SUPPORTING INFORMATION

The Role of NH_3 in the Dehydrogenation of Calcium Amidoborane Ammoniate and Magnesium Amidoborane Ammoniate: A First-Principles Study

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Table S1 Comparison of first-principles calculated structural properties of $Ca(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2{\cdot}2NH_3$, and $Mg(NH_2BH_3)_2{\cdot}NH_3$ by using generalized gradient approximation (GGA) of Perdew and Wang 1991 (PW91), GGA of Perdew–Burke–Ernzerhof (PBE) and local density approximation (LDA) and experimental data (EXP). $E_{el.tot}$ is the electronic total energy.

Compounds		GGA-PW91	GGA -PBE	LDA	EXP
$Ca(NH_2BH_3)_2$[1]	a (Å)	9.2220	9.24477	8.80922	9.100(2)
	b (Å)	4.3472	4.37205	4.02924	4.371(1)
	c (Å)	6.4996	6.56597	6.15534	6.441(2)
	α (°)	90	90	90	90
	β (°)	93.3346	93.4127	92.1574	93.19(2)
	γ (°)	90	90	90	90
	$E_{el.tot}$ (eV)	–72.81	–72.41	–77.06	--
$Ca(NH_2BH_3)_2{\cdot}2NH_3$	a (Å)	18.6301	18.7200	17.63000	18.6733
	b (Å)	5.2913	5.32884	4.95857	5.2283
	c (Å)	8.5016	8.53967	7.91976	8.5748
	α (°)	90	90	90	90
	β (°)	90	90	90	90
	γ (°)	90	90	90	90
	$E_{el.tot}$	–113.03	–112.46	–119.18	--
$Mg(NH_2BH_3)_2{\cdot}NH_3$[2]	a (Å)	8.8174	8.84655	8.16791	8.8815
	b (Å)	9.0794	9.11968	8.80380	8.9466
	c (Å)	8.1299	8.17664	7.58461	8.0701
	α (°)	90	90	90	90
	β (°)	95.2014	94.3628	96.1859	94.0744(48)
	γ (°)	90	90	90	90
	$E_{el.tot}$	–91.53	–91.08	–96.62	--

TABLE S2: Calculated structure parameters and atomic positions of $Ca(NH_2BH_3)_2$, $Ca(NH_2BH_3)_2{\cdot}2NH_3$, $Mg(NH_2BH_3)_2$ and $Mg(NH_2BH_3)_2{\cdot}NH_3$, respectively. Experimental data are displayed if available.

$Ca(NH_2BH_3)_2$							
		Calculation (GGA-PW91)			Experiment [1]		
Space group		monoclinic *C*2 (No.5)			monoclinic *C*2 (No.5)		
Lattice Parameters		*a*= 9.2220 Å	*α*= 90 º		*a*= 9.100(2) Å	*α*= 90 º	
		b= 4.3472 Å	*β*= 93.3346 º		*b*= 4.371(1) Å	*β*= 93.19(2) º	
		c= 6.4996 Å	*γ*= 90 º		*c*= 6.441(2) Å	*γ*= 90 º	
Atom	Site	*x*	*y*	*z*	*x*	*y*	*z*
H1	4c	0.92178	0.91275	0.70776	0.926	0.922	0.715
H2	4c	0.13863	0.34559	0.25596	0.145	0.344	0.212
H3	4c	0.85768	0.05412	-0.01804	0.861	0.008	0.003
H4	4c	0.64103	0.12257	0.59533	0.653	0.162	0.598
H5	4c	0.34304	0.78202	0.30588	0.345	0.803	0.320
B1	4c	0.83324	0.07946	0.79171	0.835(2)	0.064(3)	0.815(4)
N1	4c	0.67237	0.00961	0.72846	0.675(2)	0.024(1)	0.725(3)
Ca1	2a	0.00000	0.60177	0.00000	0.0	0.560(3)	0.0

$Ca(NH_2BH_3)_2 \cdot 2NH_3$							
		Calculation (GGA-PW91)			Experiment		
Space group		orthorhombic *Pna*2_1 (No.33)			orthorhombic *Pna*2_1 (No.33)		
Lattice parameters		*a*= 18.6301 Å	*α*= 90 º		*a*= 18.6733 Å	*α*= 90 º	
		b= 5.2913 Å	*β*= 90 º		*b*= 5.2283 Å	*β*= 90 º	
		c= 8.5016 Å	*γ*= 90 º		*c*= 8.5748 Å	*γ*= 90 º	
Atom	Site	*x*	*y*	*z*	*x*	*y*	*z*
H1	4a	0.84780	0.27160	0.61260	0.84780	0.27160	0.61260
H2	4a	0.92830	0.15120	0.59680	0.92830	0.15120	0.59680
H3	4a	0.85840	-0.03490	0.60020	0.85840	-0.03490	0.60020
H4	4a	0.15200	0.72780	0.77900	0.15200	0.72780	0.77900
H5	4a	0.14140	1.03440	0.79150	0.14140	1.03440	0.79150
H6	4a	0.07140	0.84850	0.79350	0.07140	0.84850	0.79350
H7	4a	0.75420	0.47530	0.56650	0.75420	0.47530	0.56650
H8	4a	0.83660	0.62400	0.44460	0.83660	0.62400	0.44460
H9	4a	0.75230	0.47070	0.33210	0.75230	0.47070	0.33210
H10	4a	0.73210	0.95810	0.54410	0.73210	0.95810	0.54410
H11	4a	0.73230	0.95860	0.35160	0.73230	0.95860	0.35160
H12	4a	0.00760	0.17160	0.43930	0.00760	0.17160	0.43930
H13	4a	0.09230	0.32290	0.33360	0.09230	0.32290	0.33360
H14	4a	-0.01310	0.64470	0.34290	-0.01310	0.64470	0.34290
H15	4a	-0.01720	0.64640	0.53320	-0.01720	0.64640	0.53320
H16	4a	0.08580	0.32090	0.56780	0.08580	0.32090	0.56780
B1	4a	0.55090	0.14810	0.44570	0.53932	0.15308	0.42306
B2	4a	0.22960	0.40060	0.94770	0.21003	0.39889	0.97491
N1	4a	0.01730	0.61780	0.44150	0.01321	0.59093	0.43370
N2	4a	0.27480	0.15400	0.94770	0.27060	0.16688	0.90051
N3	4a	0.62050	0.62500	0.15030	0.62373	0.61262	0.10811
N4	4a	0.12040	0.87460	0.74090	0.11897	0.88789	0.69925
Ca1	4a	0.88020	0.08630	0.94590	0.88318	0.11594	0.91569

