The Effect of the NH_2 Substituent on NH_3: Hydrazine as an Alternative for Ammonia in Hydrogen Release in the Presence of Boranes and Alanes

Nguyen Vinh-Son,[b,c] Saartje Swinnen,[b] Myrna H. Matus,[a] Minh Tho Nguyen*,[a,b] and David A. Dixon*,[a,1]

[a]*Department of Chemistry, The University of Alabama, Shelby Hall, Tuscaloosa, AL 35487-0336*

[b]*Department of Chemistry, University of Leuven, B-3001 Leuven, Belgium*

[c] *Department of Chemistry, Hanoi National University of Education, 136 XuanThuy Street, Hanoi, Vietnam*

Supporting Information Available. Optimized geometries (Cartesian coordinates and figures with selected parameters), CCSD(T) total energies, zero-point energies. Table S-1 lists the reaction Enthalpies and Free Energies. Table S-2 and S-3 show the Zero point energies (ZPE, kcal/mol) at MP2/aug-cc-pVDZ and CCSD(T) total energies (au) with the aVDZ, aVTZ basis sets for the points on the H_2-release pathway from N_2H_4 with a presence of borane, diborane, alane and dialane. Table S-4 lists the coordinates of all MP2/aVTZ optimized geometries. Figures S-1 and S-2 show the selected MP2/aug-cc-pVTZ geometry parameters for complexe and product for H_2-release from N_2H_4 with a presence of borane, diborane, alane and dialane.

[1] Email: dadixon@as.ua.edu

Table S-1: Reaction Enthalpies and Free Energies (kcal/mol) for H_2 elimination Reactions at MP2/aVDZ level.

Reactions	**ΔH**	**ΔG**
$BH_3 + N_2H_4 \rightarrow BH_2NHNH_2 + H_2$ (**b** + **hyz** → **bhyz-p** + H_2)	**-34.1**	**-32.7**
$B_2H_6 + N_2H_4 \rightarrow BH_2NHNH_2 + BH_3 + H_2$ (**db** + **hyz** → **bhyz-p** + **b** + H_2)	**4.4**	**7.8**
$AlH_3 + N_2H_4 \rightarrow AlH_2NHNH_2 + H_2$ (**al** + **hyz** → **alhyz-p** + H_2)	**-16.8**	**-14.3**
$Al_2H_6 + N_2H_4 \rightarrow Al_2H_5NHNH_2 + H_2$ (**dal** + **hyz** → **dalhyz-p** + H_2)	**-20.4**	**-17.6**
$BH_3AlH_3 + N_2H_4 \rightarrow AlBH_5NHNH_2 + H_2$ (**bal** + **hyz** → **balhyz-p** + H_2)	**-3.8**	**-0.9**

Table S-2: Zero point energies (ZPE, kcal/mol) at MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ, and CCSD(T) total energies (au) with the aVDZ, aVTZ basis sets for the points on the H_2-release pathway from hydrazine with a presence of borane and diborane.

Molecule	**ZPE**	**E(MP2/aVTZ)**[a]	**E(CCSD(T)/aVDZ)**[a]	**E(CCSD(T)/aVTZ)**[a]
BH_3 (**b**)	16.67	-26.5150147	-26.5122640	-26.5390576
N_2H_4 (**hyz**)	33.62	-111.6767950	-111.6081220	-111.7112807
b + hyz	50.28	-138.1918097	-138.1203860	-138.2503383
B_2H_6 (**db**)	39.87	-53.1006631	-53.0885066	-53.1464202
db + hyz	73.49	-164.7774581	-164.6966286	-164.8577009
bhyz	55.21	-138.2499776	-138.1748963	-138.3070724
b + **bhyz**	71.87	-164.7649923	-164.6871603	-164.8461300
dbhyz-com	74.37	-164.783066	-164.7030571	-164.8632920
dbhyz	75.82	-164.800436	-164.7204889	-164.8808392
bhyz-ts	51.16	-138.1851446	-138.1065475	-138.2398672
dbhyz-com-ts	74.66	-164.775863	-164.6954213	-164.8552817
dbhyz-ts	71.29	-164.754466	-164.6730815	-164.8333949
bhyz-p + H_2	47.29	-138.2455716	-138.1686549	-138.3022674
bhyz-p + **b** + H_2	63.96	-164.7605863	-164.6809189	-164.8413250

[a] Based on MP2/aug-cc-pVTZ optimized geometries.

