

## ARTICLES

 $\text{XH}_4^{2+}$  Dications and Search for  $\text{XH}_4^{3+}$  Trications ( $\text{X} = \text{N}, \text{P}, \text{and As}$ )<sup>†</sup>

Golam Rasul,\* G. K. Surya Prakash, and George A. Olah\*

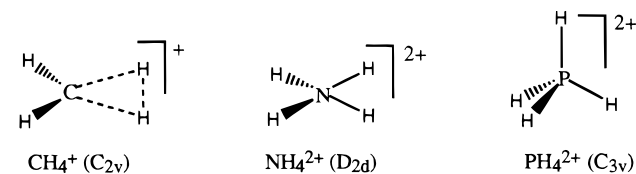
Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

Received: February 2, 1998; In Final Form: March 16, 1998

Structures and energies of  $\text{XH}_4^{2+}$  and  $\text{XH}_4^{3+}$  ( $\text{X} = \text{N}, \text{P}, \text{and As}$ ) were calculated at the ab initio MP2/6-31G\*\* and QCISD(T)/6-311G\*\* levels of theory. Contrary to previous theoretical studies, the global minimum structure of  $\text{PH}_4^{2+}$  is not  $C_{3v}$  symmetrical **2** but a  $C_s$  symmetrical **3** with a 2e-3c bond. The structure **2** is less stable than **3** by 6.5 kcal/mol. Calculations also showed that **2** if formed will spontaneously convert into **3**. The planar  $C_{2v}$  symmetric structure **6**, with a 3c-2e bond, was found to be the only minimum for  $\text{PH}_4^{3+}$ . Similarly,  $C_s$  symmetrical **8** and planar  $C_{2v}$  symmetric **10**, each containing a 2e-3c bond, were found to be the global minima of  $\text{AsH}_4^{2+}$  and  $\text{AsH}_4^{3+}$ , respectively. Thermodynamics of the deprotonation of the di- and trications studied is also discussed.

## Introduction

Onium dications are of increasing significance both in gas phase<sup>2a</sup> and in solution chemistry.<sup>2b</sup> Consequently, knowledge of the structures and bondings of such highly electron-deficient dications are of great importance. The ammonium dication,  $\text{NH}_4^{2+}$ , is isoelectronic with the methane cation,  $\text{CH}_4^+$ . But unlike  $\text{CH}_4^+$  which is of  $C_{2v}$  symmetry with a two electron three center (2e-3c) bond,<sup>3</sup> the ab initio calculated structure of  $\text{NH}_4^{2+}$  is of  $D_{2d}$  symmetry with no 2e-3c interaction as shown by Koch and Schwarz<sup>4</sup> and Pope et al.<sup>5</sup> On the other hand, the calculated structure of  $\text{PH}_4^{2+}$  is of  $C_{3v}$  symmetry with a 1e-2c bonding interaction and can be considered as a complex between  $\text{PH}_3^{2+}$  and hydrogen radical ( $\text{H}\cdot$ ) as shown by Pope et al.<sup>5</sup> The  $D_{2d}$  symmetrical structure of  $\text{PH}_4^{2+}$  was found not to be a minimum.<sup>5b</sup> In the gas phase, charge-stripping mass spectrometric study showed that the vertical ionization of the precursor  $\text{NH}_4^+$  led to a state<sup>6</sup> which is energetically higher than the transition state of deprotonation.<sup>4</sup> No experimental work on  $\text{PH}_4^{2+}$  has yet been reported.



We report now based on ab initio calculations that the global minimum structure of  $\text{PH}_4^{2+}$  is not of  $C_{3v}$  symmetry but of  $C_s$  symmetry with a 2e-3c bond. Ab initio method is particularly important to calculate such highly electron deficient species.<sup>2a</sup> The  $C_{3v}$  structure, although a minimum on the potential energy surface (PES), is significantly less stable than the  $C_s$  structure. Similar results were also found for  $\text{AsH}_4^{2+}$ . In addition, we also report the structures of trications  $\text{PH}_4^{3+}$  and  $\text{AsH}_4^{3+}$ , which

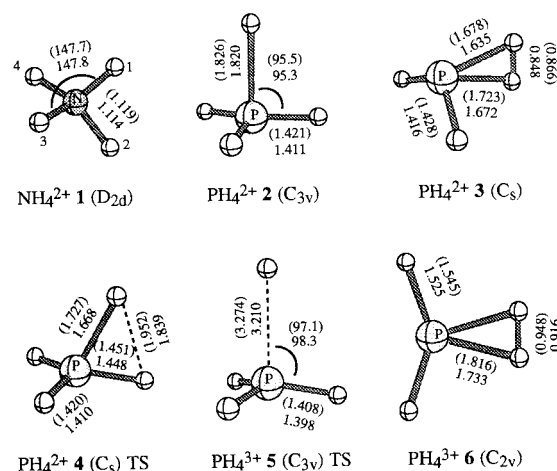


Figure 1. MP2/6-31G\*\* structures of **1–6** (QCISD(T)/6-311G\*\*).

can be derived by removing an electron from  $\text{PH}_4^{2+}$  and  $\text{AsH}_4^{2+}$ , respectively.

