Electronic Supplementary Information

Revisiting the Bonding Evolution Theory: A New Perspective on Ammonia Pyramidal Inversion and Bond Dissociations in Ethane and Borazane

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1. Optimized Cartesian coordinates for minima and TS of the pyramidal inversion of ammonia at DFT levels

ωB97X-D/6-31G(d)

Minima

H	0.00000000	0.93951400	-0.31816900
H	-0.81361300	-0.46968000	-0.31838100

H	0.81361300	-0.46968000	-0.31838100
N	0.00000000	-0.00001300	0.06938400

<u>TS</u>

H	0.00000000	0.99973900	0.0000000
H	-0.86579900	-0.49986900	0.00000000
H	0.86579900	-0.49986900	0.00000000
N	0.00000000	0.00000000	0.00000000

ωB97X-D/6-31G(d,p)

<u>Minima</u>

H	0.00000000	0.93820100	-0.31804900
H	-0.81247600	-0.46902400	-0.31826100
H	0.81247600	-0.46902300	-0.31826100
N	0.00000000	-0.00001300	0.06902300

<u>TS</u>

H	0.00000000	0.99775300	0.00000000
H	-0.86408000	-0.49887700	0.00000000
H	0.86408000	-0.49887700	0.00000000
N	0.00000000	0.00000000	0.00000000

M06-2X/6-31G(d)

<u>Minima</u>

H	0.00023000	0.93853200	-0.10127400
H	-0.81269800	-0.46946000	-0.10127000
H	0.81314900	-0.46945500	-0.09750800
N	-0.00068000	0.00038200	0.29161100

<u>TS</u>

H	0.00000000	0.99997200	0.00000000
H	-0.86600100	-0.49998600	0.00000000

| H | 0.86600100 | -0.49998600 | 0.00000000 |
| N | 0.00000000 | 0.00000000 | 0.00000000 |

M06-2X/6-31G(d,p)

<u>Minima</u>

H	0.00021800	0.93740700	-0.10072200
H	-0.81173200	-0.46888700	-0.10071800
H	0.81215900	-0.46888200	-0.09713700
N	-0.00064500	0.00036200	0.29013600

<u>TS</u>

H	0.00000000	0.99825000	0.00000000
H	-0.86449100	-0.49913200	0.00000000
H	0.86449100	-0.49913200	0.00000000
N	0.00000000	0.00001500	0.00000000

2. Optimized Cartesian coordinates for minima and TS of the pyramidal inversion of phosphine at DFT levels

ωB97X-D/6-31G(d)

<u>Minima</u>

H	0.00000000	1.19562400	-0.69484600
H	-1.03575700	-0.59836200	-0.69391400
H	1.03575700	-0.59836200	-0.69391400
P	0.00000000	0.00004600	0.06840700

<u>TS</u>

H	0.00000000	1.38355500	0.00000000
H	1.19819400	-0.69177800	0.00000000
H	-1.19819400	-0.69177800	0.00000000
P	0.00000000	0.00000000	0.00000000

ωB97X-D/6-31+G(df)

<u>Minima</u>

H	-0.00000300	1.20133000	-0.69274800
H	-1.04073000	-0.60121800	-0.69182200
H	1.04073100	-0.60122200	-0.69182100
P	0.00000100	0.00005700	0.06212400

<u>TS</u>

H	0.00000000	1.38142100	0.00000000
H	1.19634600	-0.69071000	0.00000000
H	-1.19634600	-0.69071000	0.00000000
P	0.00000000	0.00000000	0.00000000

ωB97X-D/6-31+G(df,p)

<u>Minima</u>

H	-0.00000100	1.19995200	-0.69339300
H	-1.03952400	-0.60053000	-0.69246600
H	1.03952400	-0.60053200	-0.69246600
P	0.00000100	0.00005700	0.06405800

<u>TS</u>

H	0.00000000	1.38137900	0.00000000
H	1.19631000	-0.69069000	0.00000000
H	-1.19631000	-0.69069000	0.00000000
P	0.00000000	0.00000000	0.00000000

M06-2X/6-31G(d)

<u>Minima</u>

H	0.00000000	1.18986600	-0.69605600
H	-1.03035800	-0.59554500	-0.69520700
H	1.03035800	-0.59554600	-0.69520700
P	0.00000000	0.00017100	0.07220400