Table S-3: Zero point energies (ZPE, kcal/mol) at MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ, and CCSD(T) total energies (au) with the aVDZ, aVTZ basis sets for the points on the H_2-release pathway from hydrazine with a presence of alane and dialane.

Molecule	**ZPE**	**E(MP2/aVTZ)**[a]	**E(CCSD(T)/aVDZ)**[a]	**E(CCSD(T)/aVTZ)**[a]
AlH_3 (**al**)	11.73	-243.7403261	-243.7397977	-243.7651104
N_2H_4 (**hyz**)	33.62	-111.6767950	-111.6081220	-111.7112807
al + hyz	45.35	-355.4171211	-355.3479197	-355.4763911
Al_2H_6 (**dal**)	27.76	-487.5396665	-487.5335392	-487.5895777
dal + hyz	61.39	-599.2164615	-599.1416612	-599.3008584
alhyz	48.40	-355.4662924	-355.3939515	-355.5254396
al + **alhyz**	60.14	-599.2066185	-599.1337492	-599.2905500
dalhyz	62.89	-599.247865	-599.1727911	-599.3321928
alhyz-ts	44.86	-355.4152408	-355.3376658	-355.4714282
dalhyz-ts	59.90	-599.212405	-599.1317249	-599.2937693
alhyz-p + H_2	41.81	-355.4469480	-355.3672124	-355.5033978
dalhyz-p + H_2	57.38	-599.2637824	-599.1814956	-599.3450937

[a] Based on MP2/aug-cc-pVTZ optimized geometries.

Table S-4: Zero point energies (ZPE, kcal/mol) at MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ, and CCSD(T) total energies (au) with the aVDZ, aVTZ basis sets for the points on the H_2-release pathway from hydrazine with a presence of borane-alane.

Molecule	**ZPE**	**E(MP2/aVTZ)**[a]	**E(CCSD(T)/aVDZ)**[a]	**E(CCSD(T)/aVTZ)**[a]
AlH_3 (**al**)	11.73	-243.7403261	-243.7397977	-243.7651104
$BH_3N_2H_4$ (**bhyz**)	55.21	-138.2499776	-138.1748963	-138.3070724
N_2H_4 (**hyz**)	33.62	-111.6767950	-111.6081220	-111.7112807
BH_3AlH_3 **(bal)**	33.40	-270.325378	-270.3156691	-270.3727211
bal + hyz	67.62	-382.0021725	-381.9237910	-382.0840017
al + **bhyz**	66.94	-381.9903037	-381.9146940	-382.0721828
balhyz	69.61	-382.02083	-381.9436210	-382.1028113
ts-balhyz	67.92	-381.9841234	-381.9083577	-382.0666163
balhyz-ts	66.80	-381.991311	-381.9078866	-382.0700692
balhyz-p + H_2	62.52	-382.0038754	-381.9216375	-382.0840201

Table S-5: Geometries of the Structures Considered Optimized at the MP2/aug-cc-pVTZ Level of Theory, Given in Cartesian Coordinates (Å)

1. bhyz

N	0.042692	0.548716	0.002598
H	0.074294	1.098623	0.856840
N	1.191725	-0.308406	-0.125800
H	1.939858	0.046268	0.458858
H	0.054408	1.189569	-0.784396
H	0.893111	-1.202276	0.251724
H	-2.216569	0.547128	0.099930
B	-1.353843	-0.292497	0.005938
H	-1.254562	-1.000060	0.984365
H	-1.362250	-0.898934	-1.034599

2. alhyz

N	-0.644727	0.625839	-0.003654
N	-1.623058	-0.420958	0.127506
Al	1.279920	-0.136875	-0.000837
H	-0.775919	1.262470	0.775894
H	-2.486080	-0.143362	-0.324885
H	1.584552	-0.325039	1.550944
H	-0.760297	1.161504	-0.861002
H	2.013369	1.056320	-0.773654
H	0.902967	-1.445015	-0.854989
H	-1.243049	-1.221666	-0.368390