## Methods

The geometry optimizations and frequency calculations were performed at the ab initio MP2/6-31G\*\* level.<sup>7</sup> From calculated frequencies, the optimized structures were characterized as minima (NIMAG = 0) or transition structures (NIMAG = 1). For the MP2/6-31G\*\* optimized structures further geometry optimizations were carried out at the QCISD(T)/6-311G\*\* level. For improved energy, single point energies at the CCSD(T)/cc-pVTZ<sup>8</sup> level on QCISD(T)/6-311G\*\* optimized geometries were computed. For the nitrogen and phosphorus compounds, final energies were calculated at the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G\*\* + ZPE level and for the arsenic compounds at the QCISD(T)/6-311G\*\*//QCISD(T)/6-311G\*\* + ZPE level. Calculated energies are given in Table 1. Calculations were carried out with the Gaussian 94<sup>9</sup> and Spartan<sup>10</sup> programs.

<sup>†</sup> Dedicated to Sydney Benson on the occasion of his 80th birthday.

**TABLE 1: Total Energies (-au), ZPE<sup>a</sup> (kcal/mol)**

	MP2/6-31G**//MP2/6-31G**	QCISD(T)/6-311G**//QCISD(T)/6-311G**	CCSD(T)/cc-pVTZ//QCISD(T)/6-311G**
NH <sub>4</sub> <sup>2+</sup> ( <b>1</b> )	55.841 53 (21.5)	55.886 08	55.920 47
PH <sub>4</sub> <sup>2+</sup> ( <b>2</b> )	342.126 82 (16.6)	342.192 36	342.230 30
PH <sub>4</sub> <sup>2+</sup> ( <b>3</b> )	342.141 16 (18.3)	342.207 47	342.243 40
PH <sub>4</sub> <sup>2+</sup> TS ( <b>4</b> )	342.124 44 (15.9)	342.191 18	342.229 32
PH <sub>4</sub> <sup>2+</sup> TS ( <b>5</b> )	342.102 19 (15.1)	342.159 11	342.199 26
PH <sub>3</sub> <sup>3+</sup> ( <b>6</b> )	341.177 33 (14.1)	341.245 32	341.278 04
AsH <sub>4</sub> <sup>2+</sup> ( <b>7</b> )	2233.408 77 (15.7)	2235.617 42	
AsH <sub>4</sub> <sup>2+</sup> ( <b>8</b> )	2233.427 36 (16.8)	2235.642 72	
AsH <sub>4</sub> <sup>2+</sup> TS ( <b>9</b> )	2233.402 35 (14.4)	2235.614 79	
AsH <sub>3</sub> <sup>3+</sup> ( <b>10</b> )	2232.504 75 (13.1)	2234.723 69	
PH <sub>3</sub> <sup>2+</sup>	341.577 72 (13.9)	341.634 23	341.665 42
AsH <sub>3</sub> <sup>2+</sup>	2232.863 53 (13.0)	2235.069 78	

<sup>a</sup> Zero point vibrational energies (ZPE) at MP2/6-31G\*\*//MP2/6-31G\*\* scaled by a factor of 0.93.

**TABLE 2: ΔH<sub>0</sub> of Deprotonation (in kcal/mol)<sup>a</sup>**

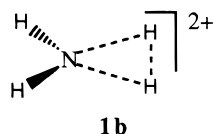
reaction	ΔH <sub>0</sub>
NH <sub>4</sub> <sup>2+</sup> ( <b>1</b> ) → NH <sub>3</sub> <sup>+</sup> + H <sup>+</sup>	-117.7
PH <sub>4</sub> <sup>2+</sup> ( <b>2</b> ) → PH <sub>3</sub> <sup>+</sup> + H <sup>+</sup>	-67.2
PH <sub>4</sub> <sup>2+</sup> ( <b>3</b> ) → PH <sub>3</sub> <sup>+</sup> + H <sup>+</sup>	-60.7
PH <sub>4</sub> <sup>2+</sup> ( <b>6</b> ) → PH <sub>3</sub> <sup>2+</sup> + H <sup>+</sup>	-243.3
AsH <sub>4</sub> <sup>2+</sup> ( <b>8</b> ) → AsH <sub>3</sub> <sup>+</sup> + H <sup>+</sup>	-41.3 <sup>b</sup>
AsH <sub>4</sub> <sup>3+</sup> ( <b>10</b> ) → AsH <sub>3</sub> <sup>2+</sup> + H <sup>+</sup>	-217.1 <sup>b</sup>

<sup>a</sup> At the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G\*\* + ZPE level.  
<sup>b</sup> QCISD(T)/6-311G\*\*//QCISD(T)/6-311G\*\* + ZPE.

