ELECTRONIC SUPPLEMENTARY INFORMATION

"Towards hydrogen-rich ionic $(NH_4)(BH_3NH_2BH_2NH_2BH_3)$ and related molecular $NH_3BH_2NH_2BH_2NH_2BH_3$"

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Contents:

1. Records of reporting synthesis of novel amidoborane and M(B3N2) salts and related compounds:

Fig. S1.1. Hydrogen content of monometallic amidoboranes (black), bimetallic amidoboranes (grey), M(B3N2) salts (magenta) and as a function of reporting date. Hydrogen content of NH_3BH_3 (19.6%), polymeric (NH_2BH_2) (14.0%) and DOE ultimate target (6.5%) given as a reference. Reports and theses marked with hollow circles.

References:

01 NaAB (9.5%) – H. I. Schlesinger, A.B. Burg, *J. Am. Chem. Soc*. 60 (1938) 290–299.
02 a-LiAB (13.7%), NaAB (9.5%) – P. M. Niedenzu, *Ph.D. Thesis*, Ohio State University, 990.
03 NaAB (9.54%) – T. Salupo, *Ph.D. Thesis*, Ohio State University, 1993.
04 α-LiAB (13.7%), NaAB (9.5%), KAB (7.3%), $Mg(AB)_2$ (12.0%), $Zn(AB)_2$ (8.1%) – A. L. DeGraffenreid, *Ph.D. Thesis*, Ohio State University, 1995.
05 α-LiAB (13.7%) – A. G. Myers, *et al., Tetrahedron Lett*. 37 (1996) 3623–3626.

06 α-LiAB (13.70%), NaAB (9.54%) – Z. Xiong, *et al., Nature Mater.* 7 (2008) 138–141.
07 $Ca(AB)_2$ (10.10%) – J. Spielmann, *et al., Angew. Chem. Int. Ed.* 47 (2008) 6290–6295.
08 $Sr(AB)_2$ (6.84%) – Q. Zhang, *et al., J. Phys. Chem. C* 114 (2010) 1709–1714.
09 β-LiAB (13.70%) – C. Wu, *et al., Inorg. Chem*. 49 (2010) 4319–4323.
10 $Y(AB)_3$ (8.47%) – R. V. Genova, *et al., J. Alloys. Comp*. 499 (2010) 144–148.
11 $Al(AB)_3$ (12.97%) – M. F. Hawthorne, *et al., Final Report*, University of Missouri, 2010.
12 KAB (7.31%) – H. V. K. Diyabalanage, *et al. J. Am. Chem. Soc*. 132 (2010) 11836–11837.
13 $Mg(AB)_2$ (12.00%) – J. Luo, J. *et al., Energy Environ. Sci*. 6 (2013) 1018–1025.
14 $Zn(AB)_2$ (8.06%) – R. Owarzany, *M.Sc. Thesis,* University of Warsaw, 2013.
15 LT-RbAB (4.37%), LT-CsAB (3.1%) – I. V. Kazakov, *et al., Polyhedron* 127 (2017) 186–190.
16 $Ba(AB)_2$ (5.12%) – N. A. Shcherbina, *et al., Rus. J. Gen. Chem.* 87 (2017) 2875–2877.
17 HT-RbAB (4.37%), HT-CsAB (3.1%) – R. Owarzany, *et al., Dalton Trans.* 46 (2017) 16315–16320.

18 $Na_2Mg(AB)_4$ (10.63%) – H. Wu, *et al., Chem. Commun*. 47 (2011) 4102–4104.
19 $NaMg(AB)_3$ (11.05%) – X. Kang, *et al., Dalton Trans*. 40 (2011) 3799–3801.
20 $LiNa(AB)_2$ (11.24%) – K. J. Fijalkowski, *et al., Dalton Trans.* 40 (2011) 4407–4413.
21 $KMg(AB)_3$ (9.88%), $RbMg(AB)_3$ (7.58%) – X. Kang, *et al., Int. J. Hydrog. Energy* 37 (2012) 4259–4266.
22 $K_2Mg(AB)_4$ (9.08%) – Y. S. Chua, *et al., Chem. Mater.* 24 (2012) 3574–3581.
23 $LiAl(AB)_4$ (13.15%) – G. Xia *et al. Mater. Chem. A*. 1 (2013) 1810–1820.
24 $NaAl(AB)_4$ (11.9%) – I. Dovgaliuk *et al.*, *Chem. Eur. J.* 21 (2015) 14562–14570
25 $Li_2Mg(AB)_4$ (12.79%) – N. Biliškov *et al., Chem. Eur. J.* 23 (2017) 16274–16282.
26 $KAl(AB)_4$ (10.87%) – K. T. Møller, *et al., Int. J. Hydrog. Energy* 43 (2018) 311–321.
27 $Li_2Ca(AB)_4$ (11.63%), $Na_2Ca(AB)_4$ (9.81%) – I. Milanovic, *et al., ACS Sustainable Chem. Eng*. 9 (2021) 2089−2099.

28 Li(B3N2) (15.22%), Na(B3N2) (12.66%) – I. C. Evans, *Ph.D. Thesis*, University of Birmingham, 2011.
29 Li(B3N2) (15.22%) – K. R. Ryan, *Ph.D. Thesis*, University of Oxford, 2011.
30 α-VB(B3N2) (3.15%) – W. C. Ewing, *et al., J. Am. Chem. Soc.* 133 (2011) 17093–17099.
31 Na(B3N2) (12.66%), (NH_4)(B3N2)/3(B3N3) (16.4%) – W. C. Ewing, *et al., Inorg. Chem.* 52 (2013) 10690–10697.
32 Li(B3N2) (15.22%), Na(B3N2) (12.66%) – K. J. Fijalkowski, *et al., Phys. Chem. Chem. Phys.* 16 (2014) 23340–23346.
33 K(B3N2) (10.83%), Rb(B3N2) (7.65%), Cs(B3N2) (5.89%), β-VB(B3N2) (3.15%) – R. Owarzany, *et al., Inorg. Chem. 55 (2016) 37.*
34 (Bu_4N)(B3N2) (3.80%), (Et_4N)(B3N2) (6.00%), $[C(N_3H_6)]$(B3N2) (13.70%), $[C(N_3H_5CH_3)]$(B3N2) (11.7%) – X. M. Chen, *Chem Asian J.* 16 (2021) 1–7.

35 (NH_4)(B3N2)/3(B3N3) (16.4%) – this study

2. Synthesis of alkali metal M(B3N2) salts:

All operations were performed under inert Ar atmosphere inside gloveboxes, MBRAUN Labmaster DP or Vigor SG1200 (O_2, H_2O < 1.0 ppm). Commercially available reagents and solvents were used: NH_3BH_3 (98%, JSC Aviabor), $NH_4B(C_6H_5)_4$ (99%, Sigma-Aldrich (later denoted as SA), C_4H_8O (99%, SA), CH_2Cl_2 (99%, SA).

Metathetic synthesis was performed using $(C_{18}H_{39}N_4PH)(BH_3NH_2BH_2NH_2BH_3)$ and $NH_4[B(C_6H_5)_4]$ in anhydrous THF at room temperature under argon atmosphere:

$$(C_{18}H_{39}N_4PH)(BH_3NH_2BH_2NH_2BH_3) + NH_4[B(C_6H_5)_4] \rightarrow (NH_4)(BH_3NH_2BH_2NH_2BH_3) + (C_{18}H_{39}N_4PH)[B(C_6H_5)_4]$$

A follow-up process of dehydrogenation of $NH_4(BH_3NH_2BH_2NH_2BH_3)$ occurs leading to neutral linear molecule $NH_3BH_2NH_2BH_2NH_2BH_3$:

$$(NH_4)(BH_3NH_2BH_2NH_2BH_3) \rightarrow NH_3BH_2NH_2BH_2NH_2BH_3 + H_2\uparrow$$

Obtained mixture of products was well soluble in THF. Side product $(C_{18}H_{39}N_4PH)[B(C_6H_5)_4]$ was precipitated by washing with anhydrous DCM.

The main product crystallises in $P2_1/c$ unit cell with the lattice parameters of: a = 13.401(11) Å, b = 13.196(8) Å, c = 17.828(12) Å, β = 128.83(4)°, V = 2556(3) Å^3 and Z = 16. The crystalline product contains two compounds: $NH_4(BH_3NH_2BH_2NH_2BH_3)$ and $NH_3BH_2NH_2BH_2NH_2BH_3$ in molar ratio 1:3. In the manuscript, the product is denoted as "main product" or "(NH_4)(B3N2)·3(B3N3)".

The synthesis of $(C_{18}H_{39}N_4PH)(BH_3NH_2BH_2NH_2BH_3)$ was performed according to the route described in our earlier paper (R. Owarzany, *et al.*, *Inorg. Chem.* 55 (2016) 37/) in a direct reaction of Verkade's Base with 3 equivalents of ammonia borane in toluene at room temperature:

$$C_{18}H_{39}N_4P + 3NH_3BH_3 \rightarrow (C_{18}H_{39}N_4PH)(BH_3NH_2BH_2NH_2BH_3) + H_2\uparrow + NH_3\uparrow$$

Different route of metathetic synthesis between $Na(BH_3NH_2BH_2NH_2BH_3)$ and NH_4Cl in glyme at room temperature for 24 hours was reported earlier (W. C. Ewing *et al. Inorg. Chem.* 52 (2013) 10690.), however, the authors were aiming $NH_3BH_2NH_2BH_2NH_2BH_3$ according to the following equation:

$$Na(BH_3NH_2BH_2NH_2BH_3) + NH_4Cl \rightarrow NH_3BH_2NH_2BH_2NH_2BH_3 + H_2\uparrow + NaCl\downarrow$$

Judging from the comparison of NMR data presented by Ewing *et al.* to our own data we strongly believe that this process leads to (NH_4)(B3N2)·3(B3N3) according to the following reaction equations:

$$Na(BH_3NH_2BH_2NH_2BH_3) + NH_4Cl \rightarrow (NH_4)(BH_3NH_2BH_2NH_2BH_3) + NaCl\downarrow$$

$$(NH_4)(BH_3NH_2BH_2NH_2BH_3) \rightarrow NH_3BH_2NH_2BH_2NH_2BH_3 + H_2\uparrow$$

3. Table of ^{11}B NMR @ THF-d_8 chemical shifts of M(B3N2) salts and ammonia borane:

Table S3. Chemical shifts, positions of multiplets, excitation frequencies and J-coupling values observed in ^{11}B NMR spectra in deuterated THF solution (δ [ppm]) of (NH_4)(B3N2)·3(B3N3) at room temperature. Results for ammonia borane [AB], precursor [β-VBH(B3N2)] and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)] at RT are shown for comparison.

	NH_3BH_3	VBH(B3N2)	M(B3N2) salts					**(NH_4)(B3N2) ·3(B3N3)**
			Li(B3N2)	Na(B3N2)	K(B3N2)	Rb(B3N2)	Cs(B3N2)	
BH_2 triplet	–	–6.590	–6.743	–7.155	–7.499	–7.410	–7.792	–9.95 | –11.78
	–	–8.184	–8.360	–8.582	–8.568	–8.424	–8.384	–10.40 | –12.26
	–	–9.716	–9.966	–10.227	–9.591	–9.491	–9.042	–10.85 | –12.70
position	–	–8.163	–8.356	–8.654	–8.553	–8.442	–8.406	–10.4 | –12.3
^1J (B,H)	–	100 Hz	103 Hz	99 Hz	101 Hz	100 Hz	101 Hz	101 Hz | 102 Hz
freq.	96.32 MHz	64.16 MHz	96.32 MHz	96.32 MHz	96.32 MHz	96.32 MHz	160.48MHz	224.62 MHz

	NH_3BH_3	VBH(B3N2)	M(B3N2) salts					**(NH_4)(B3N2) ·3(B3N3)**
			Li(B3N2)	Na(B3N2)	K(B3N2)	Rb(B3N2)	Cs(B3N2)	
BH_3 quartet	–18.184	–19.462	–20.465	–20.264	–20.613	–20.294	–20.279	–21.60
	–19.632	–20.933	–21.836	–21.693	–21.556	–21.226	–20.902	–22.01
	–21.144	–22.342	–23.314	–23.202	–22.499	–22.168	–21.479	–22.42
	–22.610	–23.752	–24.634	–24.582	–23.382	–23.105	–22.025	–22.83
position	–20.393	–21.622	–22.562	–22.435	–22.013	–21.698	–21.171	–22.21
^1J (B,H)	95 Hz	91 Hz	90 Hz	91 Hz	89 Hz	90 Hz	94 Hz	91 HZ
freq.	96.32 MHz	64.16 MHz	96.32 MHz	96.32 MHz	96.32 MHz	96.32 MHz	160.48MHz	224.62 MHz

4. Table of bands appearing in the IR spectra of M(B3N2) salts and ammonia borane:

Table S4. Absorption bands detected in IR spectra (wavenumber [cm^{-1}]) of NH_4(B3N2)·3(B3N3) at room temperature. Results for ammonia borane [AB] and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)] at RT. Absorption bands of ammonia borane at RT are shown for comparison. (ν = stretching, δ = deformation: bending and torsional modes).