TS

H	0.00000000	1.37991900	0.00000000
H	1.19504500	-0.68995900	0.00000000
H	-1.19504500	-0.68995900	0.00000000
P	0.00000000	0.00000000	0.00000000

M06-2X/6-31+G(df)

Minima

H	0.00000000	1.19589600	-0.69388200
H	-1.03563000	-0.59853300	-0.69299600
H	1.03563000	-0.59853300	-0.69299600
P	0.00000000	0.00011700	0.06560700

TS

H	0.00000000	1.19589600	-0.69388200
H	-1.03563000	-0.59853300	-0.69299600
H	1.03563000	-0.59853300	-0.69299600
P	0.00000000	0.00011700	0.06560700

M06-2X/6-31+G(df,p)

Minima

H	0.00000000	1.19531000	-0.69427300
H	-1.03512100	-0.59824200	-0.69339000
H	1.03512100	-0.59824200	-0.69339000
P	0.00000000	0.00012100	0.06678600

TS

H	0.00000000	1.37892600	0.00000000
H	1.19418500	-0.68946300	0.00000000
H	-1.19418500	-0.68946300	0.00000000
P	0.00000000	0.00000000	0.00000000

3. Optimized Cartesian coordinates for minima and TS of the pyramidal inversion of arsine at DFT levels

ωB97X-D/6-31+G(df)

<u>Minima</u>

H	-0.00000300	1.26769500	-0.82746500
H	-1.09795900	-0.63376500	-0.82742500
H	1.09796100	-0.63377000	-0.82742400
As	0.00000200	-0.00000800	0.02753200

<u>TS</u>

H	0.00000000	1.47339200	0.00000000
H	1.27599500	-0.73669600	0.00000000
H	-1.27599500	-0.73669600	0.00000000
As	0.00000000	0.00000000	0.00000000

ωB97X-D/6-31+G(df,p)

<u>Minima</u>

H	0.00000000	1.24817100	-0.82186300
H	-1.08105500	-0.62400200	-0.82181700
H	1.08105500	-0.62400200	-0.82181700
As	0.00000000	-0.00001500	0.01071400

<u>TS</u>

H	0.00000000	1.44901300	0.00000000
H	1.25488200	-0.72450600	0.00000000
H	-1.25488200	-0.72450600	0.00000000
As	0.00000000	0.00000000	0.00000000

M06-2X/6-31+G(df)

<u>Minima</u>

H	0.00000000	1.27028900	-0.82683200
H	-1.10017900	-0.63503900	-0.82675700

H	1.10017900	-0.63503900	-0.82675700
As	0.00000000	-0.00005900	0.02556300

<u>TS</u>

H	0.00000000	1.47843500	0.00000000
H	1.28036200	-0.73921700	0.00000000
H	-1.28036200	-0.73921700	0.00000000
As	0.00000000	0.00000000	0.00000000

M06-2X/6-31+G(df,p)

<u>Minima</u>

H	0.00000000	1.25134700	-0.82111400
H	-1.08357100	-0.62560000	-0.82108000
H	1.08357100	-0.62559900	-0.82107900
As	0.00000000	0.00000300	0.00849000

<u>TS</u>

H	0.00000000	1.45350800	0.00000000
H	1.25877500	-0.72675400	0.00000000
H	-1.25877500	-0.72675400	0.00000000
As	0.00000000	0.00000000	0.00000000

4. Optimized Cartesian coordinates for reactant and product of the ethane dissociation at CASSCF

CASSCF(6,6)/6-31G(d)

<u>Reactant</u>

C	-0.763558	-0.000026	-0.000246
C	0.763558	0.000026	0.000246
H	-1.160710	0.964058	0.334571
H	-1.160155	-0.771730	0.667832
H	-1.160574	-0.192005	-1.002556

H   1.160574   0.192005   1.002556

H   1.160155   0.771730   -0.667832

H   1.160710   -0.964058   -0.334571

Product

C   7.538573   0.000040   0.000144

C   -7.538543   -0.000033   -0.000168

H   7.555901   0.498551   -0.959589

H   7.542983   -1.080503   0.048472

H   7.538592   0.582131   0.911802

H   -7.540428   -0.216566   -1.059869

H   -7.553200   1.025889   0.342171

H   -7.544024   -0.809545   0.717157

5. Optimized Cartesian coordinates for reactant and products of the ammonia borane dissociation at DFT levels

ωB97X-D/6-31G(d)