3. dbhyz

N	0.678167	0.322231	0.495546
B	-0.418008	1.076359	-0.368546
N	1.485861	-0.679014	-0.179353
B	-1.838397	-0.634515	0.059993
H	-0.885734	1.968957	0.269125
H	-1.854995	-0.217693	1.185534
H	0.100099	1.376532	-1.412025
H	-1.289042	0.250837	-0.791917
H	0.221740	-0.151555	1.276270
H	1.330512	0.989967	0.899960
H	-1.132461	-1.598276	-0.120870
H	-2.899024	-0.675237	-0.490189
H	1.726745	-0.246772	-1.068510
H	0.815990	-1.408499	-0.417959

4. dalhyz

N	-1.160431	-0.417004	0.633650
N	-1.479652	-1.477975	-0.323334
Al	-0.623541	1.348255	-0.163945
Al	2.022725	-0.276850	-0.001324
H	-0.385946	-0.757666	1.211426
H	1.507651	-0.339206	1.525850
H	-1.506729	1.376108	-1.481149
H	-1.957611	-0.357547	1.262822
H	-0.694670	2.417502	0.996289
H	1.400880	-1.497302	-0.841439
H	0.946800	0.999098	-0.579183
H	3.457612	0.290755	-0.339136
H	-1.904435	-0.999648	-1.114865
H	-0.572365	-1.795503	-0.664324

5. bhyz-p

N	-0.000000	0.454740	0.000000
N	1.141603	-0.398969	-0.000000
B	-1.336462	0.070029	0.000000
H	1.080718	-0.999430	0.813493
H	0.283484	1.420798	0.000000
H	1.080718	-0.999430	-0.813493
H	-1.595496	-1.093444	-0.000000
H	-2.158339	0.930962	0.000000

6. alhyz-p

Al	-1.201094	0.128109	0.000000
N	0.460590	-0.534549	0.000000
N	1.709578	0.177629	0.000000
H	1.745210	0.778909	-0.813969
H	0.663337	-1.522690	0.000000
H	1.745210	0.778907	0.813970
H	-1.336383	1.701253	-0.000001
H	-2.394330	-0.903363	0.000000

7. dalhyz-p

N	0.000000	0.582749	0.574043
N	0.000002	1.905575	-0.044223
Al	1.350893	-0.672358	-0.103405
Al	-1.350894	-0.672356	-0.103405
H	-1.962594	-1.590373	1.024156
H	2.136932	0.055539	-1.267230
H	0.000000	0.739858	1.574947

8. bhyz-ts

N	-0.052753	-0.535080	0.002795
N	-1.287438	0.167077	-0.063011
B	1.295843	0.276655	-0.125121
H	0.806157	-0.233968	1.044164
H	-1.594052	0.385748	0.877427
H	-0.103734	-1.394593	-0.518710
H	-1.131625	1.049077	-0.540763

H	1.962591	-1.590376	1.024156
H	-0.000001	-1.534753	-0.804723
H	-2.136932	0.055541	-1.267231
H	0.811195	1.963782	-0.652152
H	-0.811196	1.963787	-0.652145

9. alhyz-ts

Al	1.206749	0.155319	-0.046762
N	-0.560332	-0.590907	-0.130500
N	-1.709173	0.272413	-0.064753
H	0.073819	-0.593546	1.112415
H	-1.943187	0.433099	0.910358
H	-0.822232	-1.452906	-0.588540
H	-1.463402	1.174427	-0.457761
H	0.793921	-0.227798	1.683009
H	1.210719	1.726168	-0.221913
H	2.349162	-0.849130	-0.462894

10. dbhyz-ts

N	0.640643	0.255599	0.481151
N	1.501772	-0.710687	-0.137441
B	-0.121788	1.241023	-0.309086
B	-1.907664	-0.538654	-0.104513
H	-0.682069	-0.440529	0.851353
H	-1.327346	-1.263147	-0.855446
H	-0.470069	2.215054	0.281402
H	1.067491	0.578969	1.337765
H	0.003850	1.226423	-1.491933
H	-1.471310	-0.740609	1.135989
H	-1.681059	0.663550	-0.284365
H	-3.061397	-0.767103	0.103010
H	1.852769	-0.304931	-0.998975
H	0.919494	-1.493902	-0.416777

11. dalhyz-ts

N	1.033889	-0.399225	0.570235
Al	0.738600	1.309963	-0.120347
Al	-1.953342	-0.182389	-0.121124
H	-0.612205	-0.758602	1.238149
H	-1.459261	-1.269860	-1.144742
H	0.859387	2.467121	0.953883
H	1.518923	-0.479933	1.455899
N	1.482281	-1.510158	-0.247194
H	1.063994	1.437096	-1.666004
H	-1.357359	-0.854961	1.532788
H	-1.091900	1.209006	-0.162538
H	-3.434949	0.035550	0.359621
H	2.031229	-1.147958	-1.020716
H	0.660602	-1.930244	-0.668501

