# Supporting Information for the paper:

# Pressure-Dependent Kinetic Analysis of the $N_2H_3$ Potential Energy Surface

Michal Keslin,[a] Kfir Kaplan,[a] Alon Grinberg Dana[a,b,*]

[a]Wolfson Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa 3200003, Israel
[b]Grand Technion Energy Program (GTEP), Technion – Israel Institute of Technology, Haifa 3200003, Israel
* Corresponding author, alon@technion.ac.il, +972-73-378-2117

**Table S1: Stationary points geometries, T1 diagnostic factors, and imaginary frequencies**

**H**

| | | | |
|---|---|---|---|
| H | 0.0 | 0.0 | 0.0 |

T1: 0.000

**H2**

| | | | |
|---|---|---|---|
| N | 0.0 | 0.0 | 0.370025 |
| N | 0.0 | 0.0 | -0.370025 |

T1: 0.012

**NH(T)**

| | | | |
|---|---|---|---|
| N | 0.0 | 0.0 | 0.517943 |
| H | 0.0 | 0.0 | -0.517943 |

T1: 0.001

**NH2**

| | | | |
|---|---|---|---|
| N | 0.000243 | 0.423545 | 0.0 |
| H | -0.803589 | -0.211311 | 0.0 |
| H | 0.803346 | -0.212233 | 0.0 |

T1: 0.008

**NNH**

| | | | |
|---|---|---|---|
| N | -0.068575 | 0.378082 | 0.0 |
| N | 0.986118 | -0.134088 | 0.0 |
| H | -0.917543 | -0.243994 | 0.0 |

T1: 0.028

**t-N2H2**

| | | | |
|---|---|---|---|
| N | -0.931858 | 0.832107 | 0.099199 |
| N | -2.169692 | 0.773196 | 0.198571 |
| H | -0.564058 | 0.953315 | 1.053457 |
| H | -2.537492 | 0.651988 | -0.755687 |

T1: 0.013

**c-N2H2**

| | | | |
|---|---|---|---|
| N | -0.929170 | 0.795957 | 0.187094 |
| N | -2.167342 | 0.719494 | 0.120147 |
| H | -0.588361 | 1.770061 | 0.108282 |
| H | -2.614630 | 1.644930 | -0.001276 |

T1: 0.013

**H2NN (singlet ground state)**

| | | | |
|---|---|---|---|
| N | -0.013141 | 0.002511 | 0.243320 |
| N | 0.996077 | -0.190324 | -0.402690 |
| H | -0.476744 | -0.727921 | 0.817821 |
| H | -0.506192 | 0.915734 | 0.281183 |

T1: 0.021

**$N_2H_3$**

| | | | |
|---|---|---|---|
| N | -0.42601000 | 0.00115600 | 0.16689800 |
| N | 0.78971200 | -0.52568500 | -0.07952700 |
| H | -1.18466200 | -0.64524000 | 0.02933400 |
| H | -0.63000700 | 0.95835800 | -0.08318900 |
| H | 1.43579600 | 0.26241300 | -0.11407100 |

T1: 0.025

**$NH_3N$**

| | | | |
|---|---|---|---|
| N | 0.57094400 | 0.08681900 | 0.23479400 |
| N | -0.76477000 | -0.11923400 | -0.32402800 |
| H | 1.15355600 | -0.75758500 | 0.25268100 |
| H | 1.10749800 | 0.83184500 | -0.22327000 |
| H | 0.43969400 | 0.37381600 | 1.20592600 |

T1: 0.012

**TS1**

| | | | |
|---|---|---|---|
| N | -1.67916600 | 0.79698300 | 0.31258100 |
| N | -3.09387500 | 0.62346800 | -0.19402200 |
| H | -1.08647400 | -0.02924200 | 0.32317000 |
| H | -1.21076700 | 1.63678400 | -0.00600500 |
| H | -2.54915800 | 1.14727500 | 0.93756800 |

imaginary frequency: 1847.05i, $cm^{-1}$
T1: 0.025

**TS2**

| | | | |
|---|---|---|---|
| N | -1.38277000 | 0.40793700 | 0.39052800 |
| N | -2.34834600 | 0.59978700 | -0.36233900 |
| H | 0.34120000 | -0.19564900 | -0.27706100 |
| H | -1.09722000 | 1.24501300 | 0.92502600 |
| H | -2.69456300 | 1.57243300 | -0.31578900 |

imaginary frequency: 600.52i, $cm^{-1}$
T1: 0.020

**TS3**

| | | | |
|---|---|---|---|
| N | -0.43791500 | -0.22586100 | -0.11221200 |
| N | -1.61889500 | -0.45151800 | 0.19390800 |
| H | 0.12795300 | -1.02752300 | 0.19605400 |
| H | 0.61674800 | 1.31230600 | 0.56814000 |
| H | -2.17138400 | 0.36078300 | -0.11336200 |

imaginary frequency: 532.85i, $cm^{-1}$
T1: 0.021

**TS4**

| | | | |
|---|---|---|---|
| N | -0.60800700 | 0.03978500 | -0.16074000 |
| N | 0.61952900 | -0.11674200 | 0.07234400 |
| H | -0.99753300 | 0.92573400 | -0.50236100 |
| H | -1.17909400 | -0.77645100 | -0.44304200 |
| H | -1.61830500 | -0.04293700 | 1.06002000 |

