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## Theoretical study of $\text{AlH}_n^{2+}$ ( $n=1-7$ ) dications

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**Abstract** The structures and stability of  $\text{AlH}_n^{2+}$  ( $n = 1 - 7$ ) 1–7 dications were calculated at the ab initio MP2/aug-cc-pVTZ level of theory. The dications  $\text{AlH}_1^{2+}$  **1** and  $\text{AlH}_2^{2+}$  **2** were characterized to be unstable thermodynamically. However, these and the stable dications,  $\text{AlH}_n^{2+}$  ( $n = 3 - 7$ ) **3–7** have considerable kinetic barriers for deprotonation. Each of the structures **3–7** contains one or more two-electron three-center (2e–3c) bonds. Aluminum atoms of these dications carry most of the positive charges, as indicated by NBO charge calculations.

**Keywords** ab initio calculations · Alane dications · Main group hydrido dications

### Introduction

The main-group hydrido dications have been a topic of numerous theoretical and experimental investigations [1]. Recently, we reported a study of structures and stabilities of  $\text{BH}_n^{2+}$  ( $n = 1 - 7$ ) dications using ab initio and density functional theory (DFT) methods at the MP2/aug-cc-pVTZ and B3LYP/ aug-cc-pVTZ levels, respectively [2]. The dications  $\text{BH}_1^{2+}$  and  $\text{BH}_2^{2+}$  were found to be highly unstable both kinetically and thermodynamically. However, dications  $\text{BH}_n^{2+}$  ( $n = 3 - 7$ ) have considerable kinetic barriers for deprotonation. Each of these structures contains at least one two-electron three-center (2e–3c) bond. We have previously

reported calculated structures and energetics of the  $\text{CH}_3^{2+}$ ,  $\text{CH}_5^{2+}$  and  $\text{CH}_6^{2+}$  carbocations [3–5]. Wong and Radom [6] have reported the calculated structure of the  $\text{CH}_4^{2+}$  dication. We have also recently reported structures and energetics of onium dications  $\text{XH}_4^{2+}$  and  $\text{XH}_5^{2+}$  ( $X=\text{N, P, and As}$ ) [7, 8], boronium  $\text{BH}_5^{2+}$  and  $\text{BH}_7^{2+}$  dications [4, 9] as well as their corresponding aluminum based analogs,  $\text{AlH}_5^{2+}$  and  $\text{AlH}_7^{2+}$  dications [10]. Koch, Frenking and Schwarz reported [11] the ab initio HF/6-31G(d) calculated structures of  $\text{SiH}_n^{2+}$  ( $n = 1 - 5$ ) dications [12]. Structures and bonding of such highly electron-deficient dications are of substantial theoretical significance. In continuation of our study of the main-group hydrido dications, we have now extended our investigations to the structures and stabilities of  $\text{AlH}_n^{2+}$  ( $n = 1 - 7$ ) dications by the ab initio method at the MP2/aug-cc-pVTZ level. The thermodynamic and kinetic barriers for deprotonation processes of dications were also estimated.

### Calculations

All calculations were carried out using the Gaussian 03 program system [13]. Initial geometry optimizations were performed at the DFT B3LYP/aug-cc-pVTZ level [14]. Vibrational frequencies at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level were used to characterize stationary points as minima (number of imaginary frequencies (NIMAG)=0) or transition state structures (NIMAG=1) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.98 [15]. Further geometry optimizations were performed at the MP2/aug-cc-pVTZ level. Final energies were calculated at the MP4(SDTQ)/aug-cc-pVTZ//MP2/aug-cc-pVTZ + ZPE level (Table 1). Atomic charges and Wiberg bond indices [16] (bond orders) were obtained at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVTZ level using the Natural Bond Orbital analysis (NBO) method [17].

