**Supplementary information**

# The Simplest Iminophosphane HPNH and Its Photoisomerization to Aminophosphinidene $H_2NP$

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**Supplementary information file includes:**

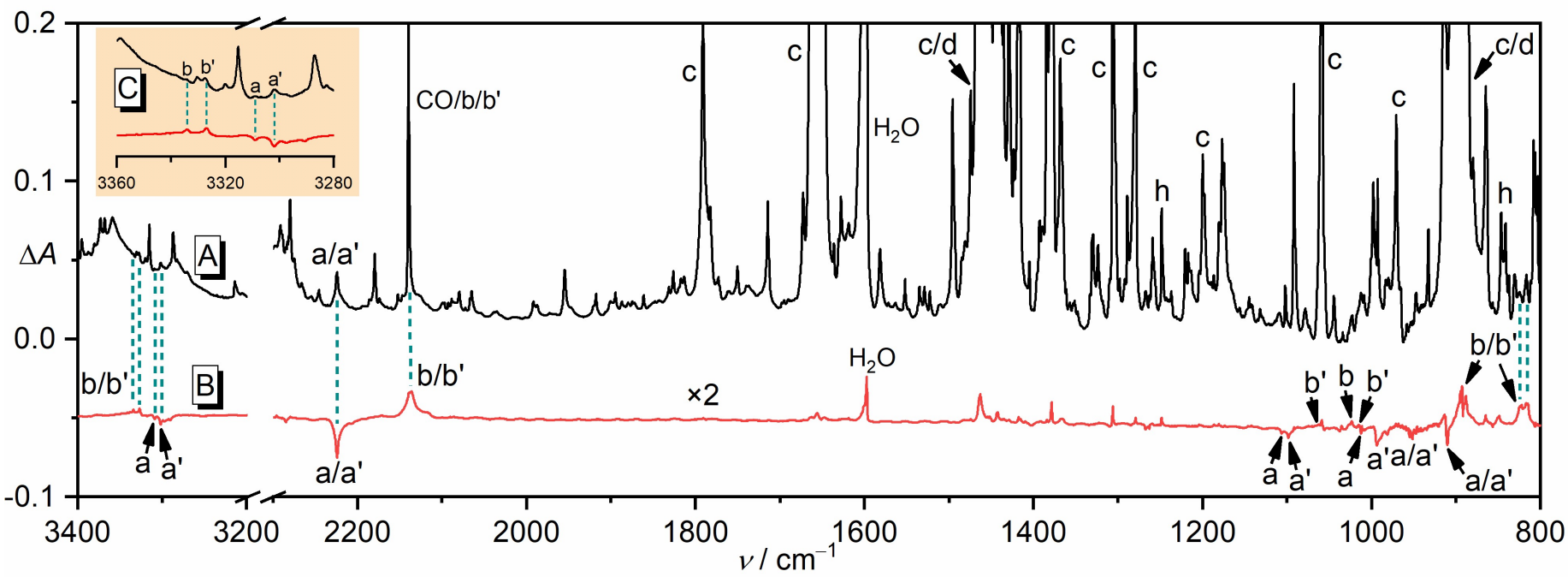


**Fig. S1.** (A) IR spectrum (3400−800 $cm^{-1}$) of the matrix-isolated pyrolysis (ca. 950 K) products of $(t\text{-Bu})_2P^{15}NH_2$ in a $N_2$-matrix at 10 K. (B) IR difference spectrum showing the isomerization from *trans*-HPNH (**a**) and *trans*-$HP^{15}NH$ (**a′**) to *cis*-HPNH (**b**) and *cis*-$HP^{15}NH$ (**b′**) in the matrix upon photoexcitation at 410 nm (10 min). (C) Expanded spectra of (A) and (B) in the range of 3360–3280 $cm^{-1}$. The IR bands for $C_4H_8$ (**c**), $C_4H_{10}$ (**d**), and HOPO (**h**) are also marked.

