

## Supporting Information

# Decomposition of fluorophosphoryl diazide: A joint experimental and theoretical study

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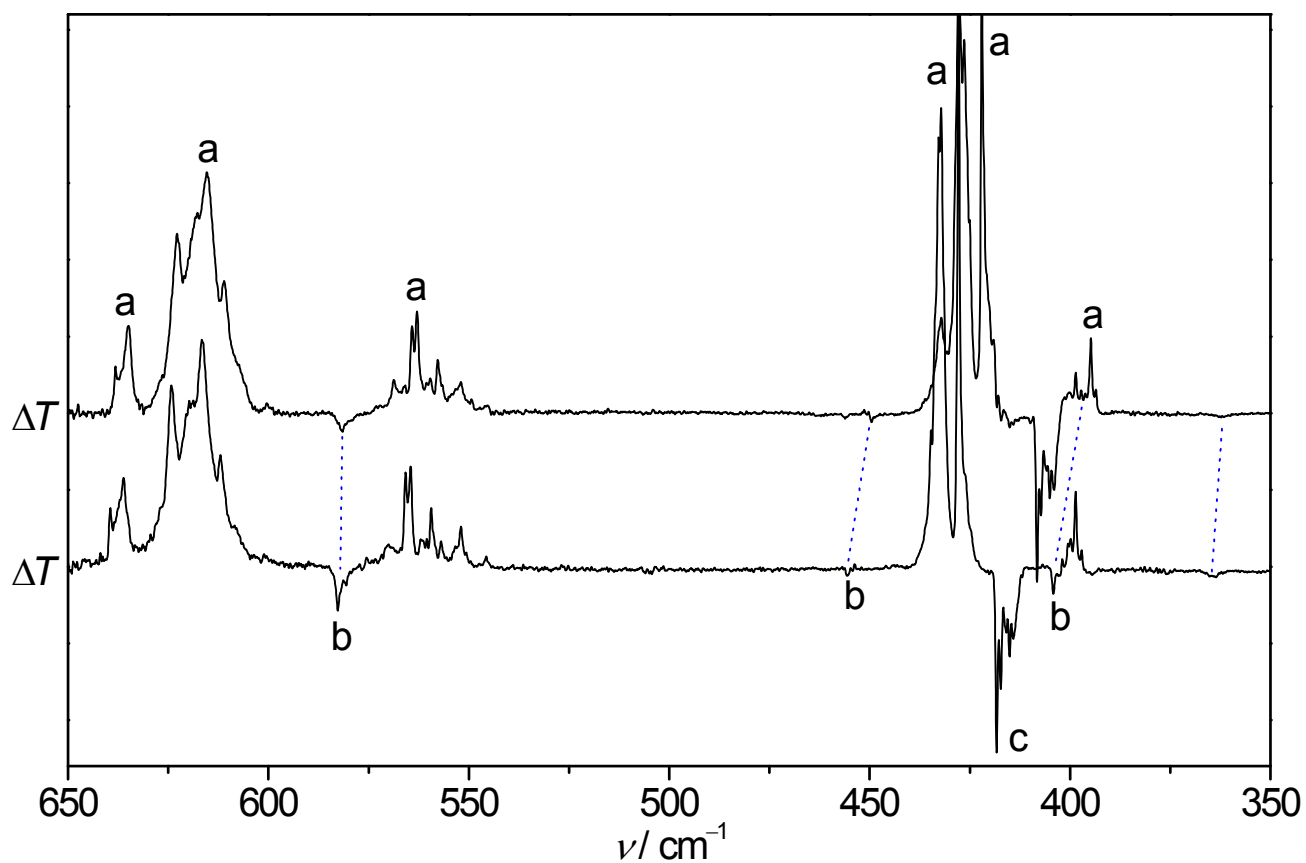
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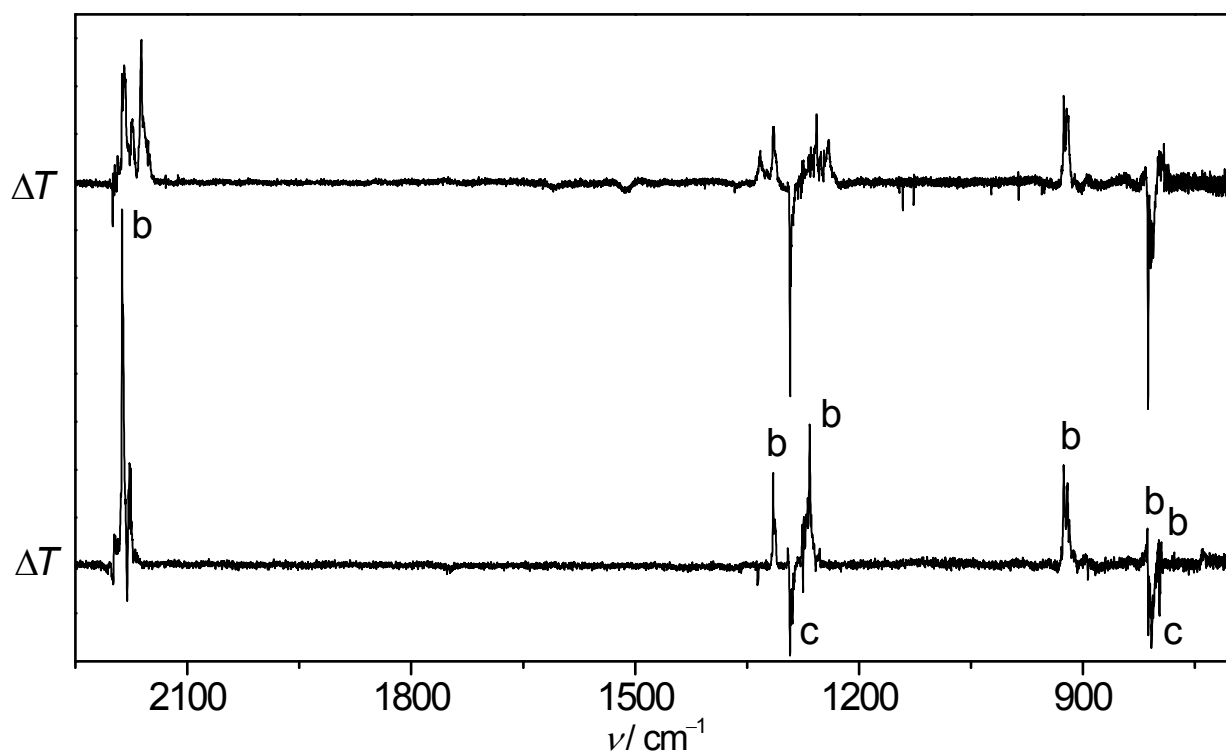