imaginary frequency: 1055.85i, $cm^{-1}$
T1: 0.047

**TS5**

| | | | |
|---|---|---|---|
| N | -0.58266300 | 0.05787000 | -0.24618300 |
| N | 0.60266300 | -0.34927700 | -0.32619100 |
| H | -0.84406700 | 1.03663300 | -0.30014700 |
| H | -1.40009100 | -0.59029700 | -0.24930700 |
| H | -1.55925200 | -0.12553900 | 1.14804900 |

imaginary frequency: 1497.90i, $cm^{-1}$
T1: 0.088

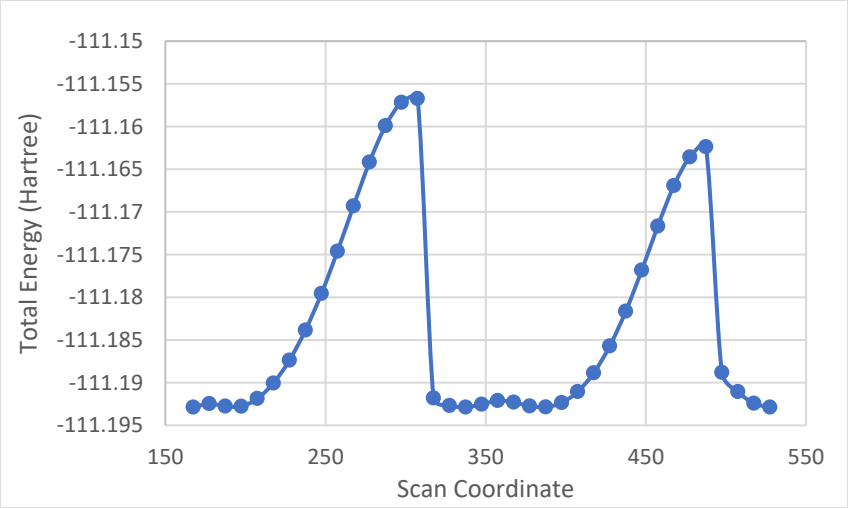


**Fig. S1:** Torsional scan of $N_2H_3$ at a resolution of 10o at the B2PLYP-D3/aug-cc-pVTZ level.

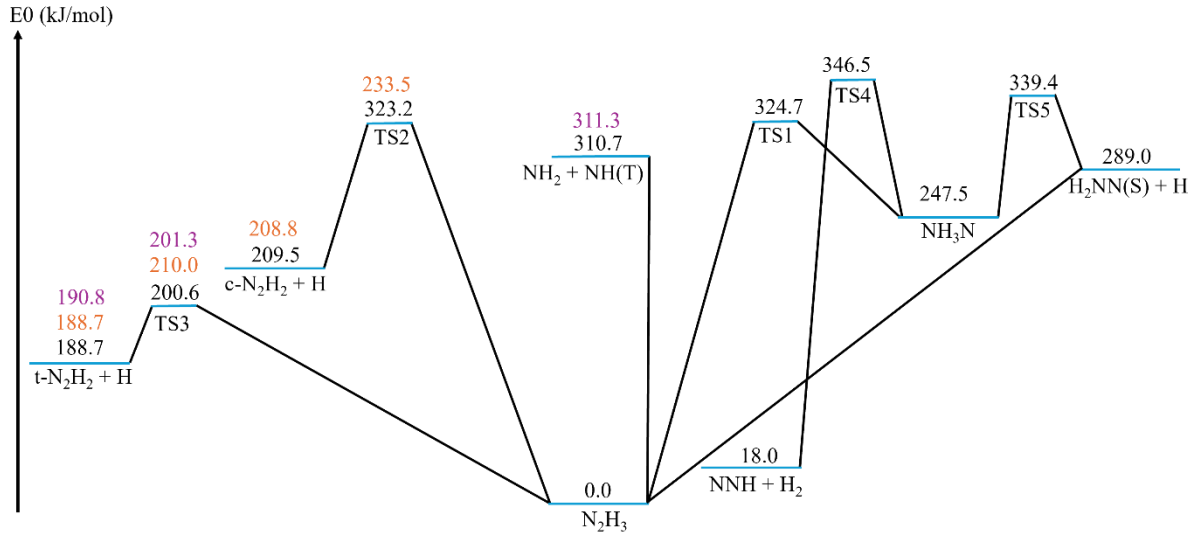


**Fig. S2:** Representation of the $N_2H_3$ PES along with energy values from previous studies.
In **black**: CCSD(T)-F12a/aug-cc-pVTZ-F12//B2PLYP-D3/aug-cc-pVTZ energies from the present work.
In **orange**: CCSD(T)/CBS//MP2/6-311++G(3df,2p) energies by Raghunath et al.[1]
In **purple**: RCCSD(T)/CBS//M06-2x-D3/aug-cc-pVTZ energies by Diévart and Catoire.[2]

**Table S2: $NH_3N$ Thermodynamic properties – Chemkin format**

```
 NH3N                    H   3N   2          G    10.000  3000.000  465.11      1
  2.11875669E+00 1.19021497E-02-6.11171276E-06 1.57914494E-09-1.62692823E-13    2
  5.57732688E+04 1.32966156E+01 4.05421786E+00-4.74258286E-03 4.75667970E-05    3
 -7.53589731E-08 4.11909655E-11 5.55932234E+04 5.44064039E+00                   4
```