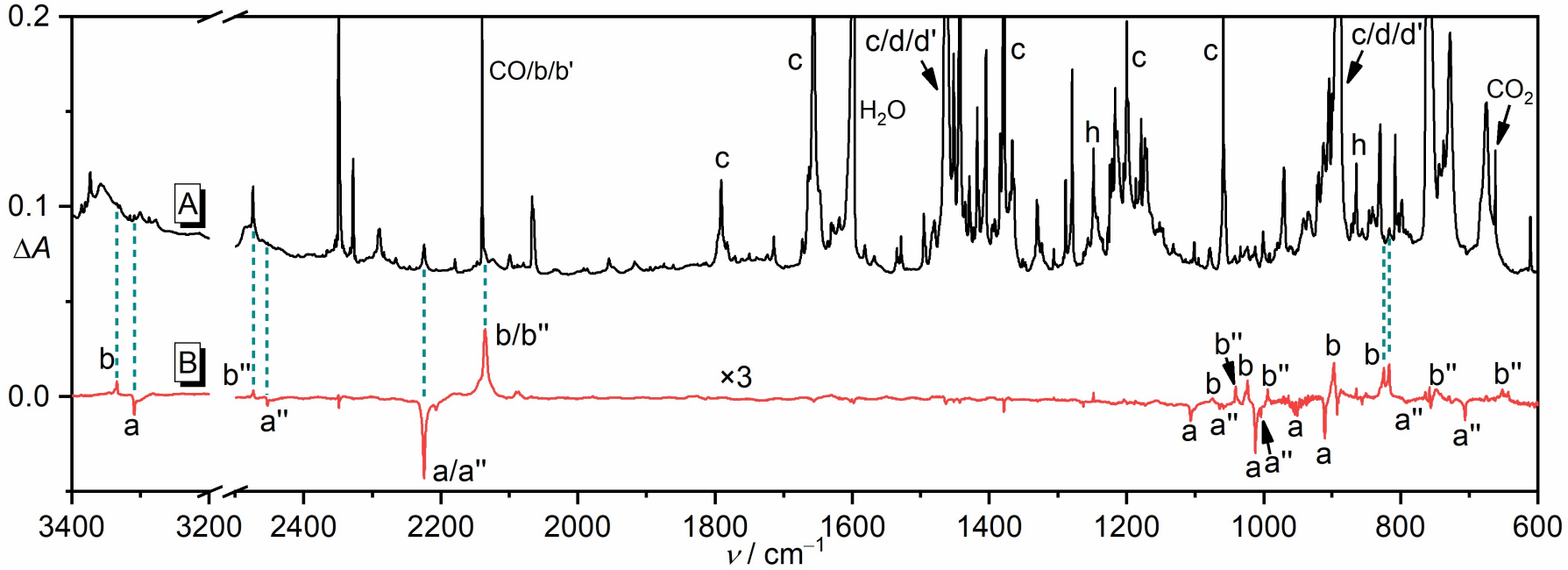


**Fig. S2.** (A) IR spectrum (3400−600 $cm^{-1}$) of the matrix-isolated pyrolysis (ca. 950 K) products of (*t*-Bu)$_2$PND$_2$ in a $N_2$-matrix at 10 K. (B) IR difference spectrum showing the isomerization from *trans*-HPND (**a"**) to *cis*-HPND (**b"**) in the matrix upon photoexcitation at 410 nm (10 min). The IR bands for $C_4H_8$ (**c**), $C_4H_{10}$ (**d**), [$D_1$]-$C_4H_{10}$ (**d′**), and HOPO (**h**) are also marked.

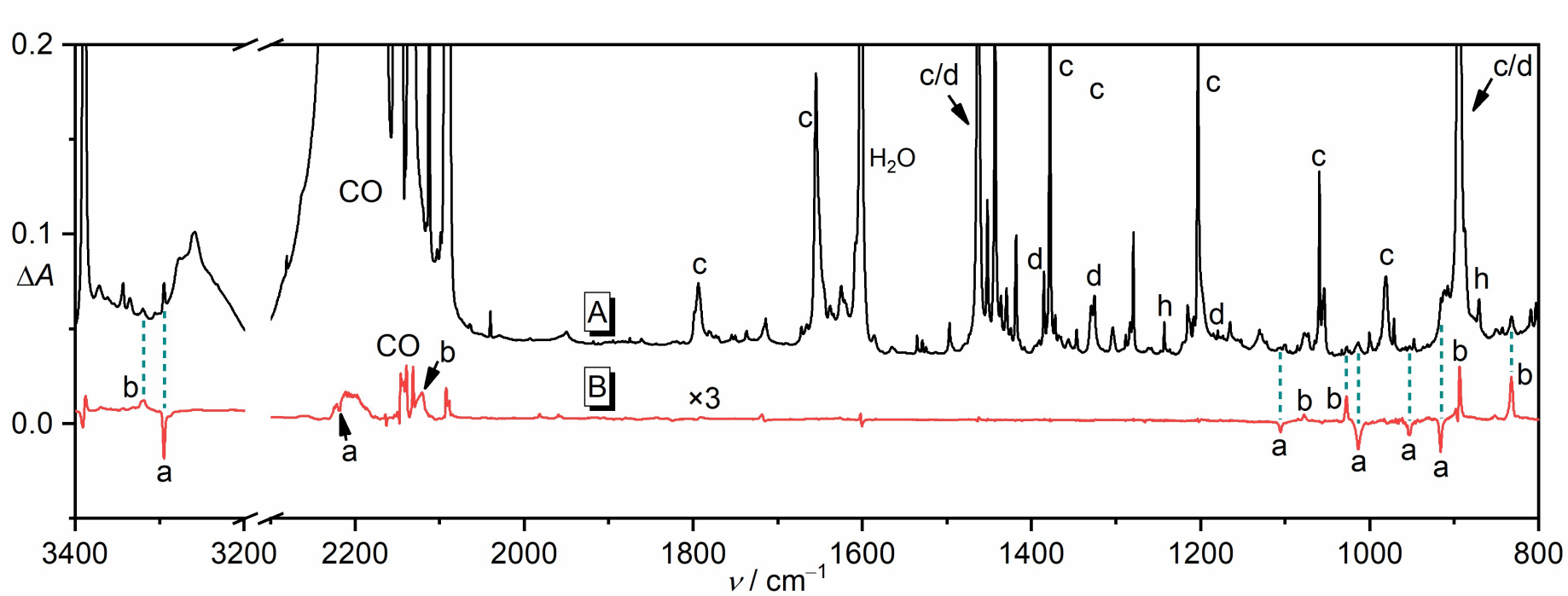


**Fig. S3.** (A) IR spectrum (3400−800 $cm^{-1}$) of the matrix-isolated pyrolysis (ca. 950 K) products of $(t\text{-Bu})_2PNH_2$ in a CO-matrix at 10 K. (B) IR difference spectrum showing the isomerization from *trans*-HPNH (**a**) to *cis*-HPNH (**b**) in the matrix upon photoexcitation at 410 nm (10 min). The IR bands for $C_4H_8$ (**c**), $C_4H_{10}$ (**d**), and HOPO (**h**) are also marked.

