)_nAsF_{3-n}$ were not reported.

Inspection of Fig. 1 reveals the usual variation of orbital energy with number and type (electronegativity) of substituted halogens. The larger the number and (or) electronegativity of the halogens the higher the orbital energies. It is worth pointing out that the HOMO orbitals (6a′ and 5a′) in the title molecules have pronounced As atomic character. This is indicated by our calculations and correlations deduced from Fig. 1. A similar conclusion was reached from MS-Xα calculations [13] on AsF_3 and $AsCl_3$. The rest of the electronic structure can be described in terms of halogen lone pairs and σ-type bonding orbitals.

Trends observed in bond lengths can be summarized by saying that the As–X (X = F, Cl) bond length decreases upon increasing halogen substitution along the sequence AsH_2X, $AsHX_2$ and AsX_3. A similar reduction of the $<$XAsX bond angle is also observed upon increased halogenation (Table 1).

The final comment refers to the results of the Mulliken population analysis (Table 4). As expected the arsenic atom accumulates a small positive charge whose magnitude depends on the degree of halogenation. Hydrogen atoms on the other hand seem unaffected by variations in halogen substitution.

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