**Table S3: $NH_3N$ Thermodynamic properties – Cantera format**

```
- name: NH3N
  composition: {N: 2, H: 3}
  thermo:
    model: NASA7
    temperature-ranges: [10.0, 465.11, 3000.0]
    data:
    - [2.11875669, 1.19021497e-02, -6.11171276e-06, 1.57914494e-09,
       -1.62692823e-13, 5.57732688e+04, 1.32966156e+01]
    - [4.05421786, -4.74258286e-03, 4.75667970e-05, -7.53589731e-08,
       4.11909655e-11, 5.55932234e+04, 5.44064039]
  note: '[NH3+][N-]'
```

**Table S4: Computed rate coefficient – Chemkin format**

```
NH3N(+M)<=>N2H3(+M)                              1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 3.164e+00    2.611e+00    -1.125e-01   -3.372e-02  /
    CHEB/ 2.506e+00    1.029e+00    4.096e-02    1.749e-02   /
    CHEB/ -4.339e-01   1.659e-01    6.194e-03    -3.833e-03  /
    CHEB/ -4.241e-01   -1.835e-03   2.004e-02    5.784e-03   /
    CHEB/ -1.475e-01   -2.299e-04   3.740e-03    2.314e-03   /
    CHEB/ -4.441e-02   -1.830e-03   -1.365e-03   -6.690e-04  /

N2H3(+M)<=>N2H2+H(+M)                         1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/  -6.79362    0.813487     -0.140865        0.0133607  /
    CHEB/  14.8198     0.820276     0.00147819     -0.02546  /
    CHEB/  -0.591313  0.239502     0.0625767       -0.0016977  /
    CHEB/ -0.304886   0.0320388   0.024277         0.00936021  /
    CHEB/ -0.133801   -0.0135305  -2.01909e-06  0.00536465  /
    CHEB/ -0.0490817 -0.015718    -0.00813631   0.00114971  /

N2H2+H(+M)<=>NH3N(+M)                         1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 1.67563         0.793494         -0.109792    -0.0300104 /
    CHEB/ 6.80705         1.06652          0.0433188    0.0147008  /
    CHEB/ -0.0113718    0.115021        0.0263406    0.00187797  /
    CHEB/ -0.197575       -0.0146724    0.020278      0.00686065  /
    CHEB/ -0.0610285     -0.00638315  0.00118585  0.000843304  /
    CHEB/ -0.0236698     -0.00743267  -0.0014863   -0.0004882  /

H2NN+H(+M)<=>N2H3(+M)                      1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 5.821e+00    1.705e+00    -1.381e-01   -4.379e-02  /
    CHEB/ 2.382e+00    3.141e-01    1.258e-01    3.047e-02   /
    CHEB/ -2.059e-01   -2.399e-02   1.439e-02    1.323e-02   /
    CHEB/ -1.624e-01   1.056e-02    -8.142e-04   -4.772e-05  /
    CHEB/ -5.628e-02   -8.414e-03   -3.273e-03   -1.149e-03  /
    CHEB/ -1.345e-02   -5.592e-03   -3.047e-03   -1.013e-03  /

NNH+H2(+M)<=>N2H3(+M)                        1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ -2.210e+01   1.843e+00    -9.439e-02   -4.106e-02  /
    CHEB/ 2.426e+01    1.492e-01    8.496e-02    3.371e-02   /
    CHEB/ -2.280e-01   6.103e-03    8.998e-03    7.083e-03   /
    CHEB/ -1.161e-01   5.985e-03    2.111e-03    4.435e-04   /
    CHEB/ -3.306e-02   -6.587e-03   -3.227e-03   -1.073e-03  /
    CHEB/ -4.288e-03   -3.689e-03   -2.450e-03   -1.089e-03  /
```

```
NH+NH2(+M)<=>N2H3(+M)                    1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 1.090e+01    1.961e+00    -2.649e-02   -1.389e-02  /
    CHEB/ -1.325e+00   4.625e-02    3.087e-02    1.595e-02   /
    CHEB/ -4.545e-01   -4.938e-03   -2.977e-03   -1.239e-03  /
    CHEB/ -1.818e-01   -1.975e-03   -1.405e-03   -8.063e-04  /
    CHEB/ -6.686e-02   -3.889e-04   -2.866e-04   -1.738e-04  /
    CHEB/ -1.792e-02   -9.773e-05   -6.817e-05   -3.804e-05  /

H2NN+H(+M)<=>NH3N(+M)                    1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 7.467e+00    1.487e+00    -1.169e-01   -2.180e-02  /
    CHEB/ 2.226e+00    5.912e-01    7.743e-02    -3.233e-03  /
    CHEB/ -4.627e-02   -8.839e-02   3.780e-02    2.130e-02   /
    CHEB/ -1.709e-01   1.987e-03    4.007e-03    3.344e-03   /
    CHEB/ -5.896e-02   7.181e-03    -5.347e-03   -1.484e-03  /
    CHEB/ -6.750e-03   -8.141e-03   -3.261e-03   -8.599e-04  /