Dedicated to Professor Dr. Paul von Ragué Schleyer on the occasion of his 75th birthday

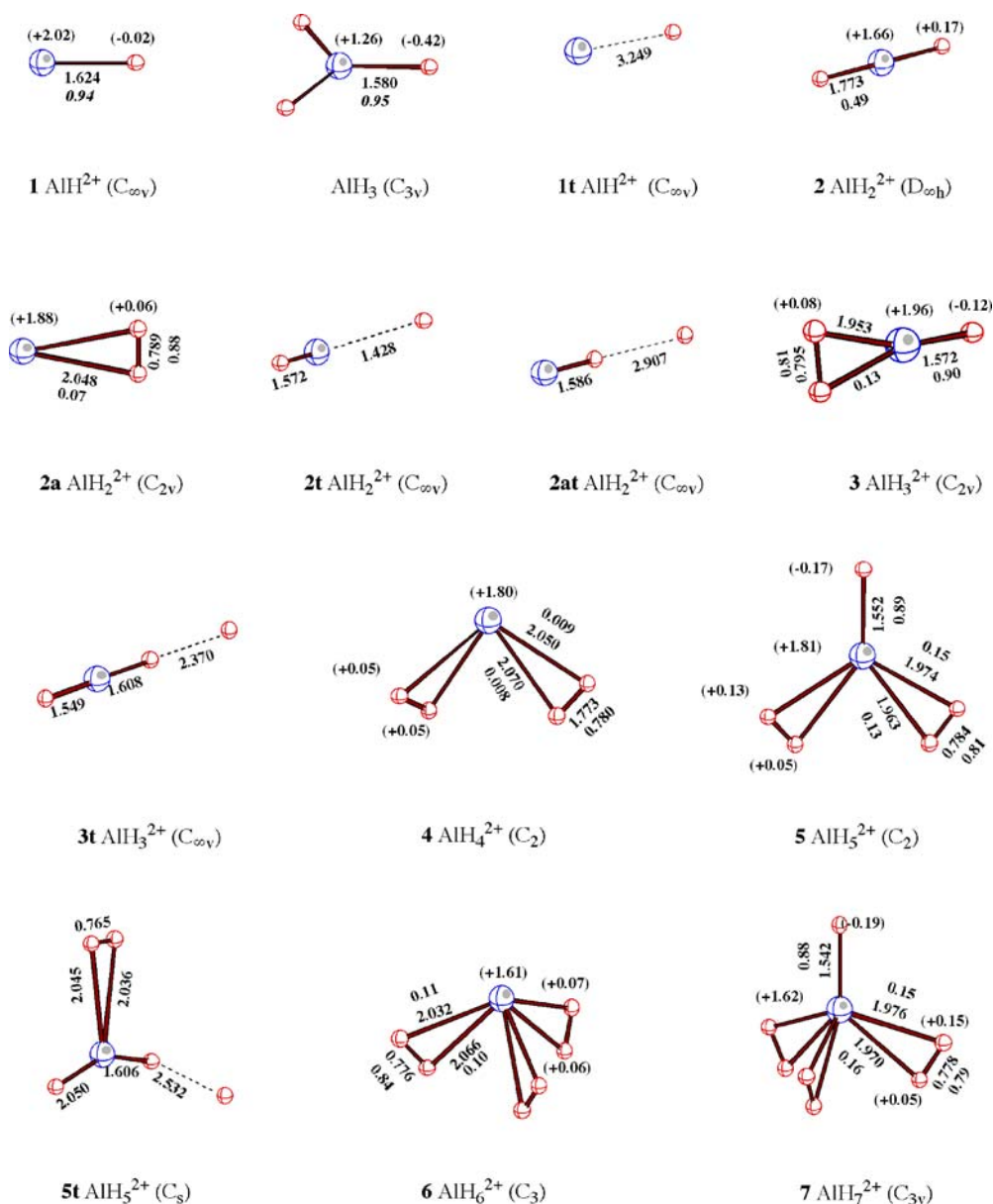
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**Table 1** Total energies (-au), ZPE<sup>a</sup> and relative energies (kcal mol<sup>-1</sup>)<sup>b</sup>