## Results and Discussion

NH<sub>4</sub><sup>2+</sup>. Koch and Schwarz<sup>4</sup> and Pope et al.<sup>5</sup> have previously reported structures and energies NH<sub>4</sub><sup>2+</sup>. We have calculated the structure of the dication only for comparison with the PH<sub>5</sub><sup>2+</sup> and AsH<sub>5</sub><sup>2+</sup>. Similar to the reported results, the *D*<sub>2d</sub> symmetrical structure **1** is found to be the only minimum on the potential energy surface of NH<sub>4</sub><sup>2+</sup> at both the MP2/6-31G\*\* and QCISD(T)/6-311G\*\* levels (Figure 1). The N–H bond distance of 1.119 Å and H<sub>1</sub>NH<sub>3</sub> angle of 147.7° of **1** at the QCISD(T)/6-311G\*\* level agree very well with the reported values of 1.126 Å and 146.2° (at the CASSCF/TZP level)<sup>5b</sup> and 1.113 Å and 147.7° (at the MP2(FULL)/6-31G\*\* level),<sup>4</sup> respectively. Dissociation of **1** into NH<sub>3</sub><sup>+</sup> and H<sup>+</sup> is exothermic by 117.7 kcal/mol and the process has a 6.6 kcal/mol barrier (Table 2), very close to the reported values of 116.5 and 7.8 kcal/mol, respectively.<sup>4</sup>

The possible structure **1b** with a 3c-2e bond was not a minimum and collapsed to **1** upon optimization at the MP2/6-31G\*\* and QCISD(T)/6-311G\*\* levels without any activation barrier.



The adiabatic ionization energy (IE<sub>a</sub>) of NH<sub>4</sub><sup>+</sup> was calculated (Table 3). The calculated IE<sub>a</sub> of NH<sub>4</sub><sup>+</sup> was 24.0 eV compared with the experimental ionization energy of 24.5 eV.<sup>6</sup>

NH<sub>4</sub><sup>3+</sup>. We also searched for any minimum-energy structure of NH<sub>4</sub><sup>3+</sup>. At the MP2/6-31G\*\* or QCISD(T)/6-311G\*\* level no structure of NH<sub>4</sub><sup>3+</sup> on its potential energy surface could be found as a minimum. Charge–charge repulsion in NH<sub>4</sub><sup>3+</sup> seems to have reached its prohibitive limit.

PH<sub>4</sub><sup>2+</sup>. Unlike NH<sub>4</sub><sup>2+</sup>, the *C*<sub>3v</sub> structure **2** and the *C*<sub>s</sub> structure **3** (Figure 1) were found to be minima on the PES of PH<sub>4</sub><sup>2+</sup> at the MP2/6-31G\*\* level as indicated by frequency calculations

**TABLE 3: Theoretical and Experimental Ionization Energies in eV<sup>a</sup>**

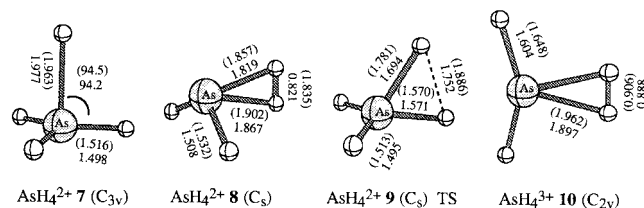
	theor IE <sub>a</sub>	exptl <sup>b</sup>
NH <sub>4</sub> <sup>+</sup>	24.0	24.5
PH <sub>4</sub> <sup>+</sup>	20.5	
PH <sub>4</sub> <sup>2+</sup>	26.1	
AsH <sub>4</sub> <sup>+</sup>	19.1 <sup>c</sup>	
AsH <sub>4</sub> <sup>2+</sup>	24.9 <sup>c</sup>	

<sup>a</sup> At the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G\*\* + ZPE level.  
<sup>b</sup> Taken from ref 6. <sup>c</sup> QCISD(T)/6-311G\*\*//QCISD(T)/6-311G\*\* + ZPE level.