Band	NH_3BH_3	M(B3N2) salts					**(NH_4)(B3N2) ·3(B3N3)**
		Li(B3N2)	Na(B3N2)	K(B3N2)	Rb(B3N2)	Cs(B3N2)	
ν(NH)	3311 vs	3310 s	3302 vs	3305 vs	3308 m	3313 w	3306 vs
					3295 m	3287 m	3288 vs
							3268 sh
	3253 vs	3273 m	3256 m	3261 m	3261 w	3261 w	3259 m
					3252 w	3235 m	3239 m
							3223 sh
	3196 s						
ν(BH)				2420 sh			2439 sh
					2390 sh	2389 sh	2407 s
		2350 vs	2364 s	2352 m	2346 s	2329 m	2357 s
	2347 vs	2322 s	2315 s				2317 vs
				2304 s			2302 sh
	2289 s	2282 vs	2286 vs	2279 s	2294 vs	2291 vs	
		2245 s		2259 s	2263 s		2260 m
					2248 sh	2248 s	
				2210 sh	2204 sh	2189 sh	
	2118 m						
δ(NH)	1611 m				1617 vw		1604 sh
						1579 vw	1572 w
		1571 vs	1576 w	1583 w	1562 sh	1565 w	1564 m
			1556 m	1568 m	1557 m	1557 vw	1556 m
							1480 w
							1428 w
							1415 m
							1392 m
							1375 w
δ(BH)		1283 m	1248 m	1244 m		1259 m	1262 s
		1226 s			1233 s	1231 s	1244 s
		1201 s	1199 vs	1202 s	1206 m	1205 s	1203 vs
			1175 m	1194 sh	1193 sh	1188 s	1179 s
	1163 vs	1148 s		1182 m	1167 s	1171 s	1168 sh
		1135 m	1129 vw	1128 w	1134 m	1127 m	1134 m
							1118 w
	1067 s		1074 m	1073 w	1065 w	1063 w	1078 w
		1044 m	1055 m	1056 w	1038 w	1043 m	1056 w
		1013 w	999 w	997 w	1012 vw	1001 w	983 w
ν(BN)		916 w	893 vw	893 vw	901 vw	902 w	
				875 w	873 vw	881 w	861 w
and		874 vw	870 w		854 vw	856 w	
other		799 vw	785 vw	781 vw	811 vw	791 vw	804 vw
				727 vw	727 vw	723 vw	749 w
							711 w

5. Table of bands appearing in the RAMAN spectra of M(B3N2) salts and ammonia borane:

Table S5. Absorption bands detected in Raman spectra (wavenumber [cm^{-1}]) of NH_4(B3N2)·3(B3N3) at room temperature. Results for ammonia borane [AB] and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)] at RT. Absorption bands of ammonia borane at RT are shown for comparison. (ν = stretching, δ = deformation: bending and torsional modes).

Band	NH_3BH_3	M(B3N2) salts					**(NH_4)(B3N2) ·3(B3N3)**
		Li(B3N2)	Na(B3N2)	K(B3N2)	Rb(B3N2)	Cs(B3N2)	
ν(NH)					3304 sh	3307 sh	
	3314 m	3314 m	3302 s	3306 s	3293 w	3303 w	3307 m
					3288 w	3292 sh	3288 m
						3279 w	
	3253 vs	3272 s	3265 vs	3263 vs	3256 m	3258 m	3260 vs
					3245 m	3232 m	3241 vs
	3177 m						
							3041 s
ν(BH)		2418 vw	2403 w				2475 sh
	2378 vs	2370 w	2373 w	2382 m	2379 m	2379 m	2442 w
				2347 m	2341 m	2343 m	2394 m
		2320 vs	2322 m				2320 vs
				2301 s	2291 vs	2286 vs	2261 s
	2284 vs	2282 m	2275 s	2274 s			
		2250 s	2243 s		2243 vs	2250 vs	
			2214 sh				
		2166 vw		2186 sh	2192 sh		
δ(NH)				1649 vw	1608 vw	1645 vw	
	1598 m			1585 vw			1578 s
	1583 m	1567 m	1539 w	1569 vw	1565 w	1566 w	1559 m
			1519 vw		1550 w	1534 w	
δ(BH)		1281 w					
		1259 vw					
		1226 w					
		1206 m	1212 w	1227 w	1207 w	1206 sh	1201 w
	1190 sh			1193 w	1188 m	1183 m	1184 w
	1168 m	1166 w	1162 w	1168 w	1155 w	1163 m	1173 w
			1132 w		1122 vw		1155 w
	1069 vw		1047 vw		1056 vw	1036 vw	1102 w
							1027 m
		1010 w	1019 vw		1004 vw	993 w	998 vs
ν(BN) and other						915 w	
		895 vw		892 vw	895 w	899 vw	
		873 w		871 w	862 w	876 vw	
			856 vw		847 w	851 w	857 w
	800 w	806 w	835 w				796 w
	785 m		749 w	778 w	779 w	783 vw	
	729w				721 w	724 w	
						715 vw	
			614 vw		653 w	643 vw	667 m
					639 vw		618 w
							604 s

6. Comparison of IR and Raman spectra of alkali metal M(B3N2) salts:

IR and Raman spectra of NH_4(B3N2)/3(B3N3) and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)]. NH and BH stretching and NH bending regions highlighted and magnified in separate figures.

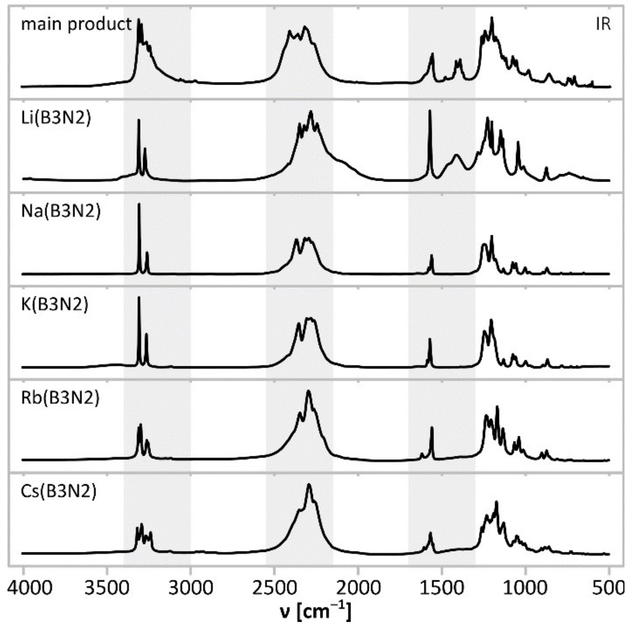

Fig. S6.1. Comparison of IR spectra of M(B3N2) salts.

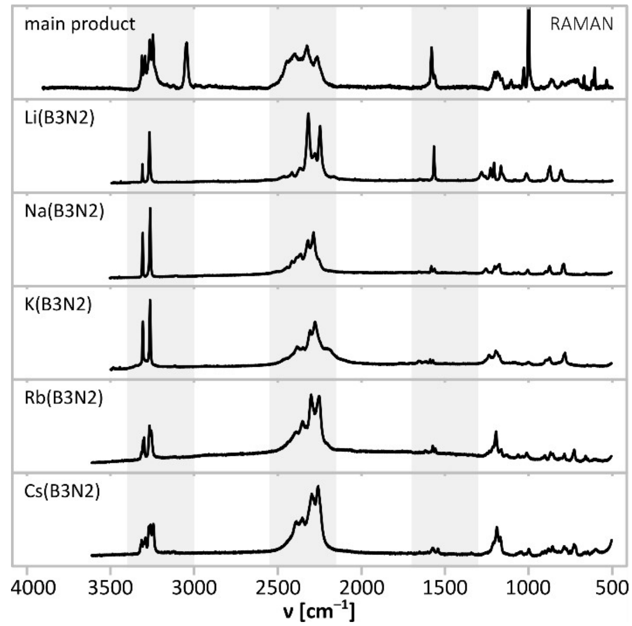

Fig. S6.2. Comparison of Raman spectra of M(B3N2) salts.

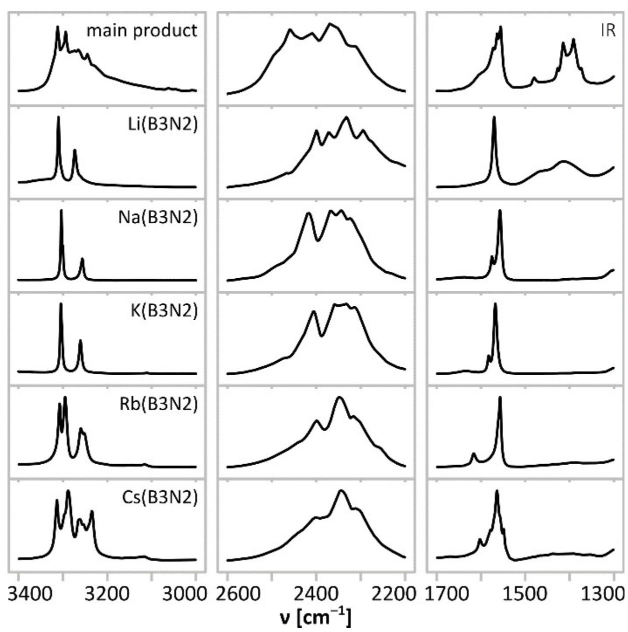

Fig. S6.3. Comparison of NH and BH stretching and NH bending regions of IR spectra of M(B3N2) salts.

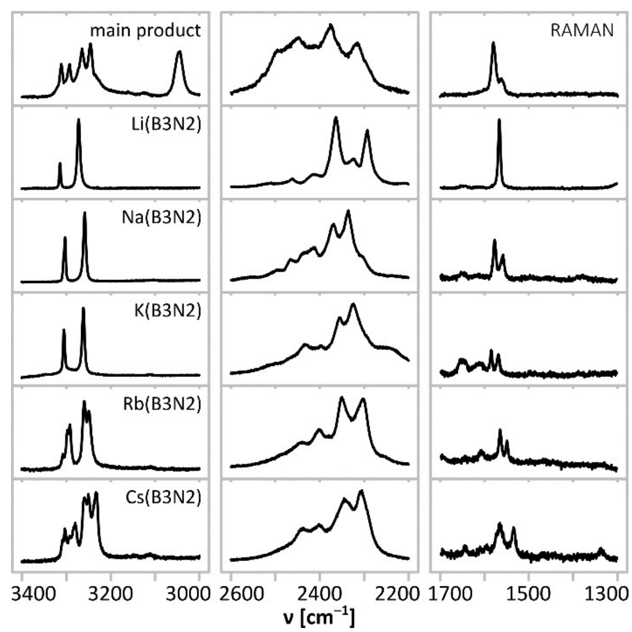

Fig. S6.4. Comparison of NH and BH stretching and NH bending regions of Raman spectra of M(B3N2) salts.

7. Thermal decomposition (TGA curves) of M(B3N2) salts:

The thermal decomposition of NH_4(B3N2)/3(B3N3) and alkali metal M(B3N2) salts occurs at the temperature range of 120–180°C.