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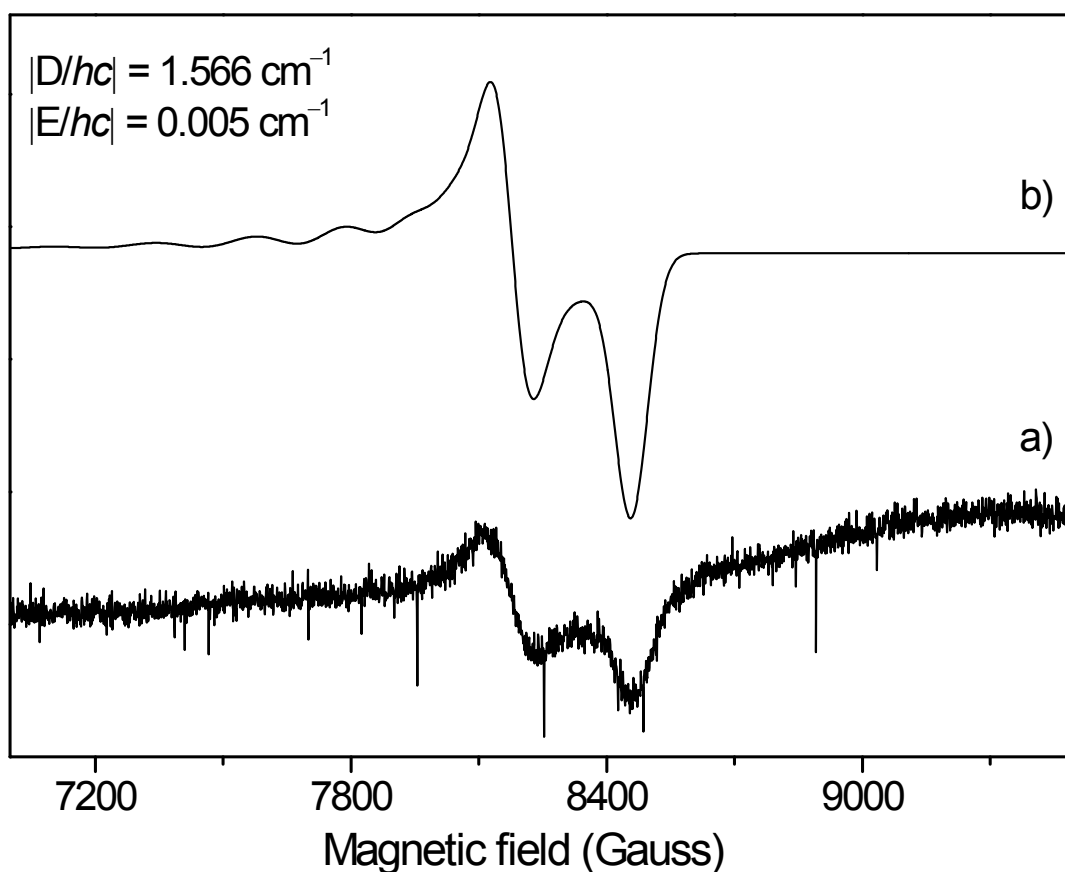
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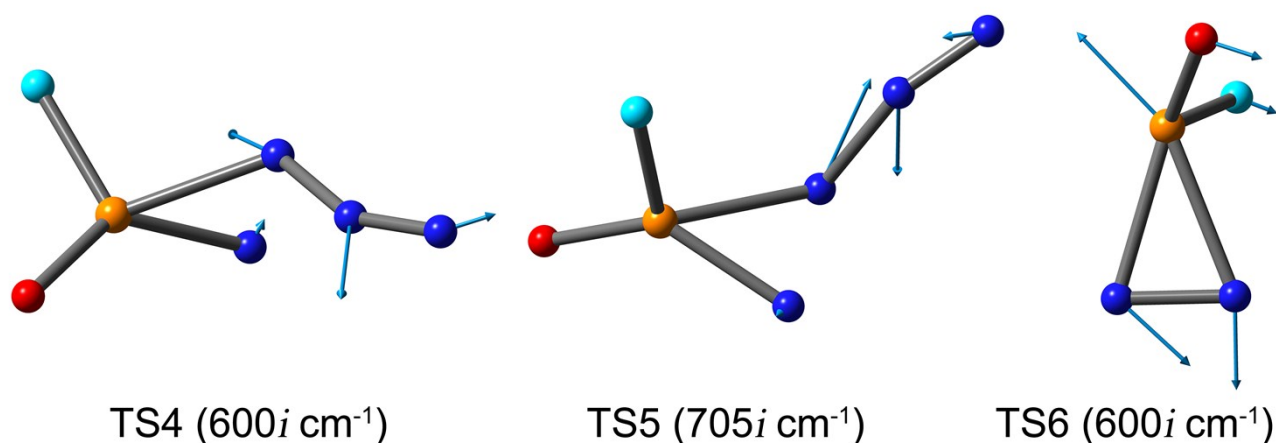
**Figure S1.** Ar-matrix IR difference spectra recorded before and after ArF laser ( $\lambda = 193 \text{ nm}$ ) photolysis of  $\text{FP}(\text{O})(\text{N}_3)_2$  (lower trace) and  $^{18}\text{O}$  labeled  $\text{FP}(\text{O})(\text{N}_3)_2$  (upper trace). Bands associated with  $\text{FP}(\text{O})(\text{N}_3)_2$ ,  $\text{FP}(\text{O})(\text{N}_3)\text{N}$  ( $^3\text{A}$ ), and FPO are marked by **a**, **b**, and **c**, respectively.