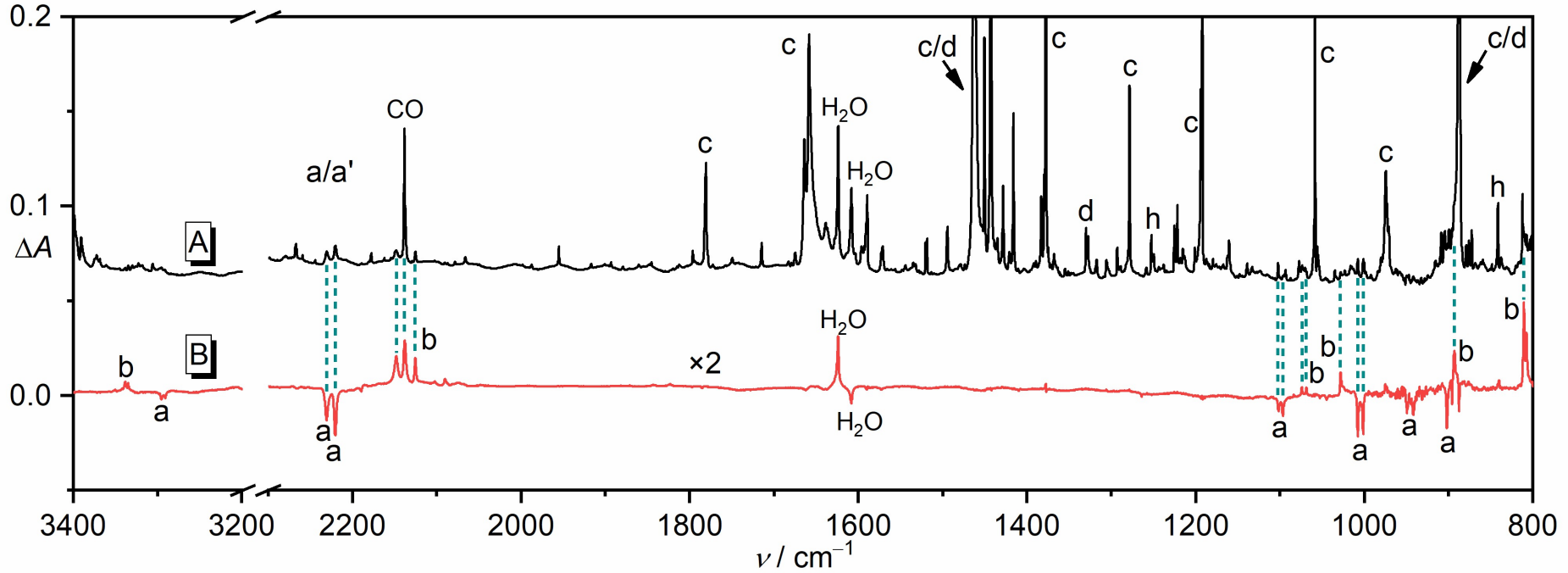


**Fig. S4.** (A) IR spectrum (3400−800 $cm^{-1}$) of the matrix-isolated pyrolysis (ca. 950 K) products of $(t\text{-Bu})_2PNH_2$ in an Ar-matrix at 10 K. (B) IR difference spectrum showing the isomerization from *trans*-HPNH (**a**) to *cis*-HPNH (**b**) in the matrix upon photoexcitation at 410 nm (10 min). The IR bands for $C_4H_8$ (**c**), $C_4H_{10}$ (**d**), and HOPO (**h**) are also marked.

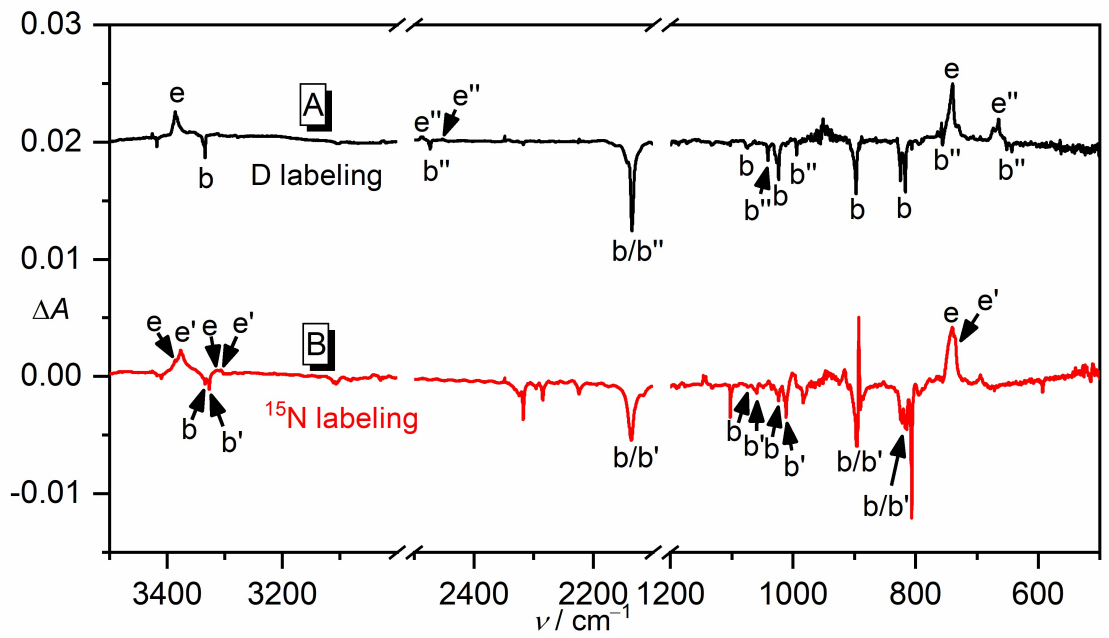


**Fig. S5**. IR difference spectra showing the isomerization from D- (panel A) and $^{15}$N-isotope labeled (panel B) *cis*-HPNH (**b**) to $H_2NP$ (**e**) upon photoexcitation at 395 nm (10 min) in the $N_2$-matrix at 10 K.

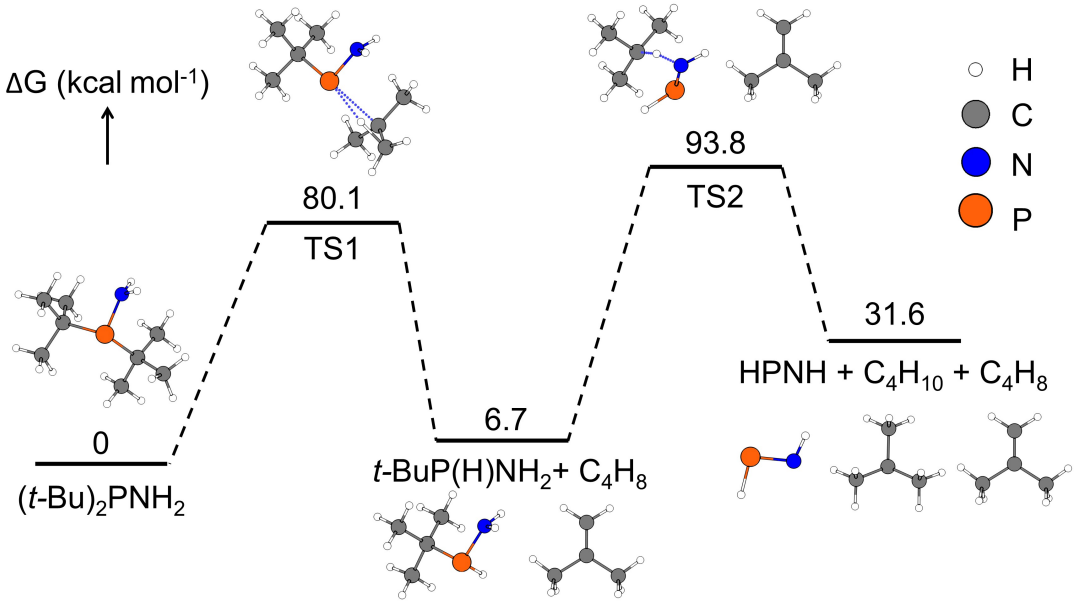


**Fig. S6.** B3LYP/6-311++G(3df,3pd) calculated relative Gibbs free energies (ΔG) for the stepwise decomposition of $(t\text{-Bu})_2PNH_2$.