NNH+H2(+M)<=>NH3N(+M)                     1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ -2.080e+01   1.795e+00    -8.408e-02   -3.411e-02  /
    CHEB/ 2.449e+01    2.239e-01    6.259e-02    2.163e-02   /
    CHEB/ -1.125e-01   -4.429e-02   2.254e-02    1.153e-02   /
    CHEB/ -1.414e-01   3.668e-02    -1.935e-03   6.527e-04   /
    CHEB/ -1.613e-02   -1.571e-02   9.475e-06    -6.765e-04  /
    CHEB/ 1.945e-04    -2.247e-03   -3.329e-03   -1.060e-03  /

NH2+NH(+M)<=>NH3N(+M)                    1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 7.426e+00    1.583e+00    -1.843e-01   -4.141e-02  /
    CHEB/ -3.808e-02   4.111e-01    1.648e-01    2.562e-02   /
    CHEB/ -1.474e-01   2.517e-02    2.471e-02    1.332e-02   /
    CHEB/ -9.065e-02   -8.933e-03   -9.601e-04   2.422e-03   /
    CHEB/ -2.653e-02   -1.214e-02   -5.249e-03   -6.964e-04  /
    CHEB/ 3.962e-05    -7.445e-03   -3.825e-03   -1.081e-03  /

H2NN+H(+M)<=>N2H2+H(+M)                  1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 7.467e+00    1.487e+00    -1.169e-01   -2.180e-02  /
    CHEB/ 2.226e+00    5.912e-01    7.743e-02    -3.233e-03  /
    CHEB/ -4.627e-02   -8.839e-02   3.780e-02    2.130e-02   /
    CHEB/ -1.709e-01   1.987e-03    4.007e-03    3.344e-03   /
    CHEB/ -5.896e-02   7.181e-03    -5.347e-03   -1.484e-03  /
    CHEB/ -6.750e-03   -8.141e-03   -3.261e-03   -8.599e-04  /
```

```
NNH+H2(+M)<=>N2H2+H(+M)                1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 13.8669          -0.0377532      -0.025426         -0.0133332  /
    CHEB/ -0.177674       0.0454564       0.0303814        0.0157223  /
    CHEB/ -0.0291851     -0.00552477    -0.00338661     -0.00147392  /
    CHEB/ -0.0104781     -0.00209585    -0.00149409     -0.000860035  /
    CHEB/ -0.00357322   -0.000355265  -0.000264803   -0.000161025  /
    CHEB/ -0.000780331 -4.76315e-05   -3.3424e-05     -1.82459e-05  /

NH2+NH(+M)<=>N2H2+H(+M)               1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 13.8669             -0.0377532     -0.025426        -0.0133332  /
    CHEB/ -0.177674         0.0454564       0.0303814       0.0157223  /
    CHEB/ -0.0291851       -0.00552477    -0.00338661    -0.00147392  /
    CHEB/ -0.0104781       -0.00209585    -0.00149409    -0.000860035  /
    CHEB/ -0.00357322     -0.000355265  -0.000264803  -0.000161025  /
    CHEB/ -0.000780331   -4.76315e-05   -3.3424e-05    -1.82459e-05  /

NNH+H2(+M)<=>H2NN+H(+M)             1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ -1.947e+01   -9.609e-02   -6.061e-02   -2.818e-02  /
    CHEB/ 2.586e+01    9.336e-02    5.761e-02    2.559e-02   /
    CHEB/ 2.971e-01    9.757e-03    7.330e-03    4.474e-03   /
    CHEB/ 1.007e-01    -2.454e-03   -1.454e-03   -5.604e-04  /
    CHEB/ 3.661e-02    -5.101e-03   -3.167e-03   -1.426e-03  /
    CHEB/ 1.424e-02    -2.476e-03   -1.622e-03   -8.077e-04  /

NH2+NH(+M)<=>H2NN+H(+M)            1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 8.088e+00    -1.695e-01   -9.938e-02   -4.034e-02  /
    CHEB/ 2.014e+00    1.866e-01    1.054e-01    3.945e-02   /
    CHEB/ 3.156e-01    -6.226e-03   1.036e-03    4.135e-03   /
    CHEB/ 9.155e-02    -5.777e-03   -3.929e-03   -1.781e-03  /
    CHEB/ 2.888e-02    -6.283e-03   -3.772e-03   -1.634e-03  /
    CHEB/ 8.379e-03    -2.481e-03   -1.645e-03   -8.323e-04  /

NH2+NH(+M)<=>NNH+H2(+M)              1.000e+00 0.000     0.000
    TCHEB/ 300.000   3000.000 /
    PCHEB/ 0.010     98.692   /
    CHEB/ 6 4/
    CHEB/ 7.385e+00    -1.138e-01   -7.213e-02   -3.391e-02  /
    CHEB/ 2.581e+00    1.180e-01    7.341e-02    3.327e-02   /
    CHEB/ 2.769e-01    3.916e-03    3.908e-03    3.086e-03   /
    CHEB/ 9.439e-02    -3.700e-03   -2.418e-03   -1.158e-03  /
    CHEB/ 3.067e-02    -5.338e-03   -3.313e-03   -1.496e-03  /
    CHEB/ 8.623e-03    -2.205e-03   -1.464e-03   -7.461e-04  /
```