**Figure S2.** Ar-matrix IR difference spectra recorded before and after near-UV irradiation ( $\lambda > 335$  nm) of the ArF laser ( $\lambda = 193$  nm) photolysis products of  $\text{FP}(\text{O})(\text{N}_3)_2$  (lower trace) and  $^{15}\text{N}$  enriched  $\text{FP}(\text{O})(\text{N}_3)_2$  (upper trace). Bands associated with  $\text{FP}(\text{O})(\text{N}_3)\text{N}$  ( $^3\text{A}$ ) and FPO are marked by **b** and **c**, respectively.



**Figure S3.** a) The  $|\Delta m_s| = 1$  EPR transitions of FP(O)(N<sub>3</sub>)N obtained after ArF excimer laser irradiation of Ar matrix isolated FP(O)(N<sub>3</sub>)<sub>2</sub> at 5 K. b) Simulated spectrum:  $g = 2.0023$ ,  $\nu = 9.60992$  GHz,  $|D/hc| = 1.566$  cm<sup>-1</sup>,  $|E/hc| = 0.005$  cm<sup>-1</sup>.



**Figure S4.** B3LYP/6-311+G(3df) calculated vibrational displacement vectors for the imaginary frequencies of the transition states.

**Calculated Energies (in Hartrees) Atomic Coordinates (in Angstroms) for All Optimized Structures at the B3LYP/6-311+G(3df) Level of Theory.**

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***syn-syn* FP(O)(N<sub>3</sub>)<sub>2</sub>**

<i>Zero-point correction=</i>			0.035596
<i>Thermal correction to Energy=</i>			0.044186
<i>Thermal correction to Enthalpy=</i>			0.045131
<i>Thermal correction to Gibbs Free Energy=</i>		-0.000488	
<i>Sum of electronic and zero-point Energies=</i>			-845.084264
<i>Sum of electronic and thermal Energies=</i>			-845.075674
<i>Sum of electronic and thermal Enthalpies=</i>			-845.074730
<i>Sum of electronic and thermal Free Energies=</i>			-845.120349

N	-1.13822500	-0.21893200	-0.80240600
N	-2.09909600	-0.77844100	-0.26559600
N	-3.00200200	-1.32172600	0.11221700
F	-0.15484600	2.02742500	-0.34898700
O	-0.09208600	0.35940400	1.58155800
P	0.00176400	0.56723300	0.14522200
N	1.45162300	0.23002900	-0.61494700
N	2.17560200	-0.67660000	-0.19568700
N	2.91264700	-1.46726700	0.09643100

***syn-anti* FP(O)(N<sub>3</sub>)<sub>2</sub>**

<i>Zero-point correction=</i>			0.035593
<i>Thermal correction to Energy=</i>			0.044138
<i>Thermal correction to Enthalpy=</i>			0.045082
<i>Thermal correction to Gibbs Free Energy=</i>		-0.000016	
<i>Sum of electronic and zero-point Energies=</i>			-845.083327
<i>Sum of electronic and thermal Energies=</i>			-845.074781
<i>Sum of electronic and thermal Enthalpies=</i>			-845.073837
<i>Sum of electronic and thermal Free Energies=</i>			-845.118936

N	1.27127600	0.03596000	-0.85405900
N	2.03527900	-0.75580400	-0.29425800
N	2.78935600	-1.47998800	0.10872100
F	0.59035800	1.27096800	1.23496500
O	-0.78778500	1.62923300	-0.89095600
P	-0.04571300	0.69773400	-0.06612800
N	-0.88654400	-0.58483600	0.61897300
N	-1.98532400	-0.91383300	0.16256200
N	-2.98479200	-1.29272600	-0.16981400