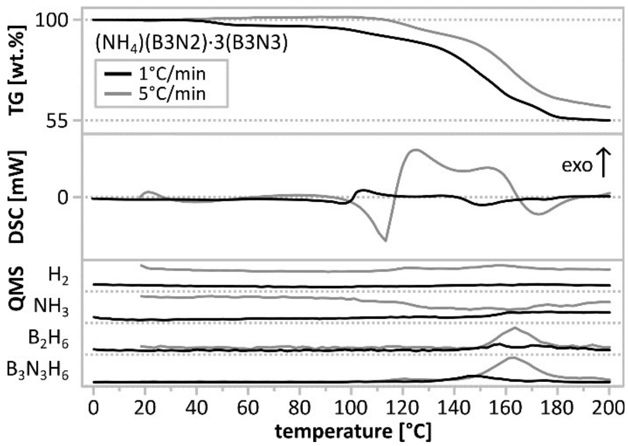

Fig.S7.1. TGA/DSC experiments of (NH_4)(B3N2)·3(B3N3) with scanning rates (1 K/min -black, 5 K/min -grey).

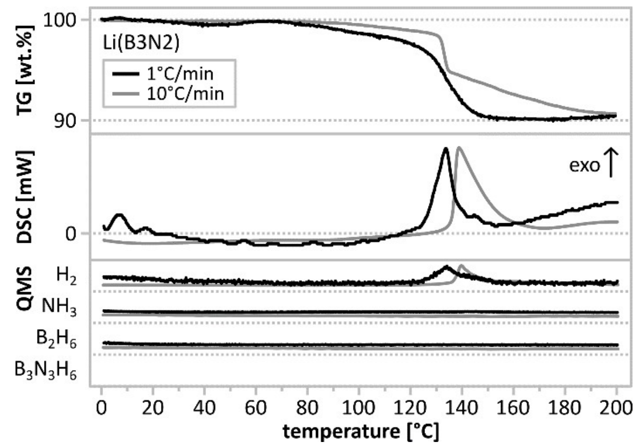

Fig.S7.2. TGA/DSC experiments of Li(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

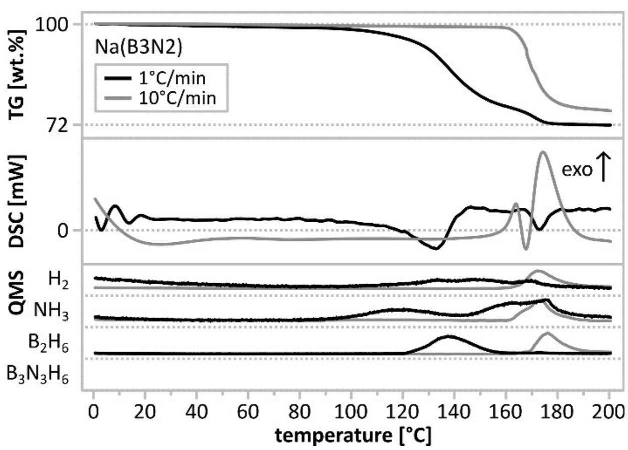

Fig.S7.3. TGA/DSC experiments of Na(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

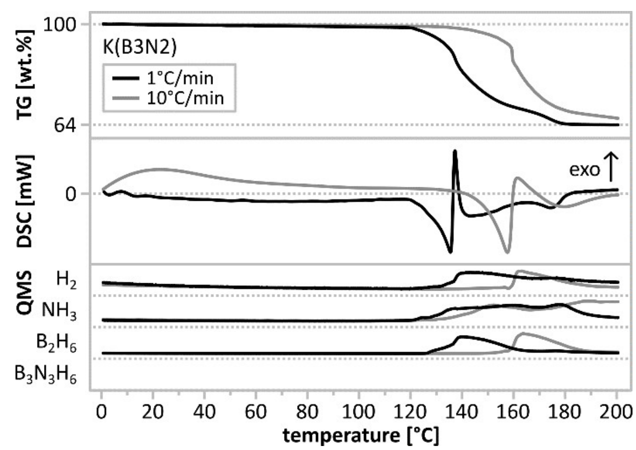

Fig.S7.4. TGA/DSC experiments of K(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

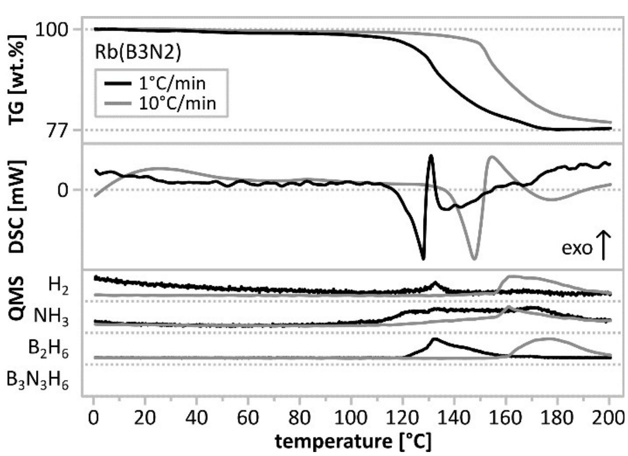

Fig.S7.5. TGA/DSC experiments of Rb(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

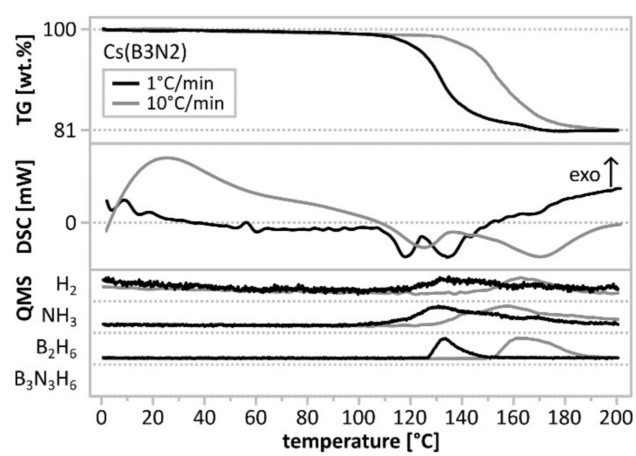

Fig.S7.6. TGA/DSC experiments of Cs(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

8. IR spectra of the products of thermal decomposition of M(B3N2) salts:

The thermal decomposition of (NH_4)(B3N2) leads to formation of boron nitride while decomposition of alkali metal M(B3N2) salts leads to formation of respective borohydrides.

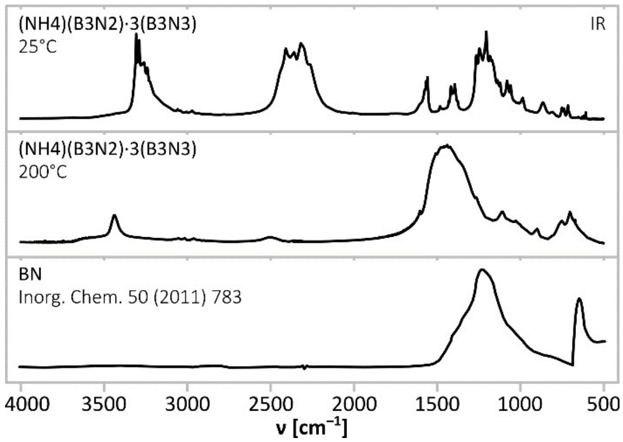

Fig. S8.1. IR spectra of the product of thermal decomposition of (NH_4)(B3N2)·3(B3N3) sample.

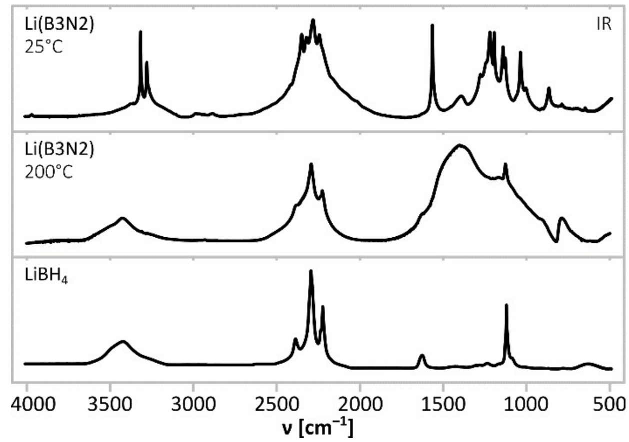

Fig. S8.2. IR spectra of the product of thermal decomposition of Li(B3N2) sample.

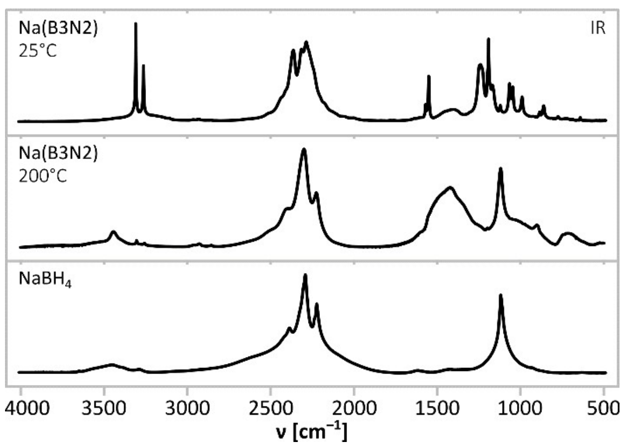

Fig. S8.3. IR spectra of the product of thermal decomposition of Na(B3N2) sample.

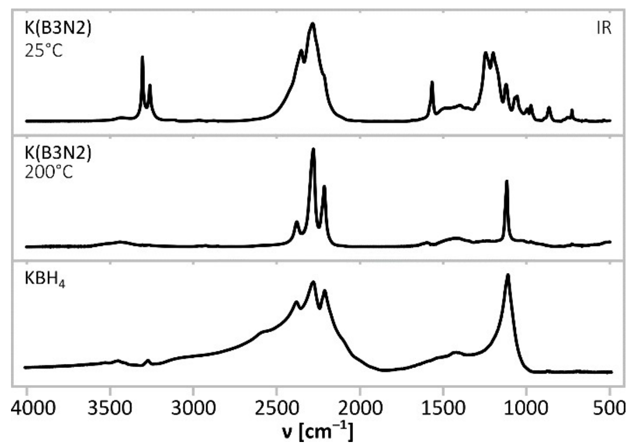

Fig. S8.4. IR spectra of the product of thermal decomposition of K(B3N2) sample.

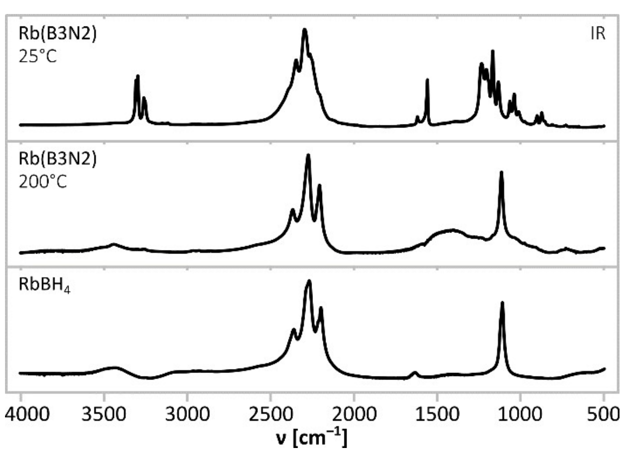

Fig. S8.5. IR spectra of the product of thermal decomposition of Rb(B3N2) sample.

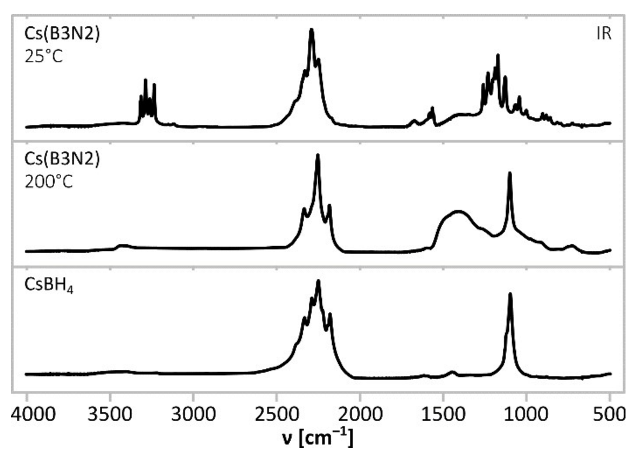

Fig. S8.6. IR spectra of the product of thermal decomposition of Cs(B3N2) sample.