(NIMAG = 0) at the same level. The structure **2** is 9.0 kcal/mol less stable than **3** at the MP2/6-31G\*\* level (Table 1). The difference becomes 9.5 kcal/mol at the higher QCISD(T)/6-311G\*\* level. At the even higher level of CCSD(T)/cc-pVTZ//QCISD(T)/6-311G\*\* the difference decreased to 8.2 kcal/mol. Including zero-point vibrational energies, i.e., at the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G\*\* + ZPE level structure **2** is still significantly less stable than **3** by 6.5 kcal/mol. Thus, structure **3** is the global minimum on the PES of PH<sub>4</sub><sup>2+</sup>. Previously Pope et al.<sup>5</sup> calculated PH<sub>4</sub><sup>2+</sup> at the ab initio HF/TZP and CASSCF/TZP levels and concluded,<sup>5b</sup> in contrast to our present results, that the global minimum for PH<sub>4</sub><sup>2+</sup> is structure **2**. The reported<sup>5b</sup> structure of **2** at the CASSCF/TZP level agrees very well with our QCISD(T)/6-311G\*\* calculated structure (Figure 1).

Structure **3** resembles a complex between PH<sub>2</sub><sup>2+</sup> and a hydrogen molecule resulting in the formation of a 2e-3c bond. The sp<sup>3</sup>-hybridized phosphorus atom of **3** possesses a formal sp<sup>3</sup>-orbital (containing a single electron) oriented pseudotetrahedrally. The electron deficient P–H bond distances in the 2e-3c bond of **3** are 1.672 and 1.635 Å at the MP2/6-31G\*\* level. These are expectedly longer than that of 2e-2c P–H bonds (1.416 Å). The H–H distance in the 2e-3c interactions of 0.848 Å is only slightly longer than H<sub>2</sub> (0.734 Å). Optimizations of structures **3** at the QCISD(T)/6-311G\*\* level changed the geometries a little. The P–H and H–H bonds become slightly longer.

Transition structure, **4** (Figure 1), for the interconversion of **2** and **3**, was also located. Structure **4** lies only 1.5 and 0.7 kcal/mol, at MP2/6-31G\*\* and QCISD(T)/6-311G\*\*, respectively, higher in energy than structure **2**. At the highest level of theory (CCSD(T)/cc-pVTZ//QCISD(T)/6-311G\*\* + ZPE) the energy difference between **3** and **4** disappeared. This shows that **2** if formed will spontaneously convert into **3**. We also have located transition structure **5** (Figure 1) for the deprotonation process in **2**. Structure **5** lies 18.0 kcal/mol higher in energy than **2**. Thus **2** has a considerable kinetic barrier for deprotonation, although the deprotonation process is exothermic by 67.2 kcal/mol. In comparison, the corresponding values for **1** are 6.6 and 117.7 kcal/mol. Deprotonation of **3** is slightly less exothermic by 60.7 kcal/mol.



**Figure 2.** MP2/6-31G\*\* (QCISD(T)/6-311G\*\*) optimized structures of 7–10.

**PH<sub>4</sub><sup>3+</sup>.** Removing an electron from PH<sub>4</sub><sup>2+</sup> dication leads to the PH<sub>4</sub><sup>3+</sup> trication. The PH<sub>4</sub><sup>3+</sup> trication is isoelectronic with the SiH<sub>4</sub><sup>2+</sup> dication. Similar to SiH<sub>4</sub><sup>2+</sup>,<sup>11</sup> the planar C<sub>2v</sub> structure **6** is found to be the only minimum on the potential energy surface of PH<sub>4</sub><sup>3+</sup> at the MP2/6-31G\*\* level (Figure 1). The planar D<sub>4h</sub> symmetrical structure of PH<sub>4</sub><sup>3+</sup> was characterized as the saddle point, as there are two imaginary frequencies (i.e., NIMAG = 2) in its calculated IR spectrum. Structure **6** is characterized with a 3c-2e bond and an empty p-orbital orthogonal to the plane of the molecule.

The transition state for deprotonation of **6** into PH<sub>3</sub><sup>2+</sup> and H<sup>+</sup> was also located. The calculated barrier for proton loss is only 4.5 kcal/mol and the deprotonation process is highly exothermic by 243.3 kcal/mol. This shows that the trication **6** if formed will easily dissociate into PH<sub>3</sub><sup>2+</sup> and H<sup>+</sup>.

The adiabatic ionization energies (IE<sub>a</sub>) of PH<sub>4</sub><sup>+</sup> and PH<sub>4</sub><sup>2+</sup> were calculated. The calculated IE<sub>a</sub>s of PH<sub>4</sub><sup>+</sup> and PH<sub>4</sub><sup>2+</sup> are 20.5 and 26.1 eV, respectively.