**syn FP(O)(N<sub>3</sub>)N (<sup>3</sup>A)**

Zero-point correction=	0.023775
Thermal correction to Energy=	0.030600
Thermal correction to Enthalpy=	0.031544
Thermal correction to Gibbs Free Energy=	-0.009146
Sum of electronic and zero-point Energies=	-735.485762
Sum of electronic and thermal Energies=	-735.478936
Sum of electronic and thermal Enthalpies=	-735.477992
Sum of electronic and thermal Free Energies=	-735.518682

N	-0.73137800	-0.78347900	-0.05750100
N	-1.83675800	-0.23315600	-0.01182200
N	-2.88489300	0.15708700	0.01876400
F	1.62197900	-0.85396000	-0.75317200
O	0.62666000	1.49209000	-0.50222900
P	0.67645700	0.12347900	-0.00552400
N	1.20189500	-0.01234700	1.60473500

**anti FP(O)(N<sub>3</sub>)N (<sup>3</sup>A)**

Zero-point correction=	0.023658
Thermal correction to Energy=	0.030506
Thermal correction to Enthalpy=	0.031450
Thermal correction to Gibbs Free Energy=	-0.009277
Sum of electronic and zero-point Energies=	-735.483651
Sum of electronic and thermal Energies=	-735.476803
Sum of electronic and thermal Enthalpies=	-735.475859
Sum of electronic and thermal Free Energies=	-735.516586

N	0.70262300	-0.86463400	0.03473600
N	1.79060800	-0.28048900	0.01072100
N	2.82849100	0.13953500	-0.00725900
F	-0.46623900	1.21127300	-0.85834300
O	-1.87423600	-0.88739200	-0.43759200
P	-0.76414800	-0.06172200	0.00279400
N	-0.94282800	0.59466100	1.55950500

**syn FP(O)(N<sub>3</sub>)N (<sup>1</sup>A) conformer I**

Zero-point correction=	0.023755
Thermal correction to Energy=	0.030403
Thermal correction to Enthalpy=	0.031347
Thermal correction to Gibbs Free Energy=	-0.007529
Sum of electronic and zero-point Energies=	-735.464314

<i>Sum of electronic and thermal Energies=</i>	-735.457666
<i>Sum of electronic and thermal Enthalpies=</i>	-735.456722
<i>Sum of electronic and thermal Free Energies=</i>	-735.495598

N	-0.71755000	-0.68866600	-0.30457000
N	-1.81109600	-0.05729200	-0.21830100
N	-2.83429100	0.38585500	-0.22386500
F	1.84038200	-0.67830700	-0.70088700
O	1.07102500	1.54873100	0.08557500
P	0.82445500	0.11875300	0.16875900
N	0.00601400	-0.79223700	1.18845100

**syn FP(O)(N<sub>3</sub>)N (<sup>1</sup>A) conformer II**

<i>Zero-point correction=</i>	0.024260
<i>Thermal correction to Energy=</i>	0.030980
<i>Thermal correction to Enthalpy=</i>	0.031924
<i>Thermal correction to Gibbs Free Energy=</i>	-0.007290
<i>Sum of electronic and zero-point Energies=</i>	-735.450867
<i>Sum of electronic and thermal Energies=</i>	-735.444147
<i>Sum of electronic and thermal Enthalpies=</i>	-735.443203
<i>Sum of electronic and thermal Free Energies=</i>	-735.482417

N	0.78380100	-0.83591900	0.02543500
N	1.84686500	-0.19549400	0.00577800
N	2.86294000	0.26823000	-0.00123500
F	-1.57216000	-1.25952200	-0.03902700
O	-0.98529300	1.04240400	0.97153900
P	-0.65858800	-0.01698500	-0.05264400
N	-0.93494800	1.22764600	-0.97732300

**anti FP(O)(N<sub>3</sub>)N (<sup>1</sup>A) conformer I**

<i>Zero-point correction=</i>	0.023643
<i>Thermal correction to Energy=</i>	0.030299
<i>Thermal correction to Enthalpy=</i>	0.031244
<i>Thermal correction to Gibbs Free Energy=</i>	-0.007600
<i>Sum of electronic and zero-point Energies=</i>	-735.464011
<i>Sum of electronic and thermal Energies=</i>	-735.457354
<i>Sum of electronic and thermal Enthalpies=</i>	-735.456410
<i>Sum of electronic and thermal Free Energies=</i>	-735.495254