12. dbhyz-com-ts

N	0.909384	-0.619531	-0.012216
N	2.002836	0.296934	-0.100369
B	-0.788659	0.560418	-0.030221
B	-2.477413	-0.154054	0.026140
H	-2.995336	-0.497408	-0.990110
H	-2.913581	-0.491255	1.082515
H	-0.447831	1.040322	1.007570
H	-1.302693	-0.664471	-0.026913
H	-2.237549	1.058319	0.009605
H	-0.489365	1.033470	-1.078331
H	0.919121	-1.157932	0.849099
H	0.971185	-1.257482	-0.797415
H	1.665430	1.177009	0.276268
H	2.775435	-0.014214	0.476210

13. dbhyz-com

N	-1.346757	0.758156	0.066974
N	-2.044050	-0.456222	-0.246228
B	1.310994	-0.740879	0.208880
B	2.580186	0.396781	-0.159348
H	2.957337	0.499368	-1.278856
H	-1.425540	0.991266	1.051185
H	1.277545	0.518585	-0.141739
H	3.040632	1.044683	0.721191
H	2.622297	-0.864891	0.181742
H	-1.790314	1.499105	-0.459204

14. ts-balhyz

N	1.642578	-0.639392	-0.010783
N	2.708516	0.309360	-0.096321
B	-0.123687	0.502144	-0.037801
Al	-2.398406	-0.043949	0.013386
H	-3.009426	-0.538312	-1.357196
H	-2.927829	-0.532079	1.420739
H	0.180838	0.969676	1.015489
H	-0.700388	-0.611945	-0.030587
H	-1.595644	1.368440	-0.009382
H	0.158009	0.968249	-1.092992

H	0.946220	-0.850970	1.332820
H	0.857302	-1.401852	-0.666029
H	-2.818592	-0.612778	0.388658
H	-1.387141	-1.215561	-0.122647

15. balhyz-ts

N	0.960374	-0.124631	0.490219
N	2.199190	-0.341321	-0.208138
B	0.137514	1.068901	-0.018754
Al	-1.727739	-0.168231	-0.061040
H	0.001589	-1.179272	-0.058337
H	-2.825634	0.118984	-1.154138
H	-0.784774	1.281166	0.785421
H	1.154936	-0.146134	1.483017
H	0.692783	2.099276	-0.260466
H	-0.613946	-1.561417	-0.551429
H	-0.373189	0.676409	-1.085897
H	-2.082772	-0.746715	1.364058
H	2.479716	0.539338	-0.631777
H	2.007383	-0.977472	-0.977733

17. balhyz-p

N	1.222264	-0.368348	-0.365019
N	2.451409	-0.059195	0.293037
B	0.090292	0.539645	-0.251094
Al	-2.004705	-0.086453	0.110783
H	-3.073377	1.058361	0.023398
H	-0.601982	0.430020	0.922432
H	1.083887	-1.365819	-0.351949
H	0.295381	1.713756	-0.315838
H	-0.797225	0.214812	-1.126307
H	-2.223729	-1.635336	0.258254
H	2.267202	0.385173	1.186831
H	2.943834	0.617508	-0.277659
H	1.663351	-1.173111	0.852642
H	1.728928	-1.278527	-0.791851
H	2.348116	1.178285	0.283655
H	3.494094	0.020160	0.474201

16. balhyz

N	1.135663	-0.333640	0.290628
N	2.407993	-0.196296	-0.362925
B	0.255565	0.997113	0.126006
Al	-2.086238	-0.176448	-0.086171
H	0.841722	1.888558	0.677645
H	0.613236	-1.088545	-0.163392
H	-0.759404	0.790634	0.803119
H	0.051530	1.152942	-1.041500
H	-2.800579	-0.440393	1.311826
H	1.232000	-0.564474	1.278043
H	-2.767107	0.763960	-1.158897
H	-1.161849	-1.398311	-0.594145
H	2.719318	0.751365	-0.177113
H	3.068818	-0.837922	0.060685

Figure S-1. Selected MP2/aVTZ geometry parameters of adducts, transition states and products related to the reaction $BH_3 + N_2H_4$ (**b + hyz**) and $B_2H_6 + N_2H_4$ (**db + hyz**). Bond distances in angstroms and bond angles in degrees.