**AsH<sub>3</sub><sup>2+</sup>.** Similar to PH<sub>4</sub><sup>2+</sup>, the C<sub>3v</sub> structure **7** and the C<sub>s</sub> structure **8** are the minima on the PES of AsH<sub>4</sub><sup>2+</sup> at the MP2/6-31G\*\* level (Figure 2). The structure **8**, with a 3c-2e bond, is lower in energy than **7** by 14.8 kcal/mol at the QCISD(T)/6-311G\*\*/QCISD(T)/6-311G\*\* + ZPE level (Table 1). The As–H bond distances in the 2e-3c bond of **8** are 1.867 and 1.819 Å, significantly longer than the 2e-2c As–H bond of 1.508 Å at the MP2/6-31G\*\* level. The H–H distance in the 2e-3c interaction is 0.821 Å at the same level. Conversion of **7** into **8** through transition structure **9** would be very facile as the barrier for the process was calculated to be only 0.4 kcal/mol. Dissociation of **8** into AsH<sub>3</sub><sup>+</sup> and H<sup>+</sup> is exothermic by only 41.3 kcal/mol (Table 2). However, no transition structure for the deprotonation of either **7** or **8** could be located.

**AsH<sub>4</sub><sup>3+</sup>.** The AsH<sub>4</sub><sup>3+</sup> trication can be formed by removing an electron from the AsH<sub>4</sub><sup>2+</sup> dication. Similar to PH<sub>4</sub><sup>3+</sup>, the planar C<sub>2v</sub> structure **10**, with a 2e-3c interaction, is the only minimum on the potential energy surface of AsH<sub>4</sub><sup>3+</sup> at the MP2/6-31G\*\* level. The D<sub>4h</sub> symmetrical structure of AsH<sub>4</sub><sup>3+</sup> is not a minimum at the MP2/6-31G\* level and contains two imaginary frequencies in its calculated vibrational frequencies. Calculated structural parameters are given in Figure 2. Calculated exothermicity of the dissociation of **10** into AsH<sub>3</sub><sup>2+</sup> and H<sup>+</sup> was found to be 217.1 kcal/mol (Table 2).

As expected, in the series NH<sub>4</sub><sup>2+</sup>, PH<sub>4</sub><sup>2+</sup>, and AsH<sub>4</sub><sup>2+</sup>, the calculated ΔH<sub>0</sub>s of deprotonation of the dications indicate an increase in the stability of the dications toward deprotonation with the increase in the size of the central atoms. Similarly, in PH<sub>4</sub><sup>3+</sup> and AsH<sub>4</sub><sup>3+</sup>, the stability of the trications toward deprotonation also increases with the increase in the size of the

central atoms, although they are still thermodynamically and kinetically extremely unstable. However, better stabilization of some of these polycations by Schmidbaur type auration<sup>12</sup> with (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PAu, an isolobal analogue of H<sup>+</sup>, should be possible. In fact, Zeller and Schmidbaur have succeeded in the preparation and identification of the hexacoordinate tripositively charged octahedral {[C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PAu]<sub>6</sub>P}<sup>3+</sup> complex in solution,<sup>13</sup> which is the isolobal analogue of PH<sub>6</sub><sup>3+</sup>.

## Conclusions

Contrary to previous theoretical studies at the HF/TZP and CASCF/TZP levels,<sup>5b</sup> present ab initio study at the MP2/6-31G\*\* and QCISD(T)/6-311G\*\* levels indicates that the global minimum structure of PH<sub>4</sub><sup>2+</sup> is not of C<sub>3v</sub> symmetric **2** but a C<sub>s</sub> symmetrical **3** with a 3c-2e bond. The C<sub>3v</sub> symmetric **2**, although a minimum on the PES, is 6.5 kcal/mol less stable than **3**. Energy calculations also indicate that conversion of **2** into **3** through transition state **4** is extremely facile. In addition the planar C<sub>2v</sub> symmetric **6**, with a 3c-2e bond, was also found to be the only minimum for PH<sub>4</sub><sup>3+</sup>. Similar to phosphorus systems, C<sub>s</sub> **8** and C<sub>2v</sub> **10**, each containing a 2e-3c bond, were found to be the global minimum of AsH<sub>4</sub><sup>2+</sup> and AsH<sub>4</sub><sup>3+</sup>, respectively. Thermodynamics of the deprotonation process of the di- and trications were also computed.

**Acknowledgment.** Support of our work by the National Science Foundation is gratefully acknowledged.

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