N	0.68692600	-0.71649600	-0.44696500
N	1.76160600	-0.07656300	-0.24288800

N	2.77859000	0.37147900	-0.14571700
F	-0.56281200	1.44232600	0.34523800
O	-2.15780300	-0.17576200	-0.65931200
P	-0.91903100	-0.06648300	0.08682000
N	-0.06809400	-1.08950500	0.95914900

**anti FP(O)(N<sub>3</sub>)N (<sup>1</sup>A) conformer II**

<i>Zero-point correction=</i>			0.024017
<i>Thermal correction to Energy=</i>			0.030864
<i>Thermal correction to Enthalpy=</i>			0.031808
<i>Thermal correction to Gibbs Free Energy=</i>		-0.007849	
<i>Sum of electronic and zero-point Energies=</i>			-735.447457
<i>Sum of electronic and thermal Energies=</i>			-735.440610
<i>Sum of electronic and thermal Enthalpies=</i>			-735.439666
<i>Sum of electronic and thermal Free Energies=</i>			-735.479324

N	-0.73713400	-0.84883900	-0.09101200
N	-1.85220500	-0.32137800	-0.00035800
N	-2.90831400	0.04123700	0.06364000
F	0.16479100	1.47783400	-0.08447800
O	1.67286500	-0.28584900	1.03359900
P	0.68082400	0.00627600	-0.06056700
N	1.91502500	-0.45785600	-0.91512500

**cis FP(O)N<sub>4</sub>**

<i>Zero-point correction=</i>			0.024361
<i>Thermal correction to Energy=</i>			0.031322
<i>Thermal correction to Enthalpy=</i>			0.032267
<i>Thermal correction to Gibbs Free Energy=</i>		-0.008296	
<i>Sum of electronic and zero-point Energies=</i>			-735.494170
<i>Sum of electronic and thermal Energies=</i>			-735.487208
<i>Sum of electronic and thermal Enthalpies=</i>			-735.486264
<i>Sum of electronic and thermal Free Energies=</i>			-735.526827

N	0.00000000	0.49187800	0.00000000
O	-0.91604000	-2.16944200	0.00000000
P	-0.96318300	-0.71622000	0.00000000
N	1.38359200	0.22793000	0.00000000
N	2.03232900	1.28845300	0.00000000
N	2.76062400	2.14795300	0.00000000
F	-2.38441800	-0.11051800	0.00000000



**trans FP(O)N<sub>4</sub>**

Zero-point correction=	0.024240
Thermal correction to Energy=	0.031247
Thermal correction to Enthalpy=	0.032192
Thermal correction to Gibbs Free Energy=	-0.008336
Sum of electronic and zero-point Energies=	-735.493015
Sum of electronic and thermal Energies=	-735.486008
Sum of electronic and thermal Enthalpies=	-735.485064
Sum of electronic and thermal Free Energies=	-735.525592

N	0.00000000	0.58038900	0.00000000
O	-2.59225600	-0.17760900	0.00000000
P	-1.16146100	-0.42739000	0.00000000
N	1.32958800	0.11974300	0.00000000
N	2.12559400	1.07551700	0.00000000
N	2.96993200	1.82111900	0.00000000
F	-0.75731500	-1.92729500	0.00000000

**cyclo-FP(O)N<sub>2</sub>**

Zero-point correction=	0.015409
Thermal correction to Energy=	0.019889
Thermal correction to Enthalpy=	0.020833
Thermal correction to Gibbs Free Energy=	-0.012413
Sum of electronic and zero-point Energies=	-626.003044
Sum of electronic and thermal Energies=	-625.998564
Sum of electronic and thermal Enthalpies=	-625.997620
Sum of electronic and thermal Free Energies=	-626.030866

N	-1.34451700	-0.17177300	0.64727900
F	0.63946300	1.38915100	0.00009300
O	1.26500000	-1.08107500	-0.00000600
P	0.19661100	-0.09672400	-0.00009700
N	-1.34467200	-0.17149800	-0.64718500