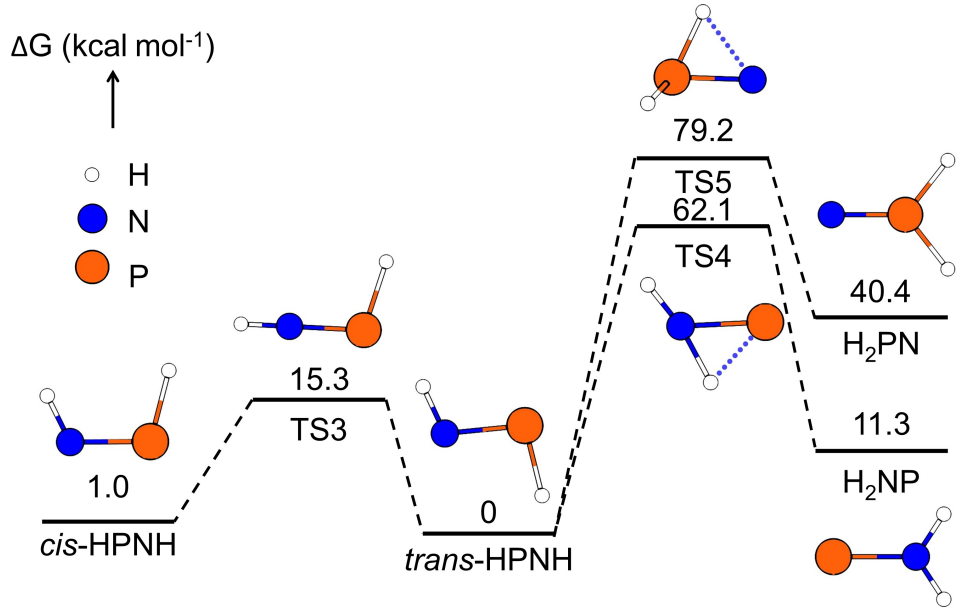


**Fig. S7.** DSD-PBEP86/aug-cc-pVTZ//CCSD(T)/CBS calculated relative Gibbs free energies (ΔG) for the isomerization of HPNH.

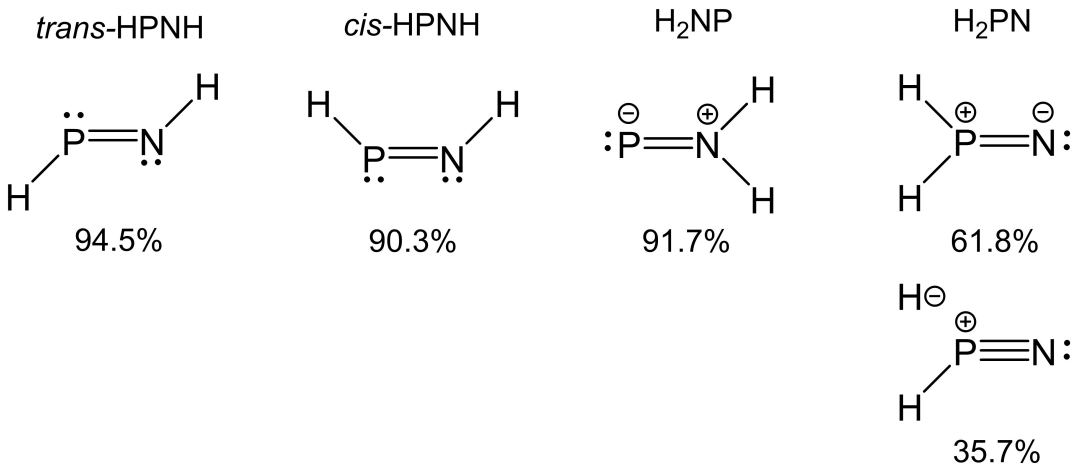


**Fig. S8.** Major Lewis resonance structures of *trans*-HPNH, *cis*-HPNH, singlet $H_2NP$, and singlet $H_2PN$ calculated by natural resonance theory (NRT).