9. Experimental crystal structure and Rietveld fit for $(NH_4)(B3N2){\cdot}3(B3N3)$:

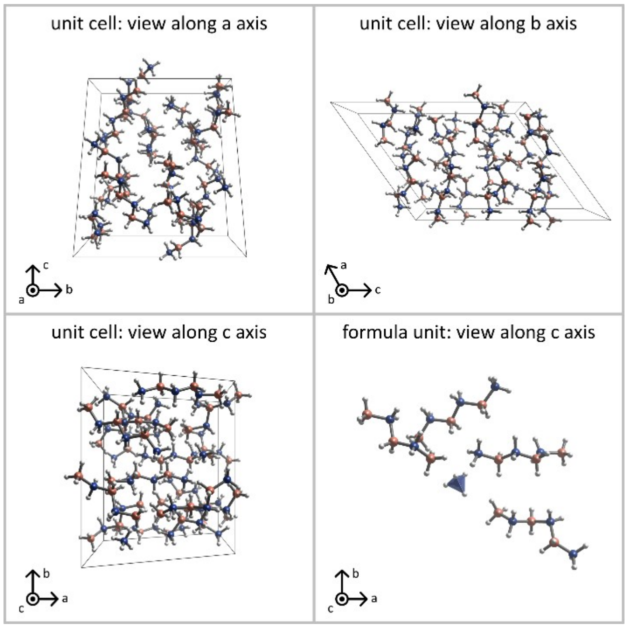

Fig. S9.1. Visualisation of the unit cell and formula unit of the main product: $(NH_4)(B3N2){\cdot}3(B3N3)$

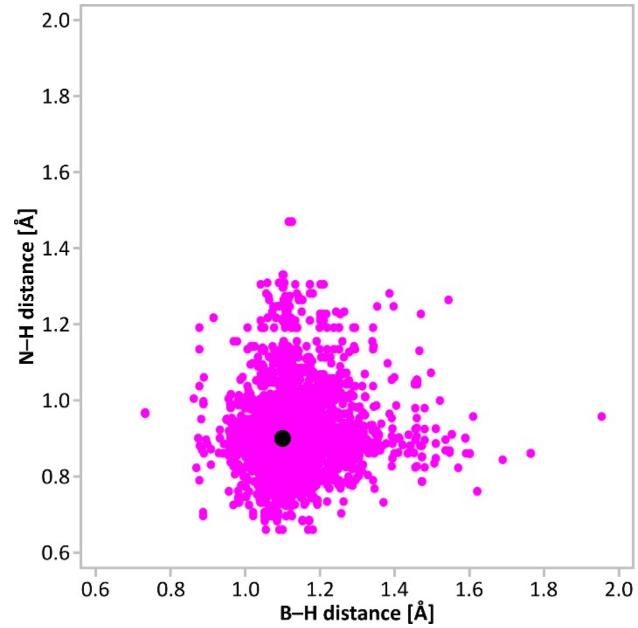

Fig. S9.2. Distribution of N-H and B-H distances in systems comprising both $[NH_x]$ and $[BH_x]$ groups found in structures in CSD database. Value of N-H and B-H distances in $(NH_4)(B3N2){\cdot}3(B3N3)$ marked with a dot.

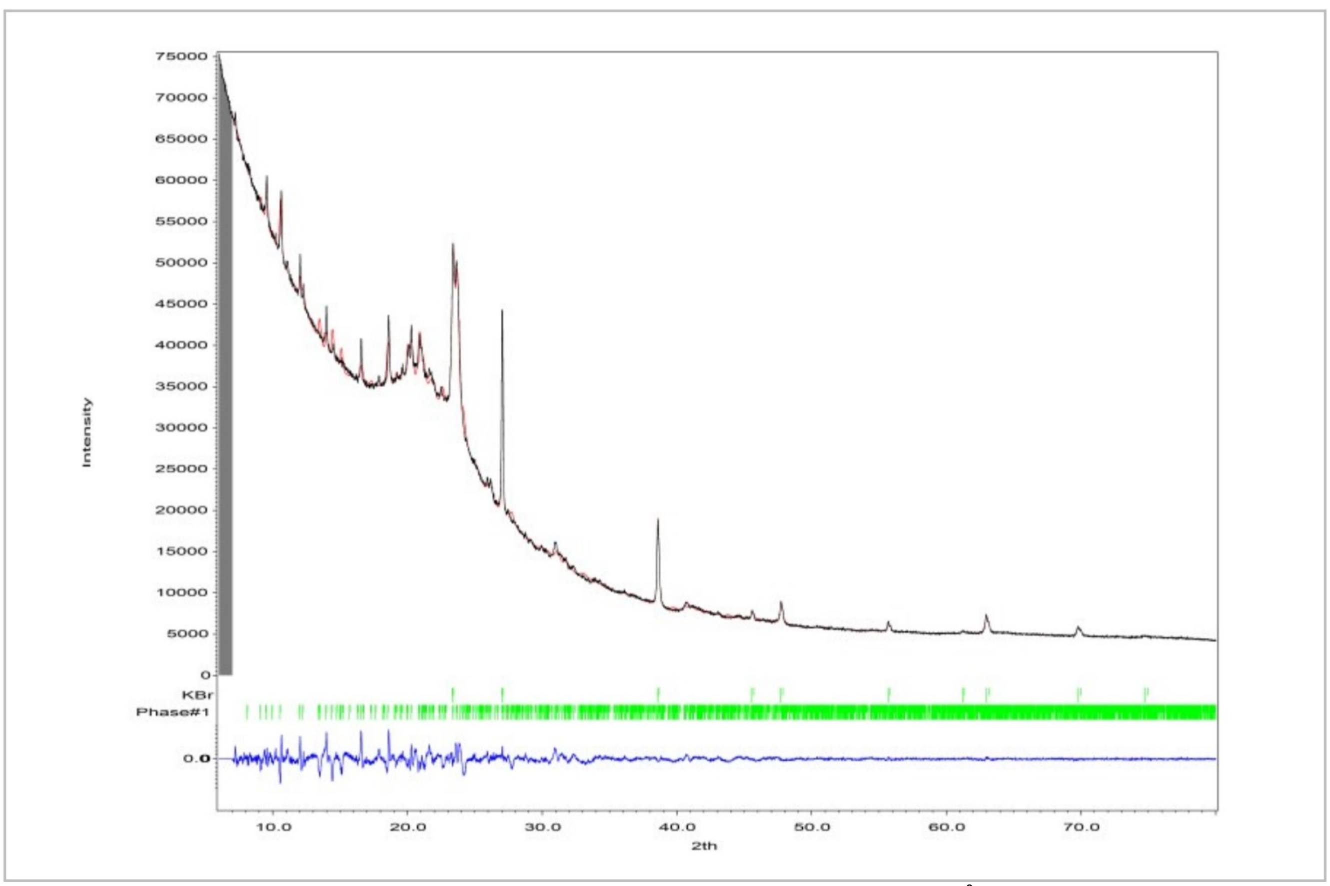

Fig. S9.3. Rietveld analysis of $(NH_4)(B3N2)/3(B3N3)$ powder pattern. $CoK_{\alpha1,2}$, λ = 1.78901 Å.

10. Table with the closest H···H distances in the crystal structure of (NH_4)(B3N2)·3(B3N3):

Table S10. List of the closest H···H distances in experimental crystal structure of (NH_4)(B3N2)·3(B3N3). Listed only strong dihydrogen bonds, < 2 Å.

H atom1	H atom2	**Length [Å]**	Length-VdW [Å]	Neighboring groups
H8	H39	1.927	-0.473	B–H···H–N
H12	H29	1.928	-0.472	B–H···H–N
H6	H52	1.931	-0.469	B–H···H–N
H12	H53	1.935	-0.465	B–H···H–N
H15	H34	1.948	-0.452	B–H···H–B
H54	H42	1.949	-0.451	B–H···H–N
H1	H51	1.951	-0.449	B–H···H–N
H50	H64	1.971	-0.429	N–H···H–N
H19	H31	1.984	-0.416	B–H···H–B
H52	H64	1.987	-0.413	N–H···H–N
H17	H47	1.993	-0.407	B–H···H–N

11. Experimental and modelled NMR spectra for various possible compositions of the main product: NMR spectra were simulated for various discussed possible compositions of the main product to ease visual examination of the experimental spectra obtained by us and reported earlier by Ewing *et al., Inorganic Chemistry* 52 (2013) 10690.

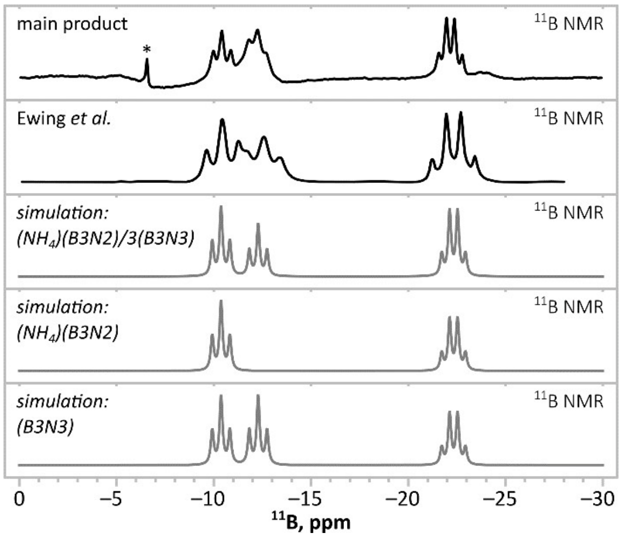

Fig. S11.1. Comparison of the experimental ^{11}B NMR spectra obtained here and reported by Ewing *et al.* (*Inorganic Chemistry* 52 (2013) 10690) with spectra simulated for various possible compositions of the main product: $(NH_4)(B3N2)\cdot 3(B3N3)$, $(NH_4)(B3N2)$ and (B3N3).

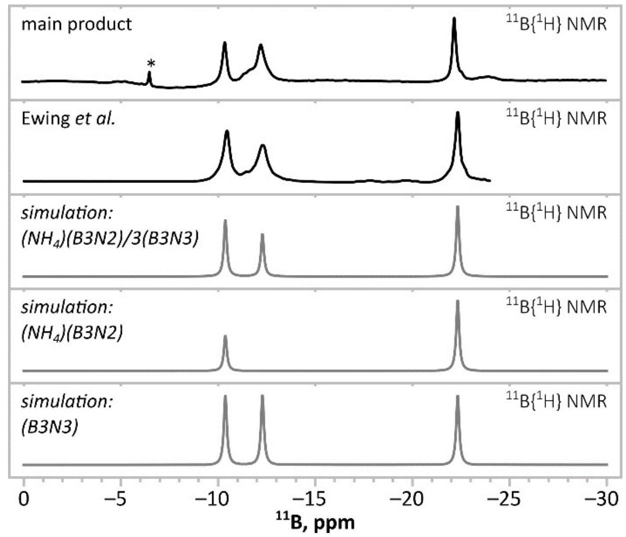

Fig. S11.2. Comparison of the experimental ^{11}B {^{1}H} NMR spectra obtained here and reported by Ewing *et al.* (*Inorganic Chemistry* 52 (2013) 10690) with spectra simulated for various possible compositions of the main product: $(NH_4)(B3N2)\cdot 3(B3N3)$, $(NH_4)(B3N2)$ and (B3N3).