**FPO**

Zero-point correction=	0.005711
Thermal correction to Energy=	0.008941
Thermal correction to Enthalpy=	0.009885
Thermal correction to Gibbs Free Energy=	-0.019541
Sum of electronic and zero-point Energies=	-516.563940

*Sum of electronic and thermal Energies=* -516.560710  
*Sum of electronic and thermal Enthalpies=* -516.559766  
*Sum of electronic and thermal Free Energies=* -516.589192

F	-1.16004500	-0.62733700	0.00000000
O	1.30505100	-0.17677900	0.00000000
P	0.00000000	0.47068400	0.00000000

## **N<sub>2</sub>**

*Zero-point correction=* 0.005573  
*Thermal correction to Energy=* 0.007934  
*Thermal correction to Enthalpy=* 0.008878  
*Thermal correction to Gibbs Free Energy=* -0.012852  
*Sum of electronic and zero-point Energies=* -109.561799  
*Sum of electronic and thermal Energies=* -109.559438  
*Sum of electronic and thermal Enthalpies=* -109.558494  
*Sum of electronic and thermal Free Energies=* -109.580224

N	0.00000000	0.00000000	0.54559100
N	0.00000000	0.00000000	-0.54559100

## **TS1**

*Zero-point correction=* 0.023313  
*Thermal correction to Energy=* 0.029547  
*Thermal correction to Enthalpy=* 0.030491  
*Thermal correction to Gibbs Free Energy=* -0.007740  
*Sum of electronic and zero-point Energies=* -735.439901  
*Sum of electronic and thermal Energies=* -735.433668  
*Sum of electronic and thermal Enthalpies=* -735.432723  
*Sum of electronic and thermal Free Energies=* -735.470954

N	0.05839600	-0.10219800	0.04642200
P	-0.04099200	0.02036900	1.64325600
N	1.61737700	-0.03570900	1.97246800
N	2.24089100	-1.09411200	1.78949200
N	2.90074600	-1.98830000	1.67223100
O	-1.00440400	-0.94111400	2.19511100
F	-0.26076900	1.45300900	2.20116300

## **TS2**

*Zero-point correction=* 0.023964

Thermal correction to Energy=	0.029962
Thermal correction to Enthalpy=	0.030906
Thermal correction to Gibbs Free Energy=	-0.006594
Sum of electronic and zero-point Energies=	-735.443574
Sum of electronic and thermal Energies=	-735.437575
Sum of electronic and thermal Enthalpies=	-735.436631
Sum of electronic and thermal Free Energies=	-735.474132

N	-0.05712700	-0.06745700	0.08800200
N	0.07744500	0.04858300	1.30567500
N	0.31883500	0.14108700	2.39569100
F	-1.79223900	1.37871500	-0.93324700
O	-1.50322500	-0.98013400	-1.94429900
P	-1.51387800	-0.13048200	-0.70299300
N	-2.70103100	-1.12198800	-0.39275800

### TS3

<i>Zero-point correction=</i>	<i>0.023196</i>
<i>Thermal correction to Energy=</i>	<i>0.029454</i>
<i>Thermal correction to Enthalpy=</i>	<i>0.030398</i>
<i>Thermal correction to Gibbs Free Energy=</i>	<i>-0.007855</i>
<i>Sum of electronic and zero-point Energies=</i>	<i>-735.436822</i>
<i>Sum of electronic and thermal Energies=</i>	<i>-735.430565</i>
<i>Sum of electronic and thermal Enthalpies=</i>	<i>-735.429620</i>
<i>Sum of electronic and thermal Free Energies=</i>	<i>-735.467873</i>

N	0.07354500	-0.00352300	0.03754700
P	-0.03708300	0.01520800	1.63729600
N	1.62356500	-0.03290300	1.92886200
N	2.24358500	0.91597700	2.43039100
N	2.90263300	1.70632300	2.86890000
O	-0.93130400	-1.03000300	2.14225400
F	-0.38586600	1.40957800	2.27328900