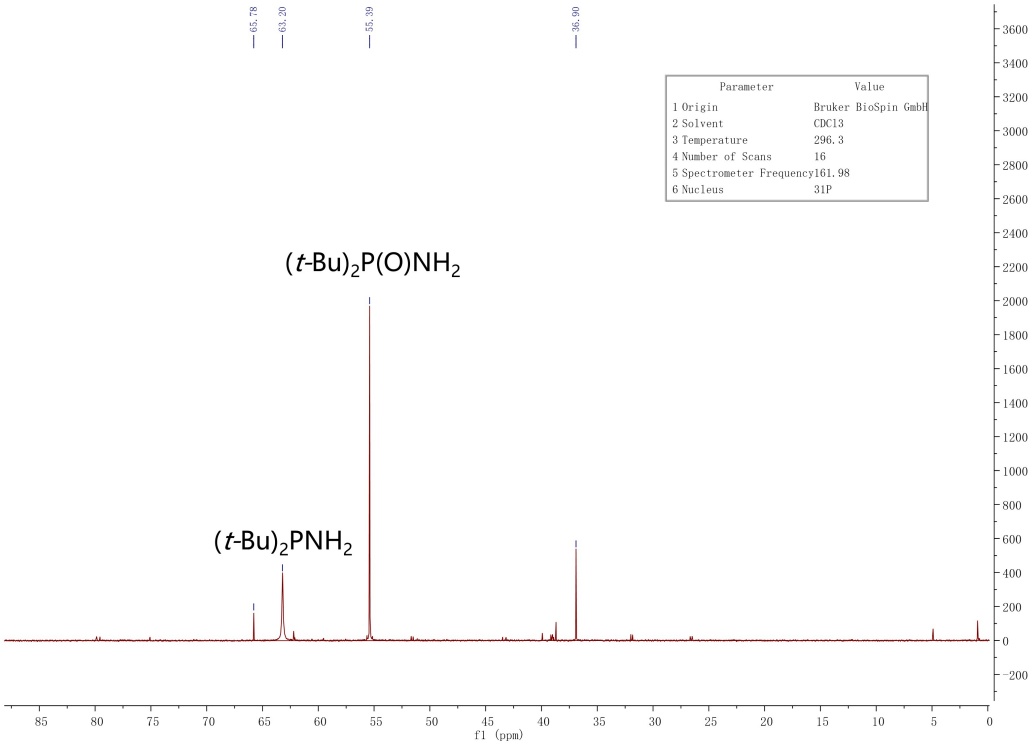


**Fig. S9.** $^{31}$P NMR spectrum of a typical sample of $(t\text{-Bu})_2PNH_2$ in $CDCl_3$, which contains the oxidation product $(t\text{-Bu})_2P(O)NH_2$. This less volatile byproduct can be mostly removed by low-temperature fractional distillation prior to the matrix-isolation experiments.

**Table S1.** Calculated vertical excitation energies ($\lambda \geq 190$ nm) and oscillator strength of *trans*-HPNH, *cis*-HPNH, singlet-$H_2NP$, triplet-$H_2NP$, singlet-$H_2PN$, and triplet-$H_2PN$ at TD-DSD-PBEP86/aug-cc-pVTZ level of theory.

| *trans*-HPNH | | *cis*-HPNH | | singlet-$H_2NP$ | | triplet-$H_2NP$ | | singlet-$H_2PN$ | | triplet-$H_2PN$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| λ/nm | oscillator strength | λ/nm | oscillator strength | λ/nm | oscillator strength | λ/nm | oscillator strength | λ/nm | oscillator strength | λ/nm | oscillator strength |
| 431.9 | 0.0025 | 376.0 | 0.0058 | 302.9 | 0.0018 | 342.2 | 0.0005 | 444.2 | 0.0000 | 535.8 | 0.0022 |
| 203.8 | 0.0757 | 262.2 | 0.0078 | 231.7 | 0.0796 | 291.8 | 0.0227 | 288.6 | 0.0736 | 407.4 | 0.0060 |
| 202.6 | 0.0051 | 204.2 | 0.0483 | 207.6 | 0.0001 | 267.0 | 0.0004 | 275.8 | 0.0095 | 290.9 | 0.0000 |
| 199.7 | 0.1832 | 191.3 | 0.1548 | 204.4 | 0.1439 | 266.8 | 0.0122 | 240.2 | 0.0060 | 287.5 | 0.4715 |
| | | | | | | 240.8 | 0.0316 | 198.4 | 0.0696 | 246.8 | 0.0014 |
| | | | | | | 228.7 | 0.0557 | | | 232.0 | 0.0148 |
| | | | | | | 211.7 | 0.0065 | | | 196.1 | 0.0355 |
| | | | | | | 198.4 | 0.0001 | | | | |

**Table S2**. Calculated and observed IR data for $H_2NPO_2$ and $H_2NNO_2$.

| $H_2NPO_2$ | | $\Delta\nu(^{16/18}O)$[c] | | Mode[d] | $H_2NNO_2$ | | Mode[d] |
|---|---|---|---|---|---|---|---|
| Cal.[a] | Obs.[b] | Cal. | Obs. | | Cal.[a] | Obs.[e] | |
| 3550.4 (82) | 3529.6 | 0 | 0 | $\nu_{as}$(HNH) | 3495.8 (50) | 3474.0 | $\nu_{as}$(HNH) |
| 3439.8 (66) | 3423.4 | 0 | 0 | $\nu_s$(HNH) | 3377.8 (26) | 3359.3 | $\nu_s$(HNH) |
| 1531.3 (65) | 1540.0 | 0 | 0 | $\delta(NH_2)$ | 1573.2 (30) | 1558.1 | $\delta(NH_2)$ |
| 1417.7 (177) | 1434.7 | −39.8 | −40.2 | $\nu_{as}$(OPO) | 1658.4 (294) | 1612.8 | $\nu_{as}$(ONO) |
| 1160.7 (133) | 1191.7 | −38.2 | −37.6 | $\nu_s$(OPO) | 1349.2 (180) | 1349.6 | $\nu_s$(ONO) |
| 950.7 (5) | n.o. | −3.5 | n.o. | $\rho(NH_2)$ | 1210.2 (22) | 1226.7 | $\rho(NH_2)$ |
| 908.0 (37) | 909.8 | −16.1 | −12.4 | ν(PN) | 975.1 (31) | 950.9 | ν(NN) |
| 488.4 (0) | n.o. | −0.7 | n.o. | $\tau(NH_2)$ | 803.9 (508) | 797.9 | ω(ONO) |
| 436.0 (50) | n.o. | −17.4 | n.o. | ω(OPO) | 715.3 (2) | 692.5 | τ(ONO) |
| 420.5 (14) | n.o. | −7.7 | n.o. | δ(OPO) | 584.8 (172) | 628.5 | ρ(ONO) |

[a] Calculated anharmonic IR frequencies (> 400 $cm^{-1}$) and intensities (km $mol^{-1}$, in parentheses) at the DSD-PBEP86/aug-cc-pVTZ level of theory. [b] Observed band position ($cm^{-1}$) for the strongest matrix site in $N_2$-matrix at 10 K. [c] Calculated and observed $^{18}O$-isotopic shifts for $H_2NP^{18}O_2$. [d] Assignment of the vibrational modes. [e] Observed band position ($cm^{-1}$) in Ar-matrix at 12 K from reference [Nonella, M., Müller, R. P. & Robert Huber, J. Infrared spectra, normal coordinate analysis, and photodecomposition of matrix-isolated $NH_2NO_2$, $^{15}NH_2NO_2$, $ND_2NO_2$, and $^{15}ND_2NO_2$. *J. Mol. Spectrosc.* **112**, 142−152 (1985)].