Reactant

B   0.93053100   0.00000600   0.00000500

H   1.23920100   -0.52975500   -1.04837000

H   1.23922200   1.17280600   0.06544400

H   1.23927000   -0.64305200   0.98295400

N   -0.72814600   0.00000000   -0.00000200

H   -1.09101900   -0.94939400   -0.05349900

H   -1.09107700   0.42836200   0.84892800

H   -1.09100200   0.52103500   -0.79545200

Ammonia

N   -2.35474700   0.00126700   0.00064600

H   -2.73871500   -0.93968500   -0.00857200

H   -2.74461700   0.46158200   0.81858700

| H | -2.74398300 | 0.47728200 | -0.80856400 |

Borane

B	2.80475400	-0.00009400	-0.00054100
H	2.80644400	-0.50869800	-1.08293500
H	2.80634600	1.19158100	0.10029600
H	2.80151800	-0.68322400	0.98109100

ωB97X-D/6-31G(d,p)

Reactant

B	0.92836500	0.00000400	0.00000400
H	1.23800300	-0.52911300	-1.04706800
H	1.23801700	1.17135700	0.06534900
H	1.23807000	-0.64224100	0.98174700
N	-0.72898500	-0.00000300	-0.00000200
H	-1.08882300	-0.94871900	-0.05347800
H	-1.08887100	0.42804100	0.84833200
H	-1.08879500	0.52068100	-0.79487600

Ammonia

N	-2.35511000	0.00126600	0.00064600
H	-2.73860000	-0.93837200	-0.00855900
H	-2.74449300	0.46093600	0.81744400
H	-2.74385900	0.47661500	-0.80743400

Borane

B	2.80475900	-0.00009300	-0.00054100
H	2.80644100	-0.50824800	-1.08197500
H	2.80634300	1.19052600	0.10020700
H	2.80151900	-0.68261900	0.98022100

M06-2X/6-31G(d)

<u>Reactant</u>

B	0.93387200	0.00001900	0.00001500
H	1.23768200	-0.52757500	-1.04451000
H	1.23777700	1.16836800	0.06536200
H	1.23778100	-0.64080300	0.97914400
N	-0.72685200	0.00001900	0.00003500
H	-1.09103700	-0.95018900	-0.05332100
H	-1.09120100	0.42892700	0.84953600
H	-1.09104100	0.52124100	-0.79625400

<u>Ammonia</u>

N	-2.35177800	0.00128400	0.00065500
H	-2.73971000	-0.93888100	-0.00857800
H	-2.74560200	0.46118700	0.81788800
H	-2.74497200	0.47685600	-0.80786800

<u>Borane</u>

B	2.80476600	-0.00010800	-0.00050000
H	2.80643300	-0.50649500	-1.07834400
H	2.80633500	1.18653000	0.09980900
H	2.80152800	-0.68036100	0.97694700

M06-2X/6-31G(d,p)

<u>Reactant</u>

B	0.93148100	0.00002000	0.00001400
H	1.23617000	-0.52698900	-1.04349700
H	1.23627600	1.16719600	0.06536600
H	1.23627600	-0.64022000	0.97812700
N	-0.72809400	0.00002200	0.00003800
H	-1.08831100	-0.94961300	-0.05320600
H	-1.08849300	0.42874100	0.84897600

H   -1.08832400 0.52085100 -0.79581200

Ammonia

N   -2.35326700 0.00127800 0.00065500

H   -2.73921800 -0.93775200 -0.00856900

H   -2.74510300 0.46063700 0.81690800

H   -2.74447400 0.47628400 -0.80689800

Borane

B   2.80476700 -0.00010700 -0.00050100

H   2.80643100 -0.50609500 -1.07749000

H   2.80633400 1.18559100 0.09973000

H   2.80153000 -0.67982300 0.97617300

Table S1. Performance of DFT levels for the pyramidal inversion of ammonia at P = 1.00 atm.