**Table S5: Computed rate coefficient – Cantera format**

```
- equation: NH3N <=> N2H3
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [3.16388, 2.61065, -0.112489, -0.0337218]
  - [2.50571, 1.02858, 0.0409628, 0.0174905]
  - [-0.433864, 0.165908, 0.00619432, -0.00383321]
  - [-0.42413, -0.00183502, 0.020043, 0.00578384]
  - [-0.147488, -0.000229917, 0.00373979, 0.00231388]
  - [-0.0444144, -0.00183023, -0.0013652, -0.000668957]

- equation: N2H3 <=> N2H2 + H
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [-6.79362,0.813487,-0.140865,0.0133607]
  - [14.8198,0.820276,0.00147819,-0.02546]
  - [-0.591313,0.239502,0.0625767,-0.0016977]
  - [-0.304886,0.0320388,0.024277,0.00936021]
  - [-0.133801,-0.0135305,-2.01909e-06,0.00536465]
  - [-0.0490817,-0.015718,-0.00813631,0.00114971]

- equation: N2H2 + H <=> NH3N
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [1.67563,0.793494,-0.109792,-0.0300104]
  - [6.80705,1.06652,0.0433188,0.0147008]
  - [-0.0113718,0.115021,0.0263406,0.00187797]
  - [-0.197575,-0.0146724,0.020278,0.00686065]
  - [-0.0610285,-0.00638315,0.00118585,0.000843304]
  - [-0.0236698,-0.00743267,-0.0014863,-0.0004882]

- equation: H2NN + H <=> N2H3
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [5.82128, 1.70499, -0.138129, -0.0437853]
  - [2.38238, 0.314136, 0.12583, 0.0304666]
  - [-0.205892, -0.0239878, 0.0143943, 0.0132256]
  - [-0.162448, 0.0105579, -0.00081423, -4.77164e-05]
  - [-0.0562824, -0.00841372, -0.00327293, -0.00114856]
  - [-0.0134511, -0.00559213, -0.00304685, -0.00101281]
```

```
- equation: NNH + H2 <=> N2H3
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [-22.0959, 1.84287, -0.0943889, -0.0410579]
  - [24.257, 0.149232, 0.084957, 0.0337131]
  - [-0.22798, 0.00610311, 0.0089977, 0.00708328]
  - [-0.116055, 0.00598474, 0.00211131, 0.000443531]
  - [-0.0330573, -0.0065871, -0.00322671, -0.00107268]
  - [-0.00428807, -0.00368917, -0.00245024, -0.00108896]

- equation: NH2 + NH <=> N2H3
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [10.8963, 1.96064, -0.0264904, -0.0138879]
  - [-1.325, 0.046248, 0.0308719, 0.0159473]
  - [-0.45446, -0.00493753, -0.00297691, -0.00123863]
  - [-0.181784, -0.00197523, -0.00140519, -0.000806267]
  - [-0.0668559, -0.000388914, -0.000286631, -0.000173789]
  - [-0.0179225, -9.77336e-05, -6.81701e-05, -3.80433e-05]

- equation: H2NN + H <=> NH3N
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [7.46678, 1.48735, -0.116947, -0.021797]
  - [2.22624, 0.591241, 0.0774315, -0.00323253]
  - [-0.0462719, -0.0883901, 0.0377971, 0.0212973]
  - [-0.17091, 0.00198697, 0.00400741, 0.00334449]
  - [-0.0589584, 0.00718057, -0.00534685, -0.00148418]
  - [-0.00675005, -0.00814075, -0.00326095, -0.000859941]

- equation: NNH + H2 <=> NH3N
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [-20.8027, 1.7952, -0.0840762, -0.03411]
  - [24.4864, 0.223914, 0.0625927, 0.0216257]
  - [-0.11247, -0.0442865, 0.0225439, 0.0115299]
  - [-0.141364, 0.0366818, -0.0019349, 0.000652662]
  - [-0.0161265, -0.0157076, 9.47483e-06, -0.000676522]
  - [0.000194453, -0.0022468, -0.00332929, -0.00105985]
```

```
- equation: NH2 + NH <=> NH3N
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [7.42567, 1.58331, -0.184293, -0.0414146]
  - [-0.0380814, 0.41113, 0.164849, 0.0256187]
  - [-0.147375, 0.025174, 0.0247136, 0.0133207]
  - [-0.090654, -0.00893325, -0.000960061, 0.00242247]
  - [-0.0265349, -0.0121359, -0.00524925, -0.000696434]
  - [3.96188e-05, -0.00744489, -0.00382456, -0.0010807]

- equation: H2NN + H <=> N2H2 + H
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [8.96391,-0.256048,-0.127045,-0.0423262]
  - [3.58104,0.282612,0.124911,0.0344487]
  - [0.208066,-0.0215834,0.00929785,0.0109161]
  - [0.0132221,0.00470197,-0.00265771,-0.0013656]
  - [0.00850942,-0.00962534,-0.00420432,-0.00163438]
  - [0.00401625,-0.00484242,-0.00302727,-0.00112655]

- equation: NNH + H2 <=> N2H2 + H
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [-18.8485,-0.141515,-0.0866854,-0.0384681]
  - [25.4015,0.140872,0.0829846,0.0345801]
  - [0.186062,0.00580615,0.00740807,0.00573263]
  - [0.0575937,0.00161044,0.000124488,-0.000371364]
  - [0.0294662,-0.00696965,-0.0038192,-0.00148802]
  - [0.0124894,-0.00349695,-0.00235714,-0.00107936]

- equation: NH2 + NH <=> N2H2 + H
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [13.8669,-0.0377532,-0.025426,-0.0133332]
  - [-0.177674,0.0454564,0.0303814,0.0157223]
  - [-0.0291851,-0.00552477,-0.00338661,-0.00147392]
  - [-0.0104781,-0.00209585,-0.00149409,-0.000860035]
  - [-0.00357322,-0.000355265,-0.000264803,-0.000161025]
  - [-0.000780331,-4.76315e-05,-3.3424e-05,-1.82459e-05]
```

```
- equation: NNH + H2 <=> H2NN + H
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [-19.4654, -0.0960863, -0.060614, -0.0281763]
  - [25.8604, 0.0933606, 0.057613, 0.0255876]
  - [0.297073, 0.00975681, 0.00732958, 0.00447352]
  - [0.100684, -0.00245421, -0.00145365, -0.000560436]
  - [0.0366116, -0.00510073, -0.003167, -0.00142605]
  - [0.0142376, -0.00247607, -0.0016218, -0.000807675]

- equation: NH2 + NH <=> H2NN + H
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [8.08802, -0.169537, -0.0993812, -0.0403407]
  - [2.01388, 0.186616, 0.105424, 0.0394484]
  - [0.315592, -0.00622597, 0.00103591, 0.00413535]
  - [0.0915501, -0.0057768, -0.00392886, -0.0017811]
  - [0.0288829, -0.0062832, -0.00377236, -0.00163368]
  - [0.00837929, -0.00248084, -0.00164509, -0.000832312]

- equation: NH2 + NH <=> NNH + H2
  type: Chebyshev
  temperature-range: [300.0, 3000.0]
  pressure-range: [0.01 atm, 98.692 atm]
  data:
  - [7.38528, -0.113782, -0.072126, -0.0339128]
  - [2.58064, 0.117989, 0.0734149, 0.0332713]
  - [0.276905, 0.00391617, 0.00390784, 0.00308579]
  - [0.0943856, -0.00369953, -0.00241765, -0.00115756]
  - [0.0306732, -0.00533849, -0.00331256, -0.0014962]
  - [0.00862349, -0.00220524, -0.0014645, -0.000746124]
```