	B3LYP/ aug-cc-pvtz	ZPE	MP2/ aug-cc-pvtz	MP4(SDTQ)/ aug-cc-pvtz// MP2/aug-cc-pvtz	Relative energy (kcal mol <sup>-1</sup> )
1	242.08106	2.1	241.61877	241.62898	0.0
1t	242.04353	0.0	241.56657	241.57523	31.6
2	242.64366	3.3	242.15951	242.16987	42.7
2a	242.70304	6.9	242.23529	242.24372	0.0
2t	242.62847	2.6	242.12291	242.13294	65.2
2at	242.63855	3.0	242.12546	242.13599	63.7
3	243.31906	10.6	242.84048	242.85704	0.0
3t	243.22642	7.1	242.73659	242.75233	62.2
4	243.91925	14.6	243.43305	243.44950	
5	244.54012	19.5	244.04686	244.07046	0.0
5t	244.42832	15.8	243.92239	243.94541	74.8
6	245.12901	22.8	244.62752	244.65187	
7	245.75552	29.3	245.24866	245.27953	

<sup>a</sup>Zero-point vibrational energies (ZPE) at B3LYP/aug-cc-pvtz//B3LYP/aug-cc-pvtz scaled by a factor of 0.98

<sup>b</sup>At MP4(SDTQ)/aug-cc-pvtz//MP2/aug-cc-pvtz + ZPE level

**Fig. 1** MP2/aug-cc-pVTZ structures, NBO charges (in parentheses) and Wiberg bond index (in italics) of 1–7

## Results and discussion

Structure **1** was found to be a minimum (Fig. 1) on the potential energy surface (PES) of singlet  $\text{AlH}^{2+}$  at the MP2/aug-cc-pVTZ level. The computed bond length of Al–H bond was found to be 1.624 Å. For comparison, we also calculated the neutral monomeric  $\text{AlH}_3$  at the same MP2/aug-cc-pVTZ level (Fig. 1). The Al–H bond of **1** is only 0.044 Å longer than the Al–H bond of  $\text{AlH}_3$ . The relative bond strength of the Al–H bond of **1** was estimated using the Wiberg bond index [16] analysis (Fig. 1). The computed bond index of Al–H bond was found to be 0.94. This is practically same as the Al–H bond index of  $\text{AlH}_3$  (0.95). NBO charge calculations show that in dication **1** the aluminum carries (+2.02) all of the charges (Fig. 1). Dissociation of **1** into  $\text{Al}^+$  and  $\text{H}^+$  was computed to be exothermic by 53.7 kcal mol<sup>-1</sup> (Table 2). The transition structure **1t** for the dissociation lies 31.6 kcal mol<sup>-1</sup> higher in energy than structure **1** at the MP4(SDTQ)/aug-cc-pVTZ//MP2/aug-cc-pVTZ + ZPE level. These results indicate that the dication **1** is quite stable kinetically. In contrast, the boron dication [2]  $\text{BH}^{2+}$  was found to be very unstable kinetically, computed at the same level.

The linear  $C_{\infty v}$  symmetric structure **2** and the trigonal  $C_{2v}$  symmetric structure **2a** were located as minima on the PES of doublet  $\text{AlH}_2^{2+}$  (Fig. 1). The structure **2** is characterized by the long Al–H bond length of 1.773. The electron deficient longer Al–H bond is expectedly weak as indicated by the calculated bond index of 0.49 (Fig. 1). On the other hand, the structure **2a** is characterized as a complex of a doubly charged aluminum atom and a hydrogen molecule. Previously Koch et al. reported [18] a detailed theoretical investigation of  $\text{CH}_2\text{XH}^{2+}$  and  $\text{CH}_3\text{X}^{2+}$  dications ( $X=\text{NH}_2, \text{OH}, \text{F}$ ). It was shown that the geometries and stabilities of these types of dications are best explained by the donor-acceptor interaction of (neutral) donor and (doubly charged) acceptor molecules. The model was also used to explain the structures, stabilities and bonding of the compounds of noble gases [19]. However, the structure **2a** is 42.7 kcal mol<sup>-1</sup> more stable than **2**. In the dication **2**, aluminum carries a charge of 1.66 and the two hydrogens carry 0.34 (Fig. 1). On the other hand, in the dication **2a**, aluminum carries a charge of 1.88 and the two hydrogens carry only 0.12. Deprotonation of both **2** and **2a** are exothermic by 45.6 and 2.9 kcal mol<sup>-1</sup> (Table 2), respectively. However, these processes have high kinetic barriers of 63.7 and 62.2 kcal mol<sup>-1</sup>, respectively, through transition states **2t** and **2at** (Fig. 1). Dissociation of **2a** into  $\text{Al}^{2+}$  and  $\text{H}_2$  is, however, quite endothermic by 25.8 kcal mol<sup>-1</sup> (Table 2).