12. Results of DFT optimisation of modelled crystal structures:

$NH_4(BH_3NH_2BH_2NH_2BH_3)\cdot 3(NH_3BH_2NH_2BH_2NH_2BH_3)$, unit cell optimised

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H18   H    0.15917  0.25731  0.52314  0.05000  Uiso  1.00
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_atom_site_adp_type
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N1    N    0.74985  0.13798  0.78118  0.05000  Uiso  1.00
B2    B    0.80335  0.24827  0.83148  0.05000  Uiso  1.00
N2    N    0.94601  0.24008  0.90513  0.05000  Uiso  1.00
B3    B    1.00612  0.33672  0.97390  0.05000  Uiso  1.00
H1    H    0.54946  0.17792  0.71315  0.05000  Uiso  1.00
H2    H    0.60187  0.18975  0.63663  0.05000  Uiso  1.00
H4    H    0.76311  0.08260  0.82641  0.05000  Uiso  1.00
H5    H    0.80196  0.11174  0.76378  0.05000  Uiso  1.00
H6    H    0.78333  0.31438  0.77695  0.05000  Uiso  1.00
H7    H    0.75652  0.27053  0.86549  0.05000  Uiso  1.00
H8    H    0.98548  0.23333  0.87482  0.05000  Uiso  1.00
H9    H    0.97069  0.17067  0.94111  0.05000  Uiso  1.00
H10   H    1.00173  0.31692  1.03399  0.05000  Uiso  1.00
H11   H    0.95188  0.41887  0.93541  0.05000  Uiso  1.00
H12   H    1.11486  0.34492  1.00700  0.05000  Uiso  1.00
B4    B    0.50969  0.43569  0.71360  0.05000  Uiso  1.00
N3    N    0.46702  0.38819  0.62292  0.05000  Uiso  1.00
B5    B    0.33020  0.34237  0.55254  0.05000  Uiso  1.00
N4    N    0.25702  0.34528  0.59044  0.05000  Uiso  1.00
B6    B    0.17134  0.44485  0.56525  0.05000  Uiso  1.00
H13   H    0.50674  0.36814  0.75773  0.05000  Uiso  1.00
H15   H    0.45024  0.51405  0.70061  0.05000  Uiso  1.00
H16   H    0.47623  0.44544  0.58905  0.05000  Uiso  1.00
H17   H    0.52384  0.32667  0.63483  0.05000  Uiso  1.00
H18   H    0.33803  0.24984  0.53711  0.05000  Uiso  1.00
H19   H    0.27691  0.39738  0.48626  0.05000  Uiso  1.00
H20   H    0.31598  0.33436  0.65830  0.05000  Uiso  1.00
H21   H    0.20393  0.27761  0.56705  0.05000  Uiso  1.00
H22   H    0.22991  0.52690  0.58489  0.05000  Uiso  1.00
H23   H    0.12913  0.44167  0.60495  0.05000  Uiso  1.00
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H24	H	0.08772	0.44511	0.48540	0.05000	Uiso	1.00
B7	B	0.27345	0.57022	-0.00885	0.05000	Uiso	1.00
N5	N	0.26635	0.66818	-0.06284	0.05000	Uiso	1.00
B8	B	0.22211	0.77997	-0.05360	0.05000	Uiso	1.00
N6	N	0.33300	0.83259	0.03608	0.05000	Uiso	1.00
B9	B	0.44363	0.86757	0.03827	0.05000	Uiso	1.00
H25	H	0.31804	0.49323	-0.01834	0.05000	Uiso	1.00
H26	H	0.33068	0.59327	0.06945	0.05000	Uiso	1.00
H28	H	0.34950	0.68144	-0.04834	0.05000	Uiso	1.00
H29	H	0.20852	0.64938	-0.12983	0.05000	Uiso	1.00
H30	H	0.19464	0.83592	-0.11562	0.05000	Uiso	1.00
H31	H	0.13695	0.76681	-0.05285	0.05000	Uiso	1.00
H32	H	0.36163	0.78334	0.08860	0.05000	Uiso	1.00
H33	H	0.29991	0.89825	0.04691	0.05000	Uiso	1.00
H34	H	0.41205	0.94339	-0.01110	0.05000	Uiso	1.00
H35	H	0.53224	0.88970	0.11504	0.05000	Uiso	1.00
H36	H	0.47107	0.79357	0.01180	0.05000	Uiso	1.00
B10	B	1.01084	1.09682	0.78046	0.05000	Uiso	1.00
N7	N	1.00571	0.98490	0.81574	0.05000	Uiso	1.00
B11	B	0.89496	0.91200	0.74411	0.05000	Uiso	1.00
N8	N	0.88698	0.81275	0.79116	0.05000	Uiso	1.00
B12	B	0.76080	0.75282	0.73529	0.05000	Uiso	1.00
H37	H	0.91116	1.14046	0.73976	0.05000	Uiso	1.00
H38	H	1.08492	1.15377	0.84346	0.05000	Uiso	1.00
H39	H	1.03831	1.08470	0.73181	0.05000	Uiso	1.00
H40	H	1.00795	0.99774	0.86972	0.05000	Uiso	1.00
H41	H	1.08598	0.94429	0.84318	0.05000	Uiso	1.00
H42	H	0.90823	0.88165	0.69059	0.05000	Uiso	1.00
H43	H	0.79993	0.96281	0.70640	0.05000	Uiso	1.00
H44	H	0.95736	0.76075	0.81376	0.05000	Uiso	1.00
H45	H	0.90141	0.83918	0.84788	0.05000	Uiso	1.00
H46	H	0.68411	0.81054	0.72636	0.05000	Uiso	1.00
H48	H	0.76990	0.66919	0.77091	0.05000	Uiso	1.00
N9	N	0.64892	0.47383	0.77073	0.05000	Uiso	1.00
H50	H	0.65955	0.53699	0.74190	0.05000	Uiso	1.00
H51	H	0.70708	0.41277	0.78183	0.05000	Uiso	1.00
H52	H	0.68082	0.49842	0.83280	0.05000	Uiso	1.00
N10	N	0.13759	0.54192	-0.04916	0.05000	Uiso	1.00
H53	H	0.10005	0.59620	-0.03170	0.05000	Uiso	1.00
H54	H	0.12833	0.46828	-0.02971	0.05000	Uiso	1.00
H55	H	0.07927	0.54020	-0.11808	0.05000	Uiso	1.00
N11	N	0.56770	0.02149	0.66238	0.05000	Uiso	1.00
H57	H	0.48257	0.01895	0.60065	0.05000	Uiso	1.00
H58	H	0.62717	-0.02152	0.65896	0.05000	Uiso	1.00
H59	H	0.55927	-0.01953	0.70490	0.05000	Uiso	1.00
N12	N	0.27916	0.22761	0.86024	0.05000	Uiso	1.00
H61	H	0.36599	0.19486	0.90001	0.05000	Uiso	1.00
H63	H	0.28219	0.29363	0.89304	0.05000	Uiso	1.00
H64	H	0.22046	0.17569	0.85841	0.05000	Uiso	1.00

13. Crystal structure (VBH)[B(C_6H_5)$_4$]

Table 13.1. Crystal structure parameters of ($C_{18}H_{39}N_4PH$)[B(C_6H_5)$_4$].

Compound	($C_{18}H_{39}N_4PH$)[B(C_6H_5)$_4$]
K_α(Å) Temperature (K)	1.54184 (Cu) 100(2)
Space group *Z*	*P*1 4
a (Å) *b* (Å) *c* (Å) *α* (°) *β* (°) *γ* (°) *V* (Å^3)	11.7376(3) 19.5388(5) 20.5479(4) 61.751(2) 73.618(2) 89.605(2) 3937.71(18)
$\rho_{calc.}$ (g cm^{-3}) $\mu_{exp.}$ (mm^{-1}) ϑ_{max} (°)	1.118 0.856 75.2030
R_1 wR_2 *GooF*	0.0695 0.2094 1.048
Crystal size (mm×mm×mm) Crystal colour	0.06 x 0.16 x 0.20 colorless
CCDC No.	2195203

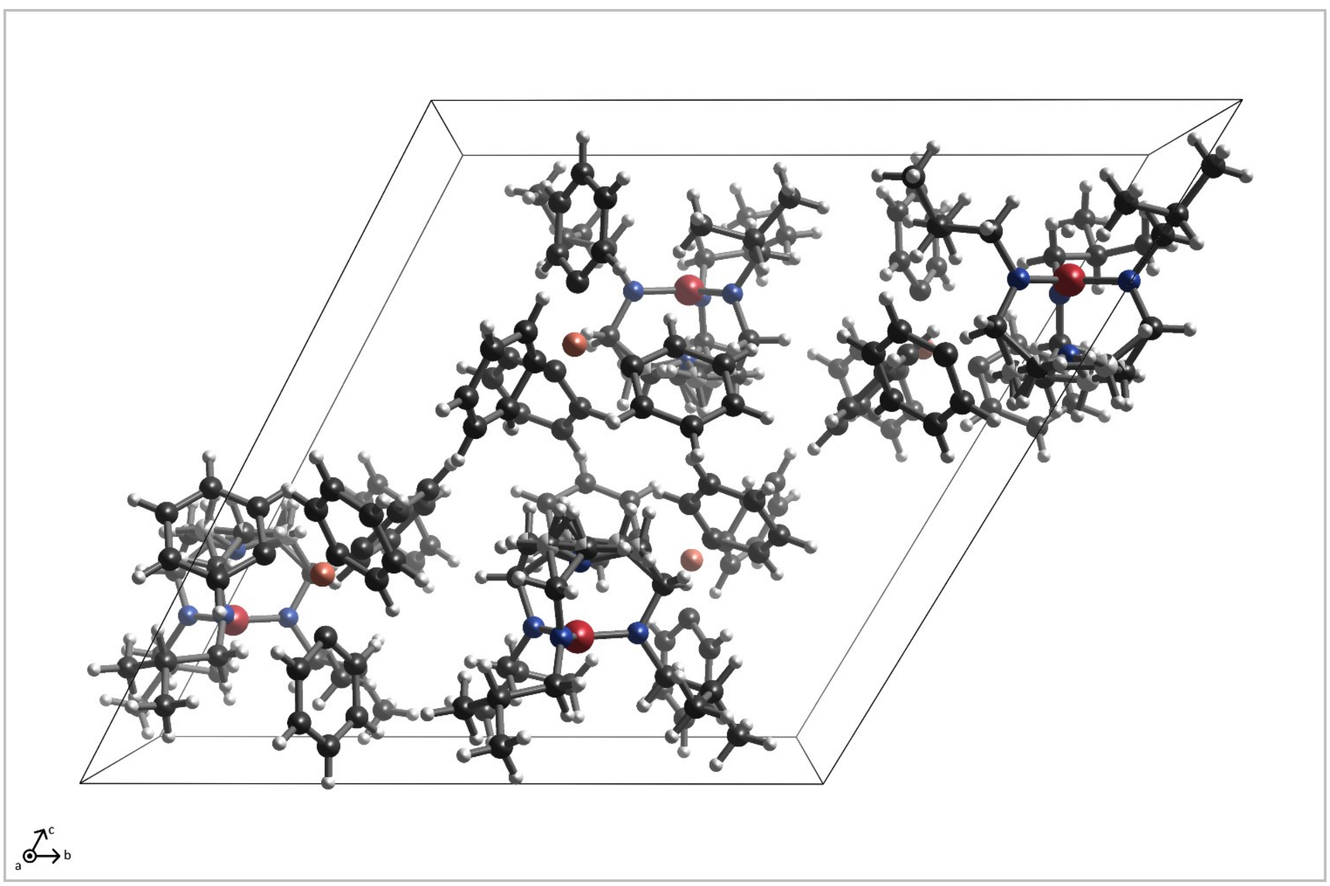

Fig. S13.2. Visualisation of the unit cell of the side product: ($C_{18}H_{39}N_4PH$)[B(C_6H_5)$_4$].

14. Molecular DFT calculations

Summary of energies and coordinates of investigated species. Three top energy values (yellow) are for r2SCAN-3c method, while the bottom (green) is single point energy obtained from ωB97X-V/def2-TZVP/D4 method. ν_{im} denotes imaginary mode in transition state. All values are calculated with CPCM solvent model.