**Geometry comparisons**:

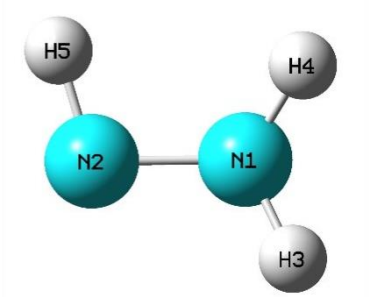


**Fig. S3:** 3D representation of $N_2H_3$, the geometry is identical to that shown in Fig. 3A, atom indices were added to give context to the parameters in Table S6.

**Table S6: Comparison of internal coordinates for the $N_2H_3$ geometry at two levels of theory, distances (r) are in Å, angles (a) and dihedral angles (d) are in degrees.**

| Description | Value CCSD | Value B2PLYP-D3 |
|---|---|---|
| rNN | 1.354 | 1.348 |
| rNH3 | 1.015 | 1.006 |
| rNH4 | 1.019 | 1.10 |
| rNH5 | 1.031 | 1.020 |
| aNNH3 | 112.532 | 113.832 |
| aNNH4 | 118.904 | 120.487 |
| aNNH5 | 105.272 | 105.999 |
| aH3N1H5 | 113.715 | 115.002 |
| dH5NNH3 | 165.572 | 167.485 |
| dH5NNH4 | 29.982 | 24.687 |

RMSD between the two methods in Table S6: 0.013.

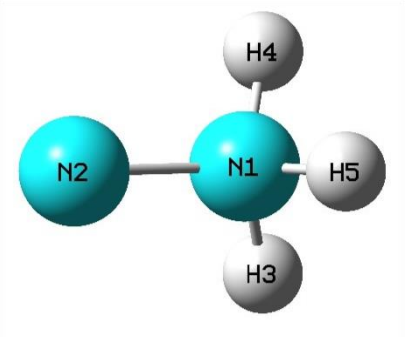


**Fig. S4:** 3D representation of $NH_3N$, the geometry is identical to that shown in Fig. 3B, atom indices were added to give context to the parameters in Table S7.

**Table S7: Comparison of internal coordinates for the $NH_3N$ geometry at two levels of theory, distances (r) are in Å, angles (a) and dihedral angles (d) are in degrees.**

| Description | Value CCSD | Value B2PLYP-D3 |
|---|---|---|
| rNN | 1.482 | 1.462 |
| rNH3 | 1.031 | 1.026 |
| rNH4 | 1.031 | 1.026 |
| rNH5 | 1.028 | 1.021 |
| aNNH3 | 113.867 | 114.612 |
| aNNH4 | 113.864 | 114.162 |
| aNNH5 | 106.714 | 106.595 |
| aH3N1H5 | 106.831 | 106.721 |
| aH4N1H5 | 106.831 | 106.721 |
| aH4N1H3 | 108.262 | 107.693 |

RMSD between the two methods in Table S7: 0.305.

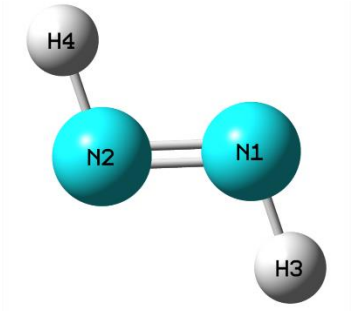


**Fig. S5:** 3D representation of t-$N_2H_2$, atom indices were added to give context to the parameters in Table S8.

**Table S8: Comparison of internal coordinates for the t-$N_2H_2$ geometry at two levels of theory, distances (r) are in Å, angles (a) and dihedral angles (d) are in degrees**.

| Description | Value experimental[3] | Value B2PLYP-D3 |
|---|---|---|
| rNN | 1.252 | 1.243 |
| rNH | 1.028 | 1.030 |
| aHNN | 106.850 | 106.685 |
| dHNNH | 180.000 | 180.000 |

RMSD between the two methods in Table S8: 0.305.