The  $C_{2v}$  symmetric structure **3** is the only minimum that was located on the PES of singlet dication  $\text{AlH}_3^{2+}$  (Fig. 1). The structure **3** is characterized with a 2e–3c bond resembling a complex between  $\text{AlH}^{2+}$  and a hydrogen molecule. The Al–H and H–H bond distances of the 2e–3c interaction are 1.953 and 0.795 Å, respectively. Deprotonation of **3** is exothermic by only 9.2 kcal mol<sup>-1</sup>, but the process has a kinetic barrier of 62.2 kcal mol<sup>-1</sup> through the

**Table 2** Dissociation energies ( $\Delta E_0$ ) and kinetic barriers at 298 K for the selected processes<sup>a</sup>

Process	$\Delta E_0$ (kcal mol <sup>-1</sup> ) <sup>a</sup>	Barrier (kcal mol <sup>-1</sup> )
$\text{AlH}^{2+}\mathbf{1} \rightarrow \text{Al}^+ + \text{H}^+$	-53.7	31.6
$\text{AlH}_2^{2+}\mathbf{2} \rightarrow \text{AlH}^+ + \text{H}^+$	-45.6	65.2
$\text{AlH}_2^{2+}\mathbf{2a} \rightarrow \text{AlH}^+ + \text{H}^+$	-2.9	63.7
$\text{AlH}_3^{2+}\mathbf{3} \rightarrow \text{AlH}_2^+ + \text{H}^+$	-9.2	62.2
$\text{AlH}_4^{2+}\mathbf{4} \rightarrow \text{AlH}_3^+ + \text{H}^+$	+14.1	
$\text{AlH}_5^{2+}\mathbf{5} \rightarrow \text{AlH}_4^+ + \text{H}^+$	+10.2	74.8
$\text{AlH}_6^{2+}\mathbf{6} \rightarrow \text{AlH}_5^+ + \text{H}^+$	+27.7	
$\text{AlH}_7^{2+}\mathbf{7} \rightarrow \text{AlH}_6^+ + \text{H}^+$	+25.7	
$\text{AlH}_2^{2+}\mathbf{2a} \rightarrow \text{Al}^{2+} + \text{H}^2$	+25.8	
$\text{AlH}_3^{2+}\mathbf{3} \rightarrow \text{AlH}^{2+}\mathbf{1} + \text{H}_2$	+33.0	
$\text{AlH}_4^{2+}\mathbf{4} \rightarrow \text{AlH}_3^{2+}\mathbf{2a} + \text{H}_2$	+19.8	
$\text{AlH}_5^{2+}\mathbf{5} \rightarrow \text{AlH}_4^{2+}\mathbf{4} + \text{H}_2$	+23.4	
$\text{AlH}_6^{2+}\mathbf{6} \rightarrow \text{AlH}_5^{2+}\mathbf{5} + \text{H}_2$	+17.2	
$\text{AlH}_7^{2+}\mathbf{7} \rightarrow \text{AlH}_6^{2+}\mathbf{6} + \text{H}_2$	+19.8	

<sup>a</sup>at MP4(SDTQ)/aug-cc-pVTZ//MP2/aug-cc-pVTZ + ZPE level

transition state **3t** (Fig. 1). However, dissociation of **3** into **1** and  $\text{H}_2$  is quite endothermic by 33.0 kcal mol<sup>-1</sup> (Table 2).