1. Decomposition of NH_4^+-(B3N2)$^-$ into $N_3B_3H_{14}$ and H_2 in THF:

$\Delta\Delta G^*$ = 69 kJ mol^{-1} (17 kcal mol^{-1})

Substrates: NH_4^+-(B3N2)$^-$		Transition state; ν_{im} = −320 cm^{-1}		Product: $B_3N_3H_{14}$ + H_2	
E	-248,4092007		-248,37501		-248.43450178
H	-248,2034667		-248,1777712		-248.23417146
G	-248,25242		-248,2261315		-248.28262085
E	-248,7570143		-248,7228562		-248.78438156
H 3.90244901624217 9.42504815708469 10.04906651434456 H 6.83353381108372 12.91820843573510 9.73238715788029 H 4.43719534906216 11.69986703130003 9.00119983920167 N 3.35862674414461 10.22123538619771 10.38092877505048 H 2.08664145131618 10.34421890053314 8.45810330345879 H 3.22180904508244 10.04317038224818 11.37568405931101 B 4.20224212731816 11.56612718028035 10.18623053147915 B 6.55213280741590 12.71639843934119 10.90468983874320 B 1.93927066092242 10.20317854563982 9.66256757334818 H 1.40424007204310 9.10583082681292 9.88380960719910 H 7.56276675279290 12.45915048747947 11.55101467613406 N 5.56960451671451 11.43711896889493 10.97525341642985 H 6.09013476343527 10.62675613008629 10.64128772462874 H 5.96807450372491 13.67664017222668 11.38440241473068 H 3.56066563888645 12.48763495472371 10.65131369665503 H 1.23545113672535 11.09142464973338 10.11752298391511 H 5.38796126729011 11.23812726099694 11.95850258491732 H 0.03017525741386 9.41187502392585 8.99311863252098 N -0.84655043457016 9.62021124500224 8.47317357925754 H -0.98311320521337 8.93077090534359 7.73492188634211 H -0.77111209349771 10.54927092937775 8.05982943839386 H -1.63920585683336 9.59758391303486 9.11384164655721		H 0.80170974429476 -0.58938294659471 0.92112336173798 H 2.66969558973920 -0.70433922319661 0.78167122769226 H 0.36495594143596 1.86894382787090 - 0.43906370692944 N 0.00846434717645 0.05845216322118 0.95595287658311 H -0.46661747709990 -0.45576680629441 - 1.23733567211541 H -0.41729221181681 -0.01334737771859 1.87670189060266 B 0.58122003140657 1.57117577845870 0.72123857557494 B 2.97933120513288 0.36151179986559 0.25811913111074 B -0.94353633117531 -0.10910243011772 - 0.20385095468940 H -1.49265637421284 -1.68457994034317 0.39895354380707 H 4.16824500072783 0.57030839062130 0.43956561509864 N 2.13623029173253 1.54375508330920 0.96807802207883 H 2.33890850007003 1.54463056086151 1.96733462842189 H 2.69610438759599 0.35743408948199 - 0.92804788099191 H 0.00579516741906 2.30510966664070 1.49538594886243 H -1.96854284261449 0.49577010842976 - 0.14690711616890 H 2.50422044235709 2.43460208115741 0.63870427237763 H -1.97107733977835 -1.68635946701670 - 0.21018432273963 N -3.32481367679018 -1.94571655131046 - 1.83094216696788 H -2.99674476800290 -2.63566492277144 - 2.49923875749211 H -3.40156928586551 -1.07181182499489 - 2.34151699858190 H -4.27203034173204 -2.21562205955953 - 1.58574151727162		H 3.33113309198864 10.46453928912834 9.56444211326653 H 5.02572135591715 9.88106982686070 11.00317297272730 H 3.84762900907083 12.88688025383359 9.07733965028903 N 2.69579559798272 11.13627610950967 10.00054716362470 H 1.60845648636007 11.68106625038090 8.05540244641130 H 2.49963888331001 10.74498040627554 10.92350538263724 B 3.51259161818743 12.49774016115045 10.17790436497004 B 5.65843982182757 10.86344232062214 10.63727985825128 B 1.36893817199600 11.28740801966533 9.17325291368432 H 3.48359085994021 7.92991002197611 9.88980668229961 H 6.73919742229469 10.89951332418051 11.20954289014780 N 4.81971458964296 12.18469419893546 11.02628277852379 H 4.60121352721698 12.15291522456638 12.02103156725538 H 5.80706285350062 10.84941951855814 9.42243569715587 H 2.80830056613616 13.29993025663493 10.76433177874059 H 0.57012404565763 11.97005305809256 9.77256642902258 H 5.43257301727170 12.99249149886208 10.93386988021092 H 2.96846927381031 7.43417532233740 9.68509172992716 N 0.70770447481291 9.81174262907880 9.02105091951508 H 1.30222300827910 9.15396018162515 8.51678164259233 H -0.16479473110288 9.87145307464581 8.49817611963089 H 0.47927038729829 9.37618697907695 9.91503489951346	

2. Decomposition of NH_4^+-BH_4^- into NH_3BH_3 and H_2 in THF

$\Delta\Delta G^* = 58$ kJ mol^{-1} (14 kcal mol^{-1})

Substrates: NH_4^+-BH_4^-		Transition state; $\nu_{im} = -192$ cm^{-1}		Product: NH_3BH_3+H_2	
E	-84,34346903		-84,30381255		-84.36551277
H	-84,2516124		-84,21922254		-84.27782184
G	-84,283986		-84,25915181		-84.31102158
E	-84,47225417		-84,43542144		-84.49696412
B -4.82982252170536 1.72053779034281 0.02367363739606 N -1.77367358139469 1.45242795552326 - 0.01414769812632 H -4.45397488619308 2.87264765918443 - 0.17619394703757 H -4.55519637579775 1.38472415937971 1.17295743090450 H -4.25235789710763 0.96441599040701 - 0.77283311497087 H -6.02965143542113 1.61290340024765 - 0.17909899434801 H -1.29474234440937 0.55767880628941 0.07770920647177 H -1.35058478382702 1.98878864032109 - 0.77020211262428 H -1.68565617843929 1.97352767555258 0.85709379486076 H -2.79574901200452 1.29909030865197 - 0.21895774962602		B -1.50287303418764 0.63876813464282 0.44569224703493 N 1.67096820610126 -0.11608199448868 0.13044477456475 H -0.83238957131596 1.55369006602716 0.08036684171849 H -1.22784572791200 0.05935014085067 1.44994762688896 H -1.06496706453873 -1.52511621206970 - 1.52727501597430 H -2.48352228729422 0.34162613383935 - 0.16220977007508 H 2.58988863001572 -0.54781171926806 0.11238143578636 H 1.75573313094210 0.74428319630006 - 0.40121193505143 H 1.51315884032439 0.16792692146426 1.09195828901368 H -0.41815112213492 -1.31663466729790 - 1.22009449390636		B -3.98602337625892 2.38548091238253 0.70841812911015 N -2.51079344393880 1.86489815834672 0.25450034458934 H -3.85675245842353 3.53856657893541 1.07580410577538 H -4.35417639142868 1.65869397734892 1.61284039523883 H -3.85295516368822 -0.63689270861993 - 1.69803943331986 H -4.70773376077587 2.29773626490969 - 0.26737675717421 H -2.52845718183990 0.89694632011587 - 0.05955104624972 H -2.12916987739779 2.41384498897070 - 0.51299544552452 H -1.83480908027833 1.91448540590981 1.01379819684301 H -3.26053828226938 -0.50701751240000 - 2.12739803638837	

3. Complexation of NH_4^+ with $B_3N_3H_{14}$ in THF:

$$NH_4^+ + B_3N_3H_{14} \xrightarrow{\Delta G = -47\ kJ/mol} [(NH_4^+)B_3N_3H_{14}]$$

$$[(NH_4^+)B_3N_3H_{14}] + B_3N_3H_{14} \xrightarrow{\Delta G = -31\ kJ/mol} [(NH_4^+)(B_3N_3H_{14})_2] + B_3N_3H_{14}$$

$$[(NH_4^+)(B_3N_3H_{14})_2] + B_3N_3H_{14} \xrightarrow{\Delta G = -19\ kJ/mol} [(NH_4^+)(B_3N_3H_{14})_3]$$

NH_4^+		$B_3N_3H_{14}$		$(NH_4^+)(B_3N_3H_{14})$	
E	-56,99274527		-247,2442444		-304,2698601
H	-56,9393111		-247,0574479		-304,0284483
G	-56,9627515		-247,0989134		-304,0796272
B -1.39495813257824 0.33929967056958 1.06916287991551 N -2.20445880584144 -0.36321058405875 -0.14819201267700 B -1.59042905375964 -1.64827802036495 -0.85488220886687 H -2.42459402852973 0.34918195621964 -0.84294611821610 H -3.11305065794379 -0.63800421413397 0.21929251238882 N -0.06459922819024 -1.30058957981328 -1.26023756554426 H -2.21175721956632 -1.91226478803726 -1.86369199693538 H -1.61411457062865 -2.57031270870798 -0.06271490095861 B 1.10830352290340 -2.09705479656034 -0.54727018566218 H 0.09168472465526 -0.30132058673718 -1.11357154655471 H 0.04509184170150 -1.44980278699727 -2.25974628123964 N 0.79935921599377 -2.03432455998856 1.03698691841691 H 2.17293231747920 -1.54970286550128 -0.73099839281503 H 1.08618816022553 -3.25721650284473 -0.88084646593162 H 0.61101004728679 -1.07863093837470 1.36145786307852 H 1.57173493962069 -2.42246771972654 1.57133490317869 H -0.04928905465051 -2.55720839413654 1.25768150201177 H -0.28111522606123 0.66358422953666 0.65998116432115 H -1.31868792080042 -0.47796636605897 1.97406236201134 H -2.00211658561593 1.32831350371642 1.42039218717870		B -1.39495813257824 0.33929967056958 1.06916287991551 N -2.20445880584144 -0.36321058405875 -0.14819201267700 B -1.59042905375964 -1.64827802036495 -0.85488220886687 H -2.42459402852973 0.34918195621964 -0.84294611821610 H -3.11305065794379 -0.63800421413397 0.21929251238882 N -0.06459922819024 -1.30058957981328 -1.26023756554426 H -2.21175721956632 -1.91226478803726 -1.86369199693538 H -1.61411457062865 -2.57031270870798 -0.06271490095861 B 1.10830352290340 -2.09705479656034 -0.54727018566218 H 0.09168472465526 -0.30132058673718 -1.11357154655471 H 0.04509184170150 -1.44980278699727 -2.25974628123964 N 0.79935921599377 -2.03432455998856 1.03698691841691 H 2.17293231747920 -1.54970286550128 -0.73099839281503 H 1.08618816022553 -3.25721650284473 -0.88084646593162 H 0.61101004728679 -1.07863093837470 1.36145786307852 H 1.57173493962069 -2.42246771972654 1.57133490317869 H -0.04928905465051 -2.55720839413654 1.25768150201177 H -0.28111522606123 0.66358422953666 0.65998116432115 H -1.31868792080042 -0.47796636605897 1.97406236201134 H -2.00211658561593 1.32831350371642 1.42039218717870		B -3.21977651162233 0.85698108237180 -0.27308569725256 N -1.66893806115107 0.62845162102579 -0.63072146820986 B -1.22135497078232 -0.87641467692306 -0.72255129427725 H -1.10626921505391 1.12098785937935 0.06203637374238 H -1.47643446617394 1.11402250507021 -1.50703374934660 N 0.33749177660046 -0.96859107958974 -1.11226174481475 H -1.86416002898519 -1.43228023661467 -1.59823427617944 H -1.36187114516945 -1.40716194741124 0.36253491174973 B 1.32095076580676 -0.20995473369159 -0.14019937475252 H 0.46115017022099 -0.65613878675463 -2.07674620883883 H 0.55694284484783 -1.96517601659965 -1.13566195946173 N 2.83902470620326 -0.55219074176528 -0.58093842560065 H 1.17263846843348 -0.61221966628137 0.99014988340315 H 1.18657880105997 0.98698169153638 -0.25440268250575 H 3.06568043885840 -1.54479368479119 -0.51739517720339 H 3.49739240107152 -0.07026605038333 0.03028309752868 H 3.06199852597102 -0.25593704344891 -1.53111251277506 H -3.43171846380942 0.33658371613133 0.82187866171214 H -3.89897346060714 0.33851958620337 -1.14504074546465 H -3.44547790769362 2.05108955515805 -0.19294875098966 N -4.19853954399310 -2.19938696994099 0.20783894429267 H -3.52529722070539 -2.50246500814299 -0.49781445334120 H -3.96879100404545 -1.21767942521280 0.46170043759037 H -4.13204870820608 -2.80368861437980 1.02616914480727 H -5.14203701337525 -2.24475228004498 -0.17578091901243	