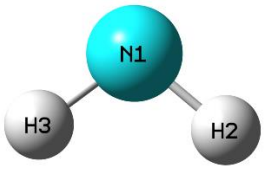


**Fig. S6:** 3D representation of $NH_2$, atom indices were added to give context to the parameters in Table S9.

**Table S9: Comparison of internal coordinates for the $NH_2$ geometry at two levels of theory, distances (r) are in Å, angles (a) and dihedral angles (d) are in degrees**.

| Description | Value experimental[3] | Value B2PLYP-D3 |
|---|---|---|
| rNH | 1.024 | 1.0243 |
| aHNH | 103.400 | 103.334 |

RMSD between the two methods in Table S9: 0.066.

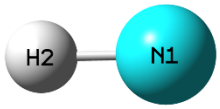


**Fig. S7:** 3D representation of $NH_2$, atom indices were added to give context to the parameters in Table S10.

**Table S10: Comparison of internal coordinates for the $NH_2$ geometry at two levels of theory, distances (r) are in Å, angles (a) and dihedral angles (d) are in degrees**.

| Description | Value experimental[3] | Value B2PLYP-D3 |
|---|---|---|
| rNH | 1.036 | 1.036 |

RMSD between the two methods in Table S10: 0.000.

**The $N_2H_3$ <=> $H_2NN$ + H reaction pathway:**

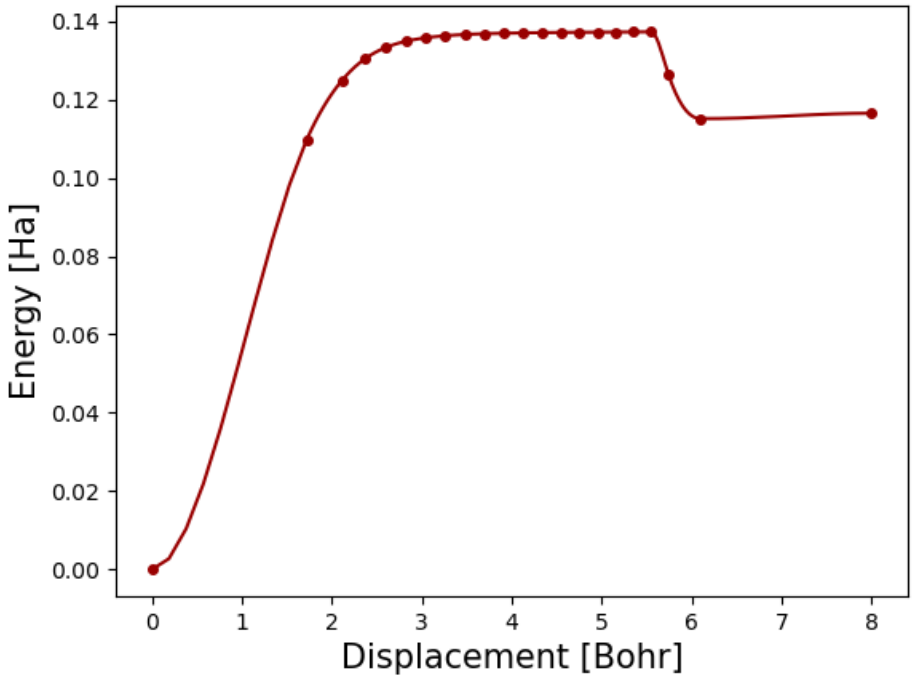


**Fig. S8:** Nudged Elastic Band (NEB) results executed in Orca of $N_2H_3$ <=> $H_2NN(S)$ + H reaction coordinate at the NEVPT2 (3,3) level of theory, energy units are Hartree