**Table S3.** Calculated PN bond orders given by the Wiberg method (WBI), Mayer approach (MBO), and Natural Resonance Theory (NRT) analysis.

| | WBI | MBO | NRT |
|---|---|---|---|
| *trans*-HPNH | 1.81 | 1.96 | 2.20 |
| *cis*-HPNH | 1.80 | 1.90 | 2.10 |
| singlet-$H_2NP$ | 1.26 | 1.57 | 2.10 |
| singlet-$H_2PN$ | 2.24 | 2.38 | 2.30 |

**Calculated atomic coordinates (in angstroms) and energies (in Hartrees) for all optimized structures.**

***trans*-HPNH**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | 0.01883700 | -0.53638200 | 0.00000000 |
| H | -1.39915000 | -0.73932700 | 0.00000000 |
| N | 0.01883700 | 1.05608700 | 0.00000000 |
| H | 0.98473900 | 1.39245000 | 0.00000000 |

Zero-point correction= 0.022462 (Hartree/Particle)
Thermal correction to Energy= 0.025440
Thermal correction to Enthalpy= 0.026384
Thermal correction to Gibbs Free Energy= -0.000742
Sum of electronic and zero-point Energies= -396.892212
Sum of electronic and thermal Energies= -396.889235
Sum of electronic and thermal Enthalpies= -396.888291
Sum of electronic and thermal Free Energies= -396.915416

CCSD(T)-F12B/VTZ-F12 ENERGY = -396.78411773

| | | | |
|---|---|---|---|
| P | 0.0000000000 | 0.0600529136 | 0.5053013166 |
| N | 0.0000000000 | -0.0968601360 | -1.0704900835 |
| H | 0.0000000000 | -1.3262601042 | 0.8506896458 |
| H | 0.0000000000 | 0.8264458824 | -1.5064921260 |

***cis*-HPNH**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | 0.09651700 | -0.53103000 | 0.00000000 |
| H | -1.30383100 | -0.90264700 | 0.00000000 |
| N | 0.09651700 | 1.05282100 | 0.00000000 |
| H | -0.81954900 | 1.49835300 | 0.00000000 |

Zero-point correction= 0.021952 (Hartree/Particle)
Thermal correction to Energy= 0.024959
Thermal correction to Enthalpy= 0.025903
Thermal correction to Gibbs Free Energy= -0.001260
Sum of electronic and zero-point Energies= -396.890736

Sum of electronic and thermal Energies= -396.887729

Sum of electronic and thermal Enthalpies= -396.886785

Sum of electronic and thermal Free Energies= -396.913948

CCSD(T)-F12B/VTZ-F12 ENERGY = -396.78235375

| | | | |
|---|---|---|---|
| P | 0.0000000000 | 0.0460427416 | -0.5051887593 |
| N | 0.0000000000 | 0.0567221244 | 1.0698266088 |
| H | 0.0000000000 | -1.3522447633 | -0.8669955458 |
| H | 0.0000000000 | -0.8509162102 | 1.5285573195 |

**singlet $H_2NP$**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | 0.66183800 | 0.00000000 | -0.00004500 |
| N | -0.97968600 | 0.00000000 | 0.00038100 |
| H | -1.53488400 | 0.84636600 | -0.00099700 |
| H | -1.53488400 | -0.84636600 | -0.00099700 |

Zero-point correction= 0.025931 (Hartree/Particle)

Thermal correction to Energy= 0.028950

Thermal correction to Enthalpy= 0.029894

Thermal correction to Gibbs Free Energy= 0.002898

Sum of electronic and zero-point Energies= -396.870708

Sum of electronic and thermal Energies= -396.867689

Sum of electronic and thermal Enthalpies= -396.866745

Sum of electronic and thermal Free Energies= -396.893740

CCSD(T)-F12B/VTZ-F12 ENERGY = -396.76444457

| | | | |
|---|---|---|---|
| P | 0.0000000000 | 0.0000000000 | -0.5810548507 |
| N | 0.0000000000 | 0.0000000000 | 1.0536986186 |
| H | 0.0000000000 | -0.8451130614 | 1.6086314481 |
| H | 0.0000000000 | 0.8451130614 | 1.6086314481 |

**triplet $H_2NP$**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | -0.68041700 | -0.00001100 | 0.00788200 |

| | | | |
|---|---|---|---|
| N | 1.02470400 | -0.00002100 | -0.07542700 |
| H | 1.51693000 | -0.83646200 | 0.20492700 |
| H | 1.51640200 | 0.83677500 | 0.20483900 |

Zero-point correction= 0.024807 (Hartree/Particle)
Thermal correction to Energy= 0.028073
Thermal correction to Enthalpy= 0.029017
Thermal correction to Gibbs Free Energy= 0.000518
Sum of electronic and zero-point Energies= -396.875360
Sum of electronic and thermal Energies= -396.872094
Sum of electronic and thermal Enthalpies= -396.871150
Sum of electronic and thermal Free Energies= -396.899649

**singlet $H_2PN$**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | -0.00002700 | -0.37032200 | 0.00000000 |
| H | 0.00029700 | -1.24370200 | 1.11746500 |
| H | 0.00029700 | -1.24370200 | -1.11746500 |
| N | -0.00002700 | 1.14889000 | 0.00000000 |

Zero-point correction= 0.019305 (Hartree/Particle)
Thermal correction to Energy= 0.022474
Thermal correction to Enthalpy= 0.023418
Thermal correction to Gibbs Free Energy= -0.003885
Sum of electronic and zero-point Energies= -396.828027
Sum of electronic and thermal Energies= -396.824858
Sum of electronic and thermal Enthalpies= -396.823914
Sum of electronic and thermal Free Energies= -396.851217

CCSD(T)-F12B/VTZ-F12 ENERGY = -396.72025223

| | | | |
|---|---|---|---|
| N | 0.0000000000 | 0.0000000000 | -1.0997894795 |
| P | 0.0000000000 | 0.0000000000 | 0.4139984849 |
| H | 0.0000000000 | -1.1179551874 | 1.2786641312 |
| H | 0.0000000000 | 1.1179551874 | 1.2786641312 |

**$H_2NPO_2$**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| N | -0.00004400 | -1.46637100 | 0.00000000 |
| H | 0.00012400 | -1.98096400 | 0.86418300 |
| H | 0.00012400 | -1.98096400 | -0.86418300 |
| P | 0.00005100 | 0.15863600 | 0.00000000 |
| O | -0.00004400 | 0.74043600 | -1.34865700 |
| O | -0.00004400 | 0.74043600 | 1.34865700 |