$[(NH_4^+)(B_3N_3H_{14})_2]$		$[(NH_4^+)(B_3N_3H_{14})_3]$			
E	-551,5445856		-798,8162026		
H	-551,1147622		-798,1981365		
G	-551,1904521		-798,2966141		
B -3.11986004524949 0.76215573551633 0.02687135332424		B -2.74981161074899 1.13506870533074 -0.04989699084143			
N -1.64743872392956 0.89634785510820 -0.60709391730230		N -1.34940611630615 1.07385926380832 -0.84182842466040			
B -0.95432825071799 -0.48071330127820 -0.91732745999767		B -0.81061774660508 -0.38639732420989 -1.06315796339265			
H -1.06995608330084 1.44650845815148 0.02712533281041		H -0.66650792187929 1.62932486290522 -0.32858165747400			
H -1.71873901349812 1.46728560692289 -1.44947723228699		H -1.46284531086275 1.56116119744841 -1.73063652499563			
N 0.47033775294366 -0.24051847493337 -1.63260493716679		N 0.57675001228961 -0.35153357885946 -1.88714862241926			
H -1.65428349734687 -1.11751677623843 -1.68472030162008		H -1.61984288398251 -1.01781398327157 -1.71889096085587			
H -0.75053890243271 -1.07106283611923 0.12435636386542		H -0.58374997293807 -0.89816420680780 0.01373223090375			
B 1.48818526612186 0.65818911686037 -0.83582363840581		B 1.72666993876936 0.50228871997024 -1.23461000889558			
H 0.31133548030767 0.12699928158070 -2.57210030911344		H 0.38889378217410 -0.04797714095678 -2.84396296812920			
H 0.85741975382638 -1.17298510341005 -1.78399405827553		H 0.86026420651351 -1.32832245788036 -1.97737864644006			
N 2.88966489630694 0.68060433037163 -1.64646543644201		N 3.07637081888178 0.29208201758057 -2.10588302835937			
H 1.70601359493412 0.17279780900042 0.24979372499201		H 1.95523360987935 0.10359152059523 -0.11646842723494			
H 1.09712992782956 1.80254757333990 -0.78917772689553		H 1.46129000554976 1.68212480835814 -1.28757635690962			
H 3.31589152690344 -0.24107763898463 -1.74393456504465		H 3.39478899054453 -0.67669817060800 -2.12848472101265			
H 3.56994428777303 1.26116133692236 -1.15734733146355		H 3.84011466320670 0.83599593678631 -1.70614543593611			
H 2.80549315901031 1.06904083233800 -2.58588646998912		H 2.98442256517201 0.59733059377464 -3.07479171446153			
H -3.03063062003186 0.07694016713273 1.04345203659699		H -2.59259312758043 0.56489389994200 1.02455815577740			
H -3.84589878907643 0.23149787460825 -0.79955434831813		H -3.59843979733198 0.57430268956494 -0.72731733767542			
H -3.53746828831985 1.86909100803453 0.32244897280417		H -3.05426555517580 2.30119239584373 0.14326192690213			
N -3.45593303413246 -2.55143517266849 0.14033883064426		N -3.40436137351559 -2.13644120425613 0.50669335442596			
H -2.55697076655568 -3.01909366809907 -0.06056447026998		H -2.57728458146402 -2.73513126376488 0.37275235591159			
H -3.30673228405240 -1.56067303199716 0.39738395926921		H -3.13644860029184 -1.14046752519274 0.54337673378521			
H -3.90968257808262 -3.05656578803449 0.90168217107346		H -3.89997429792008 -2.38875096047791 1.37254631816984			
H -4.04476736850209 -2.59270181168214 -0.69019012531722		H -4.04702563559814 -2.27203497061428 -0.27312186273353			
H -3.82192485569185 -5.32746364953546 1.24450761520394		H -3.81008640524010 -4.99808027688050 1.43413181206637			
H -2.46847979736275 -5.01104751883461 -1.11916305394685		H -2.46627212068912 -4.68273947132610 -0.87693890578797			
H -3.41629846923204 -7.31979296141109 2.68133610226729		H -3.52263629591118 -7.00153312302894 2.88477998027164			
H -1.94876724554137 -6.93734048169796 0.49177651996570		H -2.00302555857182 -6.67871063104786 0.67837108099437			
B -2.75212938380756 -5.44313235101093 1.81800461056669		B -2.75469234431700 -5.16300558872806 2.01624256438472			
N -2.95776717956341 -6.47890574909142 3.03633932452669		N -3.01619508975010 -6.18712228916998 3.23563856844959			
H -3.65171776246029 -6.04848564629801 3.64894436091237		H -3.68458287872029 -5.71051183697072 3.84278135751539			
B -1.42379955279695 -5.09634391840186 -0.49231844757904		B -1.41888498160118 -4.82631048042547 -0.26476025904556			
N -1.68392455755169 -6.00518496314754 0.81059307599722		N -1.70356317503137 -5.76322874828479 1.01359192510141			
H -0.55217074105882 -5.61356081152254 -1.17163746817266		H -0.57335403663875 -5.35490918828134 -0.97075549683143			
H -2.52547206719916 -8.65827825841582 4.80551620997253		H -2.71628367952942 -8.34801825953255 5.06246571754249			
H -2.35669341075630 -4.39334375164554		H -2.31801520910738 -4.13414185268946			

2.28589791889604 H -1.04287242437314 -3.99147398816093 - 0.11415438400579 H -0.79313574210667 -6.14293184221405 1.28627891446148 N -2.07520983715054 -7.78824193218884 5.09079019380927 B -1.65577389126226 -6.84239116581788 3.84586197545988 H -2.70328681150698 -7.33322572295090 5.75332094676226 H -0.89859885484810 -7.49109144329099 3.15990329694254 H -1.24659939125443 -8.05548721831688 5.62109895866372 H -1.16051292990348 -5.83916324548888 4.30372780502526	2.49211351480559 H -0.99875633728959 -3.75020407225487 0.14721930785591 H -0.81898062998760 -5.93950733225117 1.48781885307113 N -2.21748039953372 -7.49663483182302 5.32151034200395 B -1.73874971700232 -6.61860825098380 4.04716334847625 H -2.82196839827921 -6.98267750923446 5.96286312100030 H -1.03283448147575 -7.33842487583590 3.37678118669928 H -1.40887868247612 -7.79272142807358 5.86693476910004 H -1.17053704595792 -5.64147981190702 4.47604367237351 H -5.13740420451449 -2.80824886504039 2.74056852419030 H -6.11446342232350 -3.53278884667645 0.31514530084987 B -5.90126918534716 -1.84758834821190 2.75927419589252 H -7.68059612905569 -2.97327718259136 2.28150627733491 H -8.57714974848525 -3.79399619215984 - 0.06183326675459 B -6.84095363776522 -2.55542872736697 0.34438950948201 H -6.28273634409661 -1.64663970002707 3.90214453335991 N -7.17570486272842 -2.20499444496955 1.83987345291339 H -7.90257766667606 -3.17502996978521 - 1.39241941720272 N -8.19720622167069 -2.92734977357646 - 0.44727410212904 H -5.36537056600805 -0.85245632484656 2.29780838547558 H -6.34752394340042 -1.58851122878829 - 0.20186625243433 H -7.82216095844643 -1.41808169367191 1.88021372791635 H -10.97588824126134 -3.16602914209636 - 1.02037649484354 B -9.29305779154673 -1.79719865074552 - 0.49304922415965 H -9.73710725461541 -1.58952701757240 0.61349924408549 N -10.52988722258301 -2.32846759051453 - 1.39546025808854 H -10.26548173713014 -2.53901891352129 - 2.35811410777236 H -8.84889193316731 -0.81207066927045 - 1.03384562336816 H -11.25703022974726 -1.61600716014585 - 1.44735467844314	

4. Decomposition of $[(NH_4^+)(N_3B_3H_{14})_3]$-$(B3N2)^-$ into $(N_3B_3H_{14})_4 + H_2$

$\Delta\Delta G^*$ = 158 kJ mol^{-1} (38 kcal mol^{-1})

Note: owing very flat potential energy surface, full convergence was difficult to achieve and the structures exhibit very soft imaginary modes related to hindered rotations of entire molecules.

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Substrates: $[(NH_4^+)(N_3B_3H_{14})_3]$-$(B_3N_2)^-$		Transition state; ν_{im} = −176 cm^{-1}		Product: $(N_3B_3H_{14})_4 + H_2$	
E	-990,2437107		-990,1691194		-990.240423357142
H	-989,4749276		-989,4145655		
G	-989,5878309		-989,527105		
E	-991,6049529		-991,5306898		

B -2.45045270014242 0.97663001985663 -0.94240159205285	B 3.65707122389045 2.11166567076499 -2.22818069870608	B -2.26104092092458 0.85766465313476 -0.89464509924377
N -1.06051476994619 1.01717446105557 -1.75261924695436	N 5.02275538928323 1.66430298157141 -1.48933890391190	N -0.78591002213245 0.90790410341871 -1.53292652786250
B -0.43895882952595 -0.39776195141111 -2.04596278357475	B 4.82009779255210 0.64550880975553 -0.31227344933692	B -0.15448302967064 -0.51359264936900 -1.76472870630748
H -0.40297629625173 1.59155511290815 -1.22666078558433	H 5.48675671955213 2.50562676838191 -1.15007149032313	H -0.19088539964033 1.47067834101577 -0.92662923947340
H -1.21422874339761 1.53170792284955 -2.62034098304866	H 5.65633319418206 1.28682045293619 -2.19351301595527	H -0.83192666926596 1.43229255906463 -2.40655725277132
N 0.95458027635362 -0.23616240509669 -2.84474020908738	N 6.24994462118439 0.24161602599231 0.33118759679292	N 1.28044181003741 -0.37425227736896 -2.49456528038791
H -1.20419427491157 -1.03171130080020 -2.74919981206218	H 4.30565122977824 -0.37290584475915 -0.73799194294928	H -0.88312746288049 -1.15631473777132 -2.49670074360393
H -0.18866301624397 -0.95817257983478 -0.99754547789855	H 4.17428065538223 1.17524349675279 0.56776341038607	H 0.03239510798196 -1.05536048768044 -0.69506278519976
B 2.04113023341857 0.64583399525493 -2.12715533719284	B 7.17290078149021 1.45141162706980 0.72905115379536	B 2.32216828114796 0.55323254839690 -1.76818226393780
H 0.76332783150967 0.10560292871310 -3.78807223832081	H 6.73807681133877 -0.40386282637482 -0.29175649351973	H 1.13660629085907 -0.07895412896309 -3.46127199627963
H 1.29664573356016 -1.18852979076824 -2.98033410676248	H 6.01279830573842 -0.31902533321512 1.14821820114866	H 1.63543078172745 -1.32875031024059 -2.56586498233828
N 3.41795455231585 0.55104400842868 -2.97318535312654	N 8.34991876475359 0.89853357977865 1.69518704982774	N 3.74383308595944 0.41960086475823 -2.53473722692520
H 2.26706447666665 0.20900549280608 -1.02241678698543	H 6.54335947935226 2.26496645990928 1.36595139450592	H 2.49089439827781 0.17896168122204 -0.63095802798379
H 1.71243174416604 1.81129416327694 -2.13107129505790	H 7.71144022086666 1.91470568605062 -0.25099936565679	H 1.99013747183231 1.71407145600142 -1.85535917809307
H 3.79118322224061 -0.39674836929248 -3.03204513420952	H 7.99232172016248 0.45210303726301 2.54021922381505	H 4.12282894022621 -0.52719331963527 -2.51485347460331
H 4.14008735413082 1.11615442979612 -2.52906296594776	H 8.94022370511264 1.66926412497938 2.00514968726556	H 4.44067206142341 1.01693635272525 -2.09152757890403
H 3.33103273598992 0.89556810270251 -3.92967182370645	H 8.96862767100469 0.22472429641724 1.24413325161431	H 3.70383580896751 0.70326862051493 -3.51373572647226
H -2.23283837591041 0.45513599635410 0.14497865134990	H 2.93867617975547 2.65534500006097 -1.40329095488434	H -2.20818215103907 0.20969991911856 0.14136712855310
H -3.25629385151851 0.32397690592335 -1.58961806894551	H 3.12301447915987 1.10984925431270 -2.68183189458467	H -3.00467803858521 0.30448634686388 -1.69259922308621
H -2.85296634150095 2.11650045092522 -0.77738006302347	H 3.95017912947363 2.89114728483391 -3.12647604909542	H -2.64382859688971 1.99451435236936 -0.66560511618504
N -2.67621836311909 -2.33327910637782 -0.28418023203890	N 1.15718759940607 0.24518009977996 0.78860650128047	N -2.81609926946115 -2.62899466562874 -0.53288651143908
H -1.79447098015192 -2.73271172494911 0.06421115333268	H 1.55799062306091 0.20734628079792 1.72305953118127	H -1.94916680048878 -3.07521617598267 -0.21722161724429
H -2.61477061782091 -1.30385269785091 -0.28827090874664	H 1.77232348268049 0.81164678095955 0.21422420919621	H -2.63511808753558 -1.61751823826681 -0.54194515222468
H -3.42675906842843 -2.63626277570450 0.33899376331221	H 0.29423057934960 0.76937587707770 0.89925058991499	H -3.45550833552490 -2.80095310815449 0.24303923016918
H -2.89464708929717 -2.65933052462301 -1.23303492266033	H 0.24397862958063 -0.12870519834357 -1.66798292428128	H -4.70904528070103 -1.04930850933955 0.66348711984294
H -2.73432806788428 -5.13045480654222 0.73886848397219	H -0.54105133495013 0.18544806427354 3.27142124501266	H -3.48502881631389 -5.01561550648294 0.96811497141082
H -0.30627260444077 -4.25215945257215 0.16471804883720	H 2.10375157168273 0.52106101171587 3.94219457045441	H -1.41182224151098 -5.54022747584152 -0.73651046841868
H -3.21696370127963 -6.78199855644357 2.56343289600579	H -2.30298350756403 0.44651190733064 5.01717692625949	H -3.81451564906708 -6.49135454575638 2.95418685210442
H -0.70454052297326 -5.87894371078986 2.13972053182486	H 0.22945359917322 1.05694682710164 5.59103959092891	H -1.66912390480361 -6.80399371157794 1.45511161162825
B -2.57106749251480 -4.82165560544787 1.90558755891658	B -0.78746376170773 1.29182066316143 3.70711821195764	B -2.70060762316214 -4.96408912154915 1.89755609590071
N -3.43594853673350 -5.81760856856552	N -2.24787869355792 1.24482698174434	N -3.42706085845274 -5.57787378837774