### TS4

<i>Zero-point correction=</i>	<i>0.021691</i>
<i>Thermal correction to Energy=</i>	<i>0.028197</i>
<i>Thermal correction to Enthalpy=</i>	<i>0.029141</i>
<i>Thermal correction to Gibbs Free Energy=</i>	<i>-0.009638</i>
<i>Sum of electronic and zero-point Energies=</i>	<i>-735.460832</i>
<i>Sum of electronic and thermal Energies=</i>	<i>-735.454325</i>
<i>Sum of electronic and thermal Enthalpies=</i>	<i>-735.453381</i>

*Sum of electronic and thermal Free Energies=* -735.492161

N	0.00000000	0.00000000	0.00000000
P	0.00000000	0.00000000	1.60093800
N	1.40652200	0.00000000	0.55384200
N	2.11478000	-1.20418800	0.37297400
N	2.92118400	-1.84206600	-0.05127500
O	-0.32603900	-1.00833800	2.59694300
F	-0.01320700	1.43392300	2.20552500

### **TS5**

*Zero-point correction=* 0.021629  
*Thermal correction to Energy=* 0.028157  
*Thermal correction to Enthalpy=* 0.029101  
*Thermal correction to Gibbs Free Energy=* -0.009688  
*Sum of electronic and zero-point Energies=* -735.461181  
*Sum of electronic and thermal Energies=* -735.454653  
*Sum of electronic and thermal Enthalpies=* -735.453709  
*Sum of electronic and thermal Free Energies=* -735.492498

N	0.00000000	0.00000000	0.00000000
P	0.00000000	0.00000000	1.59842000
N	1.40520300	0.00000000	0.54199700
N	2.14725300	1.16912500	0.30525400
N	2.98271000	1.76525400	-0.12433700
O	-0.33772700	-0.99141400	2.60258400
F	-0.00341800	1.44733800	2.20470800

### **TS6**

*Zero-point correction=* 0.013335  
*Thermal correction to Energy=* 0.017846  
*Thermal correction to Enthalpy=* 0.018790  
*Thermal correction to Gibbs Free Energy=* -0.014617  
*Sum of electronic and zero-point Energies=* -625.985974  
*Sum of electronic and thermal Energies=* -625.981463  
*Sum of electronic and thermal Enthalpies=* -625.980519  
*Sum of electronic and thermal Free Energies=* -626.013926

N	0.00000000	0.00000000	0.00000000
F	0.00000000	0.00000000	2.71685200
O	2.40596500	0.00000000	1.75607400
P	0.97556000	-0.21173800	1.50405300

N	0.22532400	1.09725600	0.44091500
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**TS7**

Zero-point correction=			0.020925
Thermal correction to Energy=			0.027876
Thermal correction to Enthalpy=			0.028820
Thermal correction to Gibbs Free Energy=		-0.011221	
Sum of electronic and zero-point Energies=			-735.479267
Sum of electronic and thermal Energies=			-735.472317
Sum of electronic and thermal Enthalpies=			-735.471373
Sum of electronic and thermal Free Energies=			-735.511414

N	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	2.80480200
P	0.70431300	0.00000000	1.51880300
N	-1.06999400	0.65205400	-0.20128600
N	-1.19065500	1.20268000	-1.51678900
N	-1.79758000	1.57624300	-2.37306100
F	1.68038200	-1.22357600	1.34602100

**TS8**

Zero-point correction=			0.020779
Thermal correction to Energy=			0.027785
Thermal correction to Enthalpy=			0.028729
Thermal correction to Gibbs Free Energy=		-0.011418	
Sum of electronic and zero-point Energies=			-735.478143
Sum of electronic and thermal Energies=			-735.471137
Sum of electronic and thermal Enthalpies=			-735.470193
Sum of electronic and thermal Free Energies=			-735.510340

N	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	2.70084100
P	0.78753400	0.00000000	1.46702600
N	0.53440400	0.46239900	-1.05407200
N	0.16272300	-0.22269300	-2.25629100
N	0.00228300	-0.25888700	-3.35805800
F	1.88598400	1.14425500	1.42921800