Zero-point correction= 0.035271 (Hartree/Particle)
Thermal correction to Energy= 0.039740
Thermal correction to Enthalpy= 0.040685
Thermal correction to Gibbs Free Energy= 0.008153
Sum of electronic and zero-point Energies= -547.285261
Sum of electronic and thermal Energies= -547.280792
Sum of electronic and thermal Enthalpies= -547.279848
Sum of electronic and thermal Free Energies= -547.312379

**$H_2NNO_2$**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| N | 1.24616700 | -0.00250400 | -0.10170100 |
| H | 1.60693900 | 0.85184700 | 0.30204000 |
| H | 1.60302100 | -0.85802000 | 0.30321600 |
| O | -0.68592500 | -1.09107100 | 0.00792900 |
| O | -0.68089700 | 1.09388200 | 0.00803300 |
| N | -0.14265100 | 0.00017300 | -0.00300600 |

Zero-point correction= 0.039531 (Hartree/Particle)
Thermal correction to Energy= 0.043216
Thermal correction to Enthalpy= 0.044160
Thermal correction to Gibbs Free Energy= 0.013709
Sum of electronic and zero-point Energies= -260.706134
Sum of electronic and thermal Energies= -260.702449
Sum of electronic and thermal Enthalpies= -260.701505
Sum of electronic and thermal Free Energies= -260.731956

**(*t*-Bu)$_2$PNH$_2$**

B3LYP/6-311++G(3df,3pd)

| | | | |
|---|---|---|---|
| P | -0.00254300 | -0.58097200 | -0.69276900 |
| C | -1.56503700 | 0.25363200 | 0.01206400 |
| C | 1.57196000 | 0.24341200 | 0.01979200 |
| C | -2.71551000 | -0.38595600 | -0.79227200 |
| H | -2.74456500 | -1.46602000 | -0.65162800 |
| H | -3.67096600 | 0.02595800 | -0.45667800 |
| H | -2.61616600 | -0.18546500 | -1.85933500 |
| C | -1.83026600 | 0.01186200 | 1.50491400 |
| H | -1.07968500 | 0.46973100 | 2.14532700 |
| H | -2.79761900 | 0.44395600 | 1.77684200 |
| H | -1.87973600 | -1.05244400 | 1.73352400 |
| C | -1.55100500 | 1.76102900 | -0.27818200 |
| H | -1.29926700 | 1.97174500 | -1.31890000 |
| H | -2.54368100 | 2.17798900 | -0.08992400 |
| H | -0.84874700 | 2.29740400 | 0.35834500 |
| C | 1.84803200 | 1.53541600 | -0.76892100 |
| H | 1.12236000 | 2.31751400 | -0.55701100 |
| H | 2.83526900 | 1.92453400 | -0.50534300 |
| H | 1.83955100 | 1.35159200 | -1.84416800 |
| C | 1.58216500 | 0.53598100 | 1.52430900 |
| H | 2.57981600 | 0.86197300 | 1.83369000 |
| H | 0.88557300 | 1.32826200 | 1.79301500 |
| H | 1.33758300 | -0.34726800 | 2.11744100 |
| C | 2.70560900 | -0.75049800 | -0.29899400 |
| H | 2.71981600 | -1.01819700 | -1.35706000 |
| H | 3.66919700 | -0.29530400 | -0.05702200 |
| H | 2.61705200 | -1.66909900 | 0.28040200 |
| N | -0.10759800 | -2.09080300 | 0.11291300 |
| H | 0.31118900 | -2.86205000 | -0.38158500 |
| H | 0.07866100 | -2.15387000 | 1.10494900 |

Zero-point correction= 0.270485 (Hartree/Particle)

Thermal correction to Energy= 0.284834

Thermal correction to Enthalpy= 0.285778

Thermal correction to Gibbs Free Energy= 0.232109

Sum of electronic and zero-point Energies= -712.912930

Sum of electronic and thermal Energies= -712.898582

Sum of electronic and thermal Enthalpies= -712.897638

Sum of electronic and thermal Free Energies= -712.951307

**_t_-BuP(H)$NH_2$**

B3LYP/6-311++G(3df,3pd)

| | | | |
|---|---|---|---|
| P | 0.04654272 | -0.55965365 | -0.58896476 |
| C | 1.61764277 | 0.18293954 | -0.04803962 |
| C | 1.83058010 | 1.52218490 | -0.77788861 |
| H | 1.02402605 | 2.18633841 | -0.54708419 |
| H | 2.75424881 | 1.95876441 | -0.45987218 |
| H | 1.86141541 | 1.35196652 | -1.83381232 |
| C | 1.57326297 | 0.42792674 | 1.47170105 |
| H | 2.49693168 | 0.86450624 | 1.78971748 |
| H | 0.76670892 | 1.09208025 | 1.70250547 |
| H | 1.42531301 | -0.50258790 | 1.97880392 |
| C | 2.77847757 | -0.77294495 | -0.38022541 |
| H | 2.80931288 | -0.94316333 | -1.43614912 |
| H | 3.70214628 | -0.33636545 | -0.06220898 |
| H | 2.63052760 | -1.70345959 | 0.12687746 |
| N | -0.19543153 | -2.08152338 | 0.24040909 |
| H | 0.55835731 | -2.70222759 | 0.02470403 |
| H | -0.22424957 | -1.92244078 | 1.22725369 |
| H | -0.97107221 | 0.27829704 | -0.29776293 |

Zero-point correction= 0.156865 (Hartree/Particle)
Thermal correction to Energy= 0.165871
Thermal correction to Enthalpy= 0.166816
Thermal correction to Gibbs Free Energy= 0.124446
Sum of electronic and zero-point Energies= -555.724860
Sum of electronic and thermal Energies= -555.715854
Sum of electronic and thermal Enthalpies= -555.714909
Sum of electronic and thermal Free Energies= -555.757279