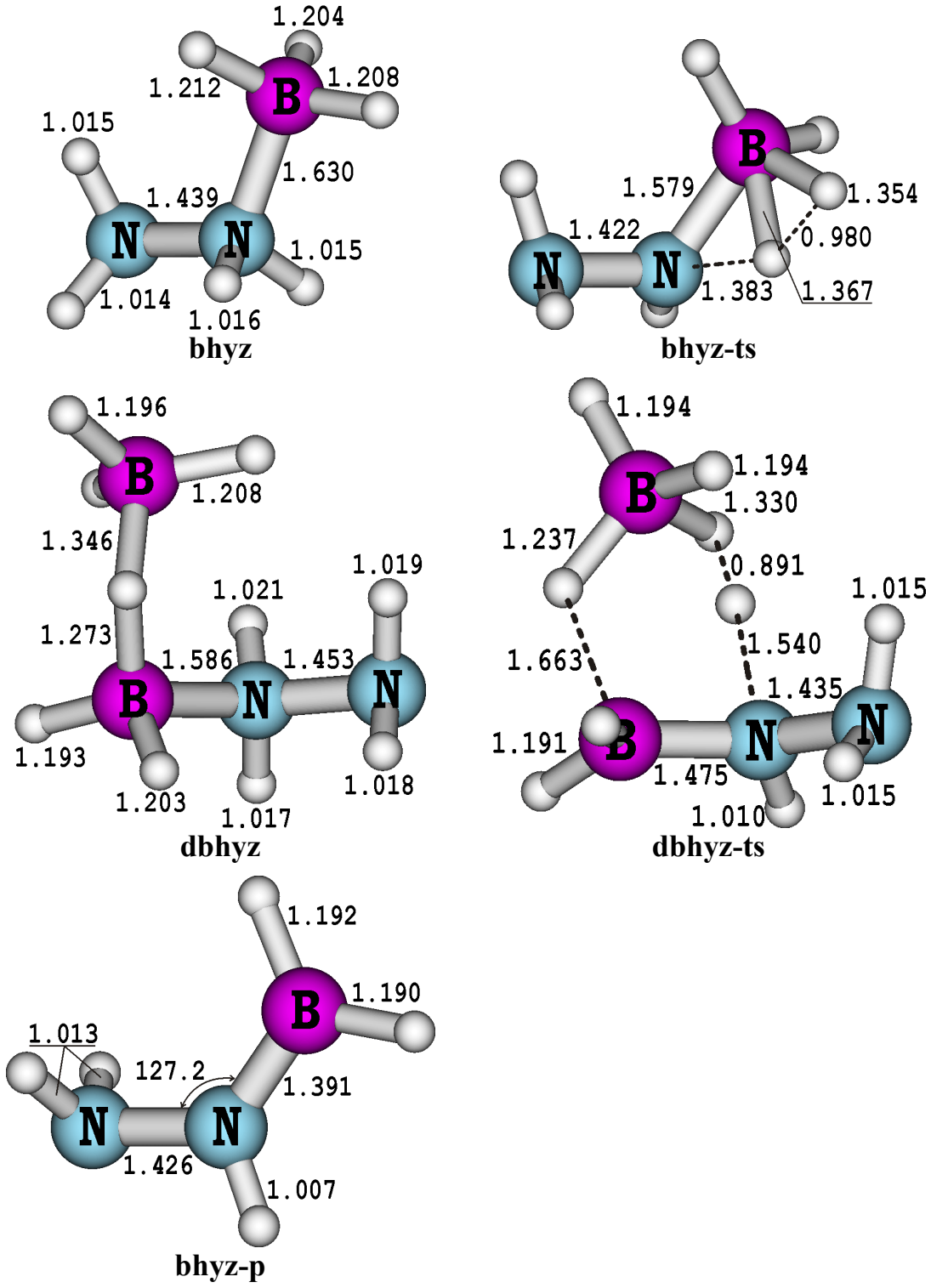

Figure S-2. Selected MP2/aVTZ geometry parameters of adducts, transition states amd products related to the reaction $AlH_3 + N_2H_4$ (**al** + **hyz**) and $Al_2H_6 + N_2H_4$ (**dal** + **hyz**). Bond distances in angstroms and bond angles in degrees.