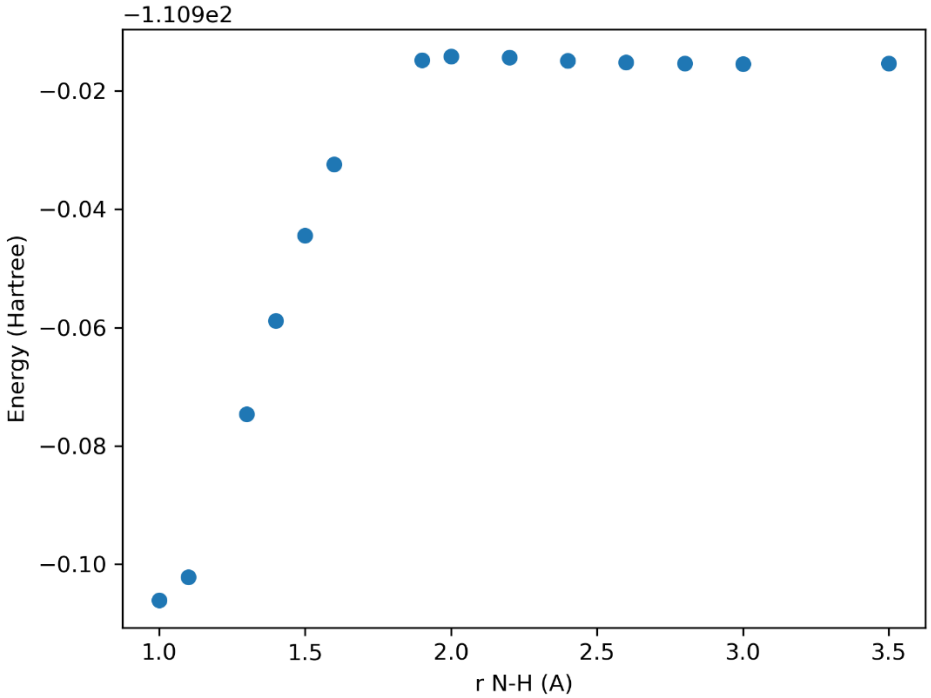


**Fig. S9:** A reaction coordinate scan of N–H distance for $H_2NN(S)$ and H radical performed at MRCI/cc-pVTZ level of theory using Molpro.

**Estimated reaction rate uncertainty based on computed energies:**

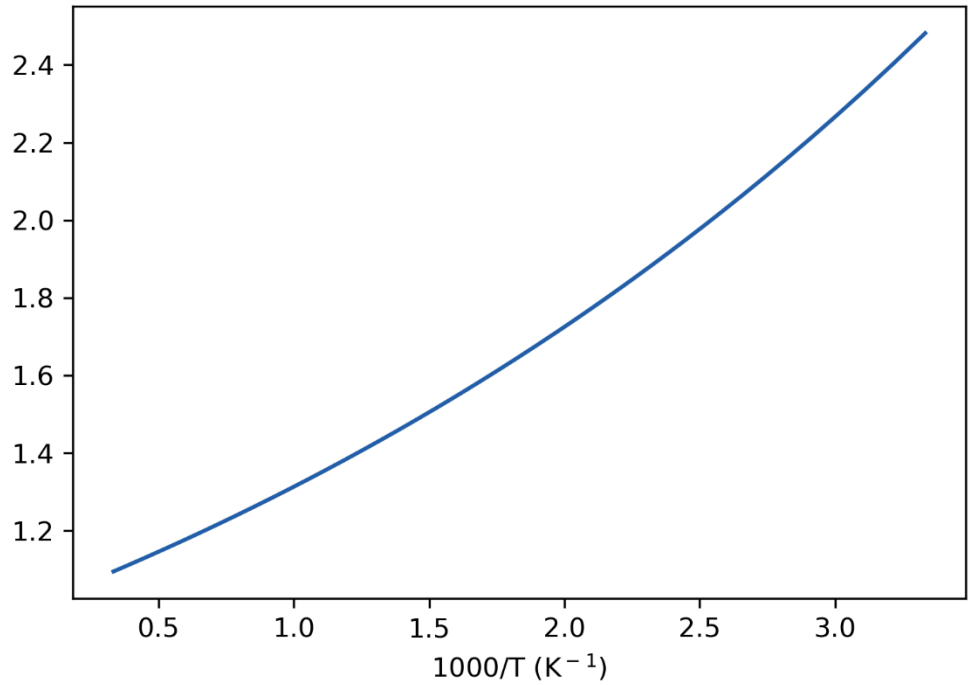


**Fig. S10:** The rate coefficient uncertainty vs. inverse temperature introduced to the high-pressure limit of computed reactions. The uncertainty was computed as $e^{2\sigma/RT}$ where $\sigma = \pm 2.3_{kJ/mol}$ is the standard deviation of E0 of all computed species on the $N_2H_3$ PES vs. the respective H0 from ATcT.

**Table S11: Comparison of computed B2PLYP-D3/aug-cc-pVTZ frequencies (scaled by a factor of 0.995) vs. experimental values taken from CCCBDB.[3]**

| | | Vibrational frequencies, $cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|
| **Trans-$N_2H_2$** | Exp. freq. | 1289 | 1316 | 1529 | 1583 | 3058 | 3120 |
| | Scaled DFT freq. | 1335 | 1347 | 1559 | 1617 | 3259 | 3293 |
| | **Deviation** | **3.6%** | **2.3%** | **1.9%** | **2.2%** | **6.6%** | **5.5%** |
| **$H_2NN(S)$** | Exp. freq. | 1003 | 1288 | 1574 | 1645 | 2805 | 2862 |
| | Scaled DFT freq. | 1007 | 1324 | 1593 | 1726 | 3062 | 3069 |
| | **Deviation** | **0.4%** | **2.8%** | **1.2%** | **4.9%** | **9.2%** | **7.2%** |
| **$NH_2$** | Exp. freq. | 1479 | 3219 | 3301 | | | |
| | Scaled DFT freq. | 1533 | 3375 | 3470 | | | |
| | **Deviation** | **3.7%** | **4.9%** | **5.1%** | | | |
| **NH** | Exp. freq. | 3283 | | | | | |
| | Scaled DFT freq. | 3296 | | | | | |
| | **Deviation** | **0.4%** | | | | | |

**References:**


[1] Putikam Raghunath and N.T. Nghia and Ming-Chang Lin, Advances in Quantum Chemistry 2014, 69, 253-301. Doi: 10.1016/B978-0-12-800345-9.00007-6

[2] Diévart, Pascal and Catoire, Laurent, The Journal of Physical Chemistry A 2020, 124(30), 6214-6236. DOI: 10.1021/acs.jpca.0c03144

[3] NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 22, May 2022, Editor: Russell D. Johnson III http://cccbdb.nist.gov/