$Mg(NH_2BH_3)_2$				
Space group		monoclinic *C*2 (No.5)		
Lattice Parameters		*a*= 8.5722 Å	*α*= 90 º	
		b= 5.6048 Å	*β*= 85.8476 º	
		c= 5.6216 Å	*γ*= 90 º	
Atom	Site	*x*	*y*	*z*
H1	4c	0.89542	0.88442	0.71438
H2	4c	0.11683	0.23641	0.25764
H3	4c	0.84195	0.04189	0.03678
H4	4c	0.63216	0.08505	0.60438
H5	4c	0.39762	0.87576	0.19833
B1	4c	0.82339	0.05324	0.81951
N1	4c	0.64574	0.04540	0.77936
Ca1	2a	-0.00000	0.76966	0.00000

$Mg(NH_2BH_3)_2 \cdot NH_3$							
		Calculation (GGA-PW91)			Experiment [2]		
Space group		monoclinic $P2_1/c$ (No.14)			monoclinic $P2_1/c$ (No.14)		
Lattice Parameters		a= 8.8174 Å	α= 90 º		a= 8.8815 Å	α= 90 º	
		b= 9.0794 Å	β= 95.2014 º		b= 8.9466 Å	β=94.0744(48) º	
		c= 8.1299 Å	γ= 90 º		c= 8.0701 Å	γ= 90 º	
Atom	Site	x	y	z	x	y	z
H1	4e	0.81817	0.92962	0.01757	0.8198(1)	-0.0570(25)	1.0231(3)
H2	4e	0.72868	0.07529	0.94230	0.6995(2)	0.0438(2)	0.9055(1)
H3	4e	0.63411	0.92884	0.99276	0.6346(1)	-0.0724(2)	1.0390(3)
H4	4e	0.60503	0.28932	0.67553	0.6203(8)	0.2751(1)	0.6851(1)
H5	4e	0.79427	0.17823	0.75396	0.8095(1)	0.1807(8)	0.7802(9)
H6	4e	0.70739	0.16250	0.51990	0.7374(1)	0.1391(7)	0.5489(1)
H7	4e	0.81683	0.40806	0.47338	0.8152(8)	0.4013(8)	0.4795(7)
H8	4e	0.94460	0.35540	0.61731	0.9543(5)	0.3477(1)	0.6089(9)
H9	4e	0.68387	0.28259	0.21758	0.6678(1)	0.2795(1)	0.1939(1)
H10	4e	0.50173	0.29549	0.05691	0.4831(1)	0.3023(1)	0.0491(6)
H11	4e	0.50289	0.14749	0.23799	0.4843(1)	0.1520(5)	0.2287(1)
H12	4e	0.51911	0.48818	0.30497	0.5186(9)	0.4959(5)	0.2932(1)
H13	4e	0.50151	0.35794	0.43907	0.5110(8)	0.3645(1)	0.4330(5)
B1	4e	0.54172	0.27410	0.20300	0.5272(1)	0.2775(7)	0.1922(7)
B2	4e	0.73086	0.24825	0.63841	0.7483(9)	0.2375(6)	0.6556(8)
N1	4e	0.47063	0.38665	0.31862	0.4709(6)	0.3934(6)	0.3145(6)
N2	4e	0.83181	0.38311	0.59648	0.8412(5)	0.3732(6)	0.6017(6)
N3	4e	0.72493	0.99484	0.03085	0.7206(6)	0.0017(6)	1.0231(6)
Mg1	4e	0.23180	0.42535	0.28130	0.2269(3)	0.4245(3)	0.2850(3)

Reference

1. Wu, H.; Zhou, W.; Yildirim, T., Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties. *Journal of the American Chemical Society* **2008,** *130* (44), 14834-14839.

2. Chua, Y. S.; Wu, G.; Xiong, Z.; Karkamkar, A.; Guo, J.; Jian, M.; Wong, M. W.; Autrey, T.; Chen, P., Synthesis, structure and dehydrogenation of magnesium amidoborane monoammoniate. *Chemical Communications* **2010,** *46* (31), 5752-5754.