Level	$\Delta H^{\ddagger}_{T=0}$[kcalmol^{-1}]	Absolute Error [kcalmol^{-1}][a]
ωB97X-D/6-31G(d)	4.93	0.33
ωB97X-D/6-31G(d,p)	4.48	0.78
M06-2X/6-31G(d)	5.43	0.17
M06-2X/6-31G(d,p)	4.81	0.45

[a] $\Delta H^{\ddagger}_{\text{exp}}(T) = E_a - RT = 5.31\,\text{kcalmol}^{-1}$ at 298 K (see M. F. Manning, *J Chem Phys*, 1935, **3**, 136–138). $\Delta H^{\ddagger}_{\text{exp}}(T) = E_a - RT = 5.21\,\text{kcalmol}^{-1}$ at 298 K (see C. C. Costain and G. B. B. M. Sutherland, *J Phys Chem*, 1952, **56**, 321–324). The absolute error was computed using the average of the experimental values.

Table S2. Performance of DFT levels for the pyramidal inversion of phosphine at P = 1.00 atm.

Level	$\Delta H^{\ddagger}_{T=0}$[kcalmol^{-1}]	Absolute Error [kcalmol^{-1}][a]
ωB97X-D/6-31G(d)	33.80	10.05
ωB97X-D/6-31+G(df)	31.18	7.43
ωB97X-D/6-31+G(df,p)	31.11	7.36
M06-2X/6-31G(d)	34.68	10.93
M06-2X/6-31+G(df)	31.86	8.11
M06-2X/6-31+G(df,p)	31.80	8.05

[a] $\Delta H^{\ddagger}_{exp}(T) = E_a - RT = 30.99\,\text{kcalmol}^{-1}$ at 298 K (see R. E. Weston, , J Am Chem Soc, 1954, **76**, 2645–2648).
$\Delta H^{\ddagger}_{exp}(T) = E_a - RT = 16.51\,\text{kcalmol}^{-1}$ at 298 K (see C. C. Costain and G. B. B. M. Sutherland, *J Phys Chem*, 1952, **56**, 321–324). The absolute error was computed using the average of the experimental values.

Table S3. Performance of DFT levels for the pyramidal inversion of arsine at P = 1.00 atm.

Level	$\Delta H^{\ddagger}_{T=0}$[kcalmol^{-1}]	Absolute Error [kcalmol^{-1}][a]
ωB97X-D/6-31+G(df)	39.33	7.82
ωB97X-D/6-31+G(df,p)	37.60	6.09
M06-2X/6-31+G(df)	36.76	5.25
M06-2X/6-31+G(df,p)	35.22	3.71

[a] $\Delta H^{\ddagger}_{exp}(T) = E_a - RT = 31.51\,\text{kcalmol}^{-1}$ at 298 K (see C. C. Costain and G. B. B. M. Sutherland, *J Phys Chem*, 1952, **56**, 321–324).

Table S4. Performance of CASSCF and CASPT2 methods combined with the 6-31(d) basis set for the ethane dissociation at P = 1.00 atm.

Level	$\Delta H_{diss,0K}$[kcalmol^{-1}]	$\Delta H_{diss,298K}$[kcalmol^{-1}]	Absolute Error [kcalmol^{-1}][a]
CASSCF(6,6)	88.04	80.79	-
CASSCF(8,8)	77.47	66.61	-
CASPT2(6,6)	95.58	88.34	1.56
CASPT2(8,8)	92.64	81.75	8.15

[a] $\Delta H^{0}_{diss}(\text{exp}) = 89.9\,\text{kcalmol}^{-1}$ at 298 K (see A. Haaland, Chem Int Ed Engl, 1989, 28, 992–1007). The absolute error was computed for CASPT2 only.

Table S5. Performance of DFT levels for the ammonia borane dissociation at P = 1.00 atm.

Level	$\Delta H_{diss,0K}$ [kcalmol^{-1}]	$\Delta H_{diss,298K}$ [kcalmol^{-1}]	**Absolute Error [kcalmol^{-1}][a]**
ωB97X-D/6-31G(d)	29.30	31.11	3.19
ωB97X-D/6-31G(d,p)	28.79	30.59	3.71
M06-2X/6-31G(d)	30.17	31.97	2.33
M06-2X/6-31G(d,p)	29.64	31.45	2.85

[a] $\Delta H_{diss}^0 (exp) = 31.1 \, kcalmol^{-1}$ at 298 K (see A. Haaland, Chem Int Ed Engl, 1989, 28, 992–1007). [a] $\Delta H_{diss}^0 (exp) = 37.5 \, kcalmol^{-1}$ at 298 K (see L. V. Gurvich, I. V. Veyts and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th edn., 1994, Vol. 3.). The absolute error was computed for enthalpies at 298 K taking the average of experimental values.