2.81227234252672
H -4.40430060893840 -5.68593994700825
2.50118157503268
B -0.11439604630933 -3.96050470641967
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N -1.03919356932342 -4.92139788157418
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H 1.05748754738529 -4.13355280015511
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H -4.65717098496188 -7.29747212982246
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H -2.95529168545551 -3.69485485479486
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H -0.43953719337666 -2.80248485252492
1.56362399631073
H -0.87471108597513 -4.69626658995166
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H -3.64139343598174 -2.52679997290261 -

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H -6.35142528707451 -0.95930807812568 -5.98222451542640	H -0.37042604105596 -3.37326859774143 -5.65156596617817	H -5.57232851876223 -0.22801784799885 -4.01994756819247
B -6.35172444465070 -2.38313432143847 -4.35687543646739	B -0.94567412074293 -2.78513176896134 -3.65586041393652	B -5.52449054000253 -2.10223786223792 -2.93965571883580
H -8.60755635056070 -0.56283021894363 -4.81472656287485	H -2.69392970169147 -2.33938941223529 -5.97739335689899	H -8.07182690560947 -0.57602842304007 -3.49243412110827
N -4.80338287677326 -2.71326440319982 -4.41927733467855	N 0.58660425812486 -2.98666254089487 -3.06553309497818	N -3.93328496872300 -2.22803975364388 -2.90783770775522
H -4.73486530030004 -4.55508965734203 -3.03093568304795	H 0.05949541935957 -2.95950057009183 -0.83286863301398	H -3.96825571242119 -4.22214453990551 -1.73933168490171
H -4.27161204533088 -1.85747347804267 -4.57559666598130	H 1.27880935911173 -2.59710156943196 -3.70624222431574	H -3.49645277261708 -1.30700222432812 -2.80554369750814
B -4.26077632833148 -3.43237833981028 -3.09408702453409	B 0.81826460767882 -2.54834375979215 -1.64976872065530	B -3.22441228592620 -3.29147538817247 -1.94301526405673
H -3.03461644000549 -3.48509356617226 -3.12100436489471	H 1.78057880311700 -1.90607287771543 -1.39264918773973	H -2.18392765178568 -3.63658532615937 -2.46324193638247
H -6.51321977521847 -1.53853442835827 -3.49066042057411	H -1.09861028289508 -1.61087242559697 -3.88962482684422	H -5.94311746890761 -1.60454101943400 -1.91208996255461
H -4.63216393706986 -2.76209094657814 -2.13999463894711	H -0.20992353310031 -0.19226734744219 -2.26354519341510	H -5.21080190892674 -1.17737105863830 0.13161202749128

5. Dehydrogenation and cyclisation of $B_3N_3H_{14}$ in THF:

$\Delta\Delta G^*$ = 178 kJ mol^{-1} (42 kcal mol^{-1})

Substrates: $B_3N_3H_{14}$		Transition state; ν_{im} = −204 cm^{-1}		Product: $B_3N_3H_{12}$ + H_2	
E	-247,2662843		- 247,1909889		-247.2758594
H	-247,0800285		-247,0140584		-247.09599548
G	-247,122004		-247,056871		-247.1401522
E	-247,6042227		-247,5260112		-247.615999430351
B -1.54021257597342 0.33518671174295 1.07577370926230 N -2.24767204444348 -0.33042947009478 - 0.20922419342796 B -1.57323874628140 -1.62812148879007 - 0.82251153718234 H -2.36885303399078 0.37840621104163 - 0.93273756662568 H -3.20055415994328 -0.58220939306202 0.04784336455853 N -0.05306778392926 -1.27039042657532 - 1.20802912397333 H -2.16130522345302 -1.97512119634289 - 1.83132178985886 H -1.59490616256961 -2.50272191323365 0.02462030764529 B 1.08471963587744 -2.16782663650063 - 0.57211131460446 H 0.13118542431796 -0.29102437783617 - 0.97948961602105 H 0.05330732904628 -1.32118846610820 - 2.21877626243848 N 0.95090690216052 -2.02817310679335 1.02344567239229 H 2.18331899032538 -1.75744906541819 - 0.88629277415234 H 0.90558643810501 -3.32963856256439 - 0.86323586078577 H 1.10087813560022 -1.07544998540478 1.35674157184943 H 1.62488982651624 -2.62421572413340 1.49981066964694 H 0.01905738657255 -2.29634404797524 1.34632461587986 H -0.41757243547574 0.71491413564573 0.75907621668372 H -1.47267349918011 -0.51662152655766 1.95055380606411 H -2.20666011758149 1.29044227696042 1.44479472218780		B -1.48933548070614 1.69028293241534 0.90952371791048 N -1.85061940734333 0.92150461988765 - 0.31643842195996 B -0.93913373012405 -0.47915801785037 - 0.59589234652356 H -1.79710832135936 1.48517055476195 - 1.16522278719921 H -2.80211009606767 0.55991781489787 - 0.25633786656530 N 0.48767158852963 -0.05588078907379 - 1.05889053135279 H -1.51968856915579 -1.05946462599117 - 1.48427034984702 H -0.93573380788072 -1.07462538528650 0.45178627304930 B 1.64043202083740 -1.18915138157626 - 0.70463415973849 H 0.81827190266837 0.80016205317940 - 0.61449110767296 H 0.50251634779866 0.13922908914621 - 2.05815800567083 N 1.87528485855925 -1.13969342475653 0.80358309791266 H 2.63650492534253 -0.84869498524101 - 1.33498074665712 H 1.19011999695609 -2.25120319562546 - 1.11988736557730 H 0.56815563848040 0.38891158646307 1.58311457552563 H 2.83270699754095 -0.97135760170923 1.08219371490947 H 1.54148565654742 -1.93788083128647 1.32768021977848 H 0.10573093295074 0.94800854425153 1.85041175125671 H -2.05714121760914 1.41641296341921 1.91771864565424 H -0.80801023596524 2.65751007997451 0.78319169276753		B -1.05546083732234 -0.41491796481028 0.84291476154349 N -2.23684857660377 -0.91969834364003 - 0.11330653157109 B -1.80421480810396 -1.92209161250638 - 1.28561819864657 H -2.69636405569349 -0.10002906118230 - 0.50417598451900 H -2.96033401902721 -1.37634735397911 0.43780385624553 N -0.30373233495498 -1.56140637107804 - 1.66317454603026 H -2.53519517305881 -1.77642429940327 - 2.24736246474465 H -1.82745726278180 -3.06065148394025 - 0.85728652509533 B 0.75196939449638 -1.85385643859558 - 0.49921432702027 H -0.24282395674732 -0.59079310583134 - 1.96914911118958 H -0.03854229702164 -2.10426766553993 - 2.48205568866728 N 0.01646247417678 -1.58592224999171 0.89373437355813 H 1.68971120870533 -1.08447644258186 - 0.59086250003938 H 1.09061109315911 -3.01978437925855 - 0.57092239841860 H 1.85476940905151 0.81187245722791 2.92647131209845 H 0.72147721480060 -1.34978556074013 1.58848093224413 H -0.41488708302660 -2.44019711608998 1.24525703793069 H 1.23351096842995 0.99093586508606 2.55996998978200 H -1.49213942052244 -0.18211820439285 1.95457680356297 H -0.53337765225509 0.56198327914812 0.33917382607667	

6. Decomposition of NH_3BH_3 via intermolecular H-H coupling in THF:

$\Delta\Delta G^{*}$ = 234 kJ mol^{-1} (56 kcal mol^{-1})

Substrates: NH_3BH_3-NH_3BH_3		Transition state; ν_{im} = −398 cm^{-1}		Product: $B_2N_2H_{10}$ + H_2	
E	-166,3762763		-166,2993303		-166.40021646
H	-166,2248895		-166,1591102		-166.2557570
G	-166,2652426		-166,2001		-166.29789097
E	-166,6379647		-166,5376871		-166.64088737
B -2.38802484572491 2.91204211672677 0.95553559629116 N -3.59460107020342 1.93839093891025 0.47577935726196 H -1.45246917778288 2.75513917252628 0.19701513936704 H -2.09842828934953 2.58578716202429 2.09496590784631 H -2.81265684261429 4.05505155217783 0.90788091263165 H -4.40942254583189 2.02860674154634 1.08823878930229 H -3.90956332488206 2.14846201933829 - 0.46905010942889 H -3.32587025519320 0.95672283876557 0.48383429107018 H -3.62717797010433 3.89629075839835 2.87591054037878 H -4.12754750310937 3.78055059674458 4.43348089074959 N -4.44203288198516 3.98850855025422 3.48802707862085 H -4.71021533324017 4.97030642737220 3.47766707344280 H -5.22385536548494 1.87138863528488 3.05899105321156 B -5.64871137004771 3.01425581314372 3.00986425492581 H -5.93846317948459 3.33891220829129 1.87002116122901 H -6.58426543836136 3.17210906069501 3.76819322379979		B 1.17802562560649 0.24807060287034 - 1.30111656047350 N 0.35252917973386 -1.01857255796370 - 1.12348832007337 H 2.27450643126923 0.10208199995796 - 1.73023537420129 H 2.56580191086223 0.28456456579400 0.51581958427068 H 0.60562257623616 1.28094725757088 - 1.25906457998112 H -0.43140303861209 -0.91218596489681 - 0.42752163615396 H -0.10431651149796 -1.24745258361255 - 2.01404823641472 H 0.90382536514622 -1.84239090428124 - 0.87706687914468 H 1.85514833259062 0.39251112931152 0.76161528516905 H -0.23641515850994 0.33445073650433 2.26677275896971 N -0.40446822735139 0.66296011652211 1.32004421685270 H -0.38325261470850 1.67613943252819 1.38248041823231 H -1.67375565259136 -1.08951646247121 0.57562924827017 B -1.76287244032122 0.14662480989853 0.75885676086020 H -1.98746499931990 0.67684801971950 - 0.33406842635950 H -2.75151077853243 0.30491980254814 1.48539174017732		B -3.42137861966307 2.93167561462684 1.29084413951406 N -4.19200561125328 1.70166452483815 0.59083253048053 H -2.25332901894857 2.61482981877786 1.39324432606630 H -1.27490449489458 4.91424880903867 2.89557228167457 H -3.59073751003527 3.90470592005182 0.58818238373643 H -5.19382711846080 1.88409759386304 0.51739730243204 H -3.83733468608333 1.54077432457612 - 0.34995639728083 H -4.09340744473607 0.82261541239944 1.09770543299171 H -0.88099751526103 4.87072093951393 3.52382414568928 H -3.71272556542333 2.52931185523065 3.39378077751019 N -4.08940885638064 3.17194519088480 2.69836332303267 H -3.78858894768645 4.08963732705960 3.02108422013436 H -6.05373233756791 1.95451820506417 2.63370464052930 B -5.70487343612638 3.12072869804726 2.75544311693162 H -6.13412063411801 3.79951589798047 1.83293283487361 H -6.07193359655973 3.56153446034606 3.83340010218345	