The  $C_2$  symmetric form **4** was located as a minimum for doublet  $\text{AlH}_4^{2+}$  (Fig. 1). The structure **4** resembles a complex between  $\text{Al}^{2+}$  and two hydrogen molecules resulting in the formation of two 2e–3c bonds. The calculated charges of aluminum and each of the hydrogen of **4** are +1.80 and +0.05, respectively (Fig. 1). The deprotonation of **4** is endothermic by 14.1 kcal mol<sup>-1</sup> (Table 2). However, no transition state could be located for the deprotonation of **4**.

Olah and Rasul have previously reported [10] the structure and energetics of  $\text{AlH}_5^{2+}$  at the MP2/6-31G(d,p) level of theory. At the MP2/6-31G(d,p) level, the planar  $C_{2v}$ -symmetric form was found to be the minimum. However, at the MP2/aug-cc-pVTZ level, a slightly different  $C_2$ -symmetric form **5** with two 2e–3c bonds was located as the only minima for singlet  $\text{AlH}_5^{2+}$  (Fig. 1). The optimized structure of  $\text{AlH}_5^{2+}$  (**5**) is shown in Fig. 1. Structure **5** resembles a complex between  $\text{AlH}^{2+}$  and two hydrogen molecules with an empty  $p$ -orbital orthogonal to the plane of the molecule. Deprotonation of **5** is endothermic by 10.2 kcal mol<sup>-1</sup>, but the process has a kinetic barrier of 74.8 kcal mol<sup>-1</sup> through the transition state **5t** (Fig. 1).

The six coordinate propeller-shaped  $C_3$ -symmetrical structure **6** with three 2e–3c bonds is the only minimum on the PES of doublet  $\text{AlH}_6^{2+}$  (Fig. 1). The Al–H bond distances of **6** are 2.032 and 2.066 Å, slightly shorter than those in  $\text{AlH}_4^{2+}$  **4** (2.050 and 2.070 Å). The six hydrogen atoms bear charges of only +0.39. The deprotonation process in **6** is endothermic by 27.7 kcal mol<sup>-1</sup>. Even the trication  $\text{AlH}_6^{3+}$  was found to be a minimum, as shown in earlier calculations [10].

The structure and energetics of seven-coordinate  $\text{AlH}_7^{2+}$  at the MP2/6-31G\*\* level were also reported previously [10]. Similar to the reported results, our present calculations also indicate that the propeller-shaped  $C_{3v}$ -symmetrical structure **7** with three 2e–3c bonds is the only minimum on the PES of singlet  $\text{AlH}_7^{2+}$  (Fig. 1). Structure **7** is isostructural with that of the carbon analog  $\text{CH}_7^{3+}$  [20]. We also searched for eight-coordinate minimum-energy structure for  $\text{AlH}_8^{2+}$ . No structure could be located as a minimum for doublet  $\text{AlH}_8^{2+}$  at the MP2/aug-cc-pVTZ level.

## Conclusions

Structures and stabilities of  $\text{AlH}_n^{2+}$  ( $n = 1 - 7$ ) dications were calculated at the *ab initio* MP2/aug-cc-pVTZ level of theory. The structures **1–7** were found to be the minima on the PES. The dication  $\text{AlH}_2^{2+}$  **1** is unstable (by 53.7 kcal mol<sup>-1</sup>) thermodynamically towards deprotonation, although the process has to overcome a kinetic barrier of 31.6 kcal mol<sup>-1</sup>. Deprotonation in  $\text{AlH}_2^{2+}$  **2a** also has a high kinetic barrier of 63.7 kcal mol<sup>-1</sup>. The deprotonation process in **2a** was found to be exothermic by only 2.9 kcal mol<sup>-1</sup>. Calculations indicate that each of the structures **3–7** contains one or more 2e–3c bond. The Wiberg bond indices and charge distributions of the structures by the NBO method were also computed. Aluminum atoms of these dications carry most of the positive charge. Although such small alane dications are thermodynamically unstable, their computational characterization gives additional support for their transient existence in gas phase ion-molecule reactions.

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