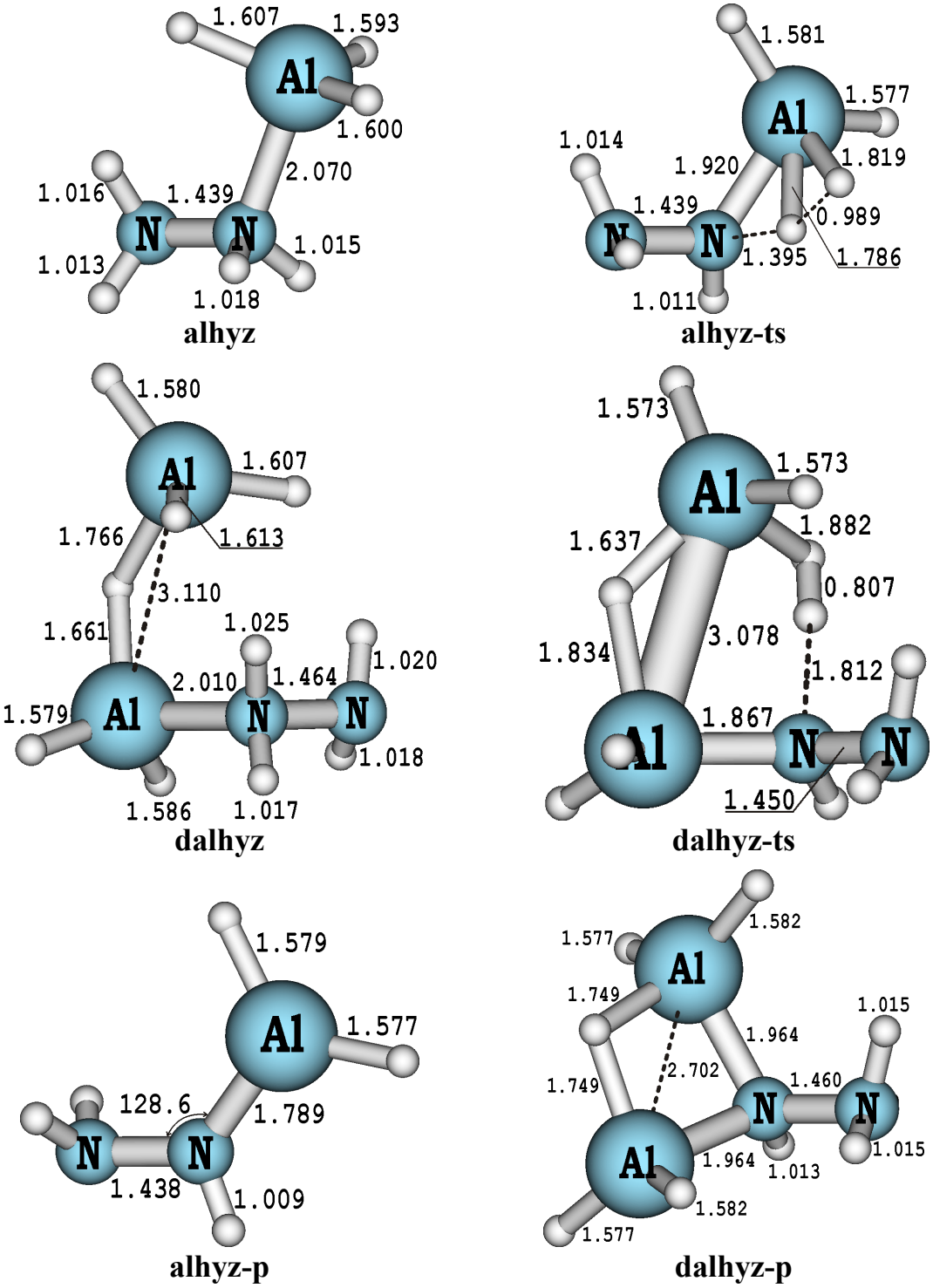

Figure S-3. Selected MP2/aVTZ geometry parameters of adducts, transition states amd products related to the reaction $BH_3AlH_3 + N_2H_4$ (**bal** + **hyz**). Bond distances in angstroms and bond angles in degrees.