**TS1**

B3LYP/6-311++G(3df,3pd)

| | | | |
|---|---|---|---|
| P | 0.32217900 | 0.57714400 | -0.71090700 |

| | | | |
|---|---|---|---|
| C | -2.31109400 | -0.25804600 | 0.03808700 |
| C | -2.11588600 | -1.74252400 | 0.04590900 |
| H | -1.34639000 | -2.04711800 | 0.75021900 |
| H | -3.06593100 | -2.20613200 | 0.34206700 |
| H | -1.86359700 | -2.12127800 | -0.94254200 |
| C | -2.32393000 | 0.45568700 | 1.35131000 |
| H | -3.30742400 | 0.29912800 | 1.81249800 |
| H | -1.55856700 | 0.07986200 | 2.02606200 |
| H | -2.19468500 | 1.53011400 | 1.22691600 |
| C | -2.97941600 | 0.33459300 | -1.06950600 |
| H | -1.62412100 | 0.35887000 | -0.97574300 |
| H | -3.22078800 | -0.25495200 | -1.94031800 |
| H | -3.35227900 | 1.34472900 | -1.00234900 |
| N | 0.41278300 | 2.11283700 | 0.07780300 |
| H | 0.16895500 | 2.91374800 | -0.48130500 |
| H | 0.09981600 | 2.22234700 | 1.03337100 |
| C | 1.81977400 | -0.33001400 | 0.02972300 |
| C | 1.81788600 | -1.74409200 | -0.56550900 |
| H | 0.93050500 | -2.30660700 | -0.27155300 |
| H | 1.85231400 | -1.71620400 | -1.65602700 |
| H | 2.69224200 | -2.30135900 | -0.21886800 |
| C | 3.10400400 | 0.40325800 | -0.38669300 |
| H | 3.98159500 | -0.10249700 | 0.02993500 |
| H | 3.21058800 | 0.42656300 | -1.47157600 |
| H | 3.10145400 | 1.43133400 | -0.02621000 |
| C | 1.74795100 | -0.40501500 | 1.56029900 |
| H | 0.86527700 | -0.95205500 | 1.89558900 |
| H | 2.62809700 | -0.91880600 | 1.96025600 |
| H | 1.72503100 | 0.59021000 | 2.00684500 |

Zero-point correction= 0.261129 (Hartree/Particle)

Thermal correction to Energy= 0.276839

Thermal correction to Enthalpy= 0.277783

Thermal correction to Gibbs Free Energy= 0.218937

Sum of electronic and zero-point Energies= -712.787288

Sum of electronic and thermal Energies= -712.771577

Sum of electronic and thermal Enthalpies= -712.770633

Sum of electronic and thermal Free Energies= -712.829480

**TS2**

B3LYP/6-311++G(3df,3pd)

| | | | |
|---|---|---|---|
| P | -1.38163400 | 0.64710700 | -0.10059200 |
| C | 0.77299500 | -0.05082900 | -0.01125100 |
| C | 1.37463900 | 1.31841800 | 0.29639300 |
| H | 1.10986100 | 1.66637500 | 1.29469900 |
| H | 2.46613700 | 1.25099400 | 0.25155000 |
| H | 1.06491900 | 2.07473300 | -0.42601900 |
| C | 1.18872700 | -1.07023700 | 1.06500800 |
| H | 2.27186200 | -1.21705500 | 1.02146300 |
| H | 0.92958900 | -0.71786700 | 2.06312800 |
| H | 0.71704200 | -2.04386000 | 0.92077000 |
| C | 1.13198100 | -0.53045100 | -1.41362500 |
| H | 0.86625800 | 0.20999100 | -2.16880800 |
| H | 2.20683000 | -0.71745800 | -1.49071600 |
| H | 0.62150800 | -1.46350700 | -1.66194000 |
| N | -2.02974700 | -0.85259300 | 0.19670900 |
| H | -2.37977300 | -1.24030100 | -0.67662300 |
| H | -0.53555300 | -0.63913400 | 0.14143700 |
| H | -1.21599100 | 1.09723100 | 1.24382800 |

Zero-point correction= 0.150581 (Hartree/Particle)

Thermal correction to Energy= 0.159543

Thermal correction to Enthalpy= 0.160487

Thermal correction to Gibbs Free Energy= 0.117522

Sum of electronic and zero-point Energies= -555.592232

Sum of electronic and thermal Energies= -555.583270

Sum of electronic and thermal Enthalpies= -555.582326

Sum of electronic and thermal Free Energies= -555.625291

**TS3**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | 0.52671800 | -0.10996600 | -0.00005300 |
| H | 1.03963700 | 1.26455100 | 0.00000400 |
| N | -0.99307400 | 0.04587000 | 0.00008800 |

| | | | |
|---|---|---|---|
| H | -1.98889100 | 0.06385100 | 0.00017500 |

Zero-point correction= 0.020011 (Hartree/Particle)
Thermal correction to Energy= 0.023037
Thermal correction to Enthalpy= 0.023981
Thermal correction to Gibbs Free Energy= -0.003048
Sum of electronic and zero-point Energies= -396.869334
Sum of electronic and thermal Energies= -396.866308
Sum of electronic and thermal Enthalpies= -396.865364
Sum of electronic and thermal Free Energies= -396.892393

**TS4**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | 0.62341700 | -0.04676700 | 0.00000500 |
| H | -0.44026800 | 1.14164200 | 0.00050100 |
| N | -1.03371700 | 0.04516400 | -0.00018000 |
| H | -1.67496400 | -0.75629100 | 0.00067600 |

Zero-point correction= 0.017283 (Hartree/Particle)
Thermal correction to Energy= 0.020736
Thermal correction to Enthalpy= 0.021680
Thermal correction to Gibbs Free Energy= -0.006240
Sum of electronic and zero-point Energies= -396.800070
Sum of electronic and thermal Energies= -396.796618
Sum of electronic and thermal Enthalpies= -396.795674
Sum of electronic and thermal Free Energies= -396.823593

**TS5**

DSD-PBEP86/AVTZ

| | | | |
|---|---|---|---|
| P | -0.45909100 | 0.03643500 | -0.10508300 |
| H | -1.13682700 | -0.88148600 | 0.79449500 |
| H | 0.11237500 | 1.11004900 | 0.69163100 |
| N | 1.13011800 | -0.11072600 | 0.01287400 |

Zero-point correction= 0.016132 (Hartree/Particle)
Thermal correction to Energy= 0.019166
Thermal correction to Enthalpy= 0.020110

| | |
|---|---|
| Thermal correction to Gibbs Free Energy= | -0.007187 |
| Sum of electronic and zero-point Energies= | -396.766148 |
| Sum of electronic and thermal Energies= | -396.763114 |
| Sum of electronic and thermal Enthalpies= | -396.762170 |
| Sum of electronic and thermal Free Energies= | -396.789467 |