Theoretical Prediction of a New Dinitrogen Reduction Process: The Utilization of four Dihydrogen Hydrogen Molecules and Zr₂Pt₂ Clusters

Djamaladdin G. Musaev*

Cherry L. Emerson Center for Scientific Computation, Emory University, 1515 Dickey Dr., Atlanta, GA 30322

Supporting Information Available
Total (4 pages)

Table 1S. Cartesian Coordinates (in Å) of all calculated reactants, transition states, intermediates and products of the reactions studied in this paper.

Structure I, Zr₂Pt₂: Singlet State

Zr -0.22587 1.34322 0.00000
Pt -0.22587 -0.14087 2.15324
Pt -0.22587 -0.14087 -2.15324
Zr 1.10674 -0.79382 0.00000

Structure I, Zr₂Pt₂: Triplet State

Zr -0.25716 1.46777 0.00000
Pt -0.25716 -0.17246 1.98328
Pt -0.25716 -0.17246 -1.98328
Zr 1.26009 -0.79516 0.00000

Structure I, Zr₂Pt₂: Quintet State

Zr -0.38298 1.97119 0.00000
Pt -0.38298 -0.72007 1.21483
Pt -0.38298 -0.72007 -1.21483
Zr 1.87662 0.83706 0.00000

Structure II: Zr₂Pt₂(□-1,2-N₂); Singlet State

Zr 0.00012 -0.69224 1.43616
Pt 1.82898 -0.37309 -0.41237
Pt -1.82896 -0.37320 -0.41236
Zr -0.00004 1.50750 -0.38364
N -0.00033 2.44132 1.38376
N -0.00031 1.21580 1.79172

Structure II: Zr₂Pt₂(□-1,2-N₂); Triplet State

Zr -0.00002 -0.97034 1.25717
Pt 1.83280 -0.27995 -0.44322
Pt -1.83283 -0.27987 -0.44322
Zr 0.00006 1.51459 -0.19423
N 0.00063 2.17817 1.85146
N -0.00055 0.94982 1.95210

Structure II: Zr₂Pt₂(□-1,2-N₂); Quintet State

Zr 0.00045 -1.48811 0.51881
Pt 1.84949 -0.00044 -0.48808
Pt -1.84948 -0.00080 -0.48812
Zr -0.00040 1.49181 0.51952
N -0.00039 0.60400 2.46766
N 0.00001 -0.61134 2.47678

TS1 (Isomer_2): Singlet State:

Zr 0.09032 -1.36685 0.84110
Zr -0.05091 1.47140 0.35988
H 0.94706 -2.05069 2.50134
H 0.84177 -0.79355 2.52934
N -0.05828 0.13785 2.13046
N -0.05548 1.40507 2.38190
Pt -1.88763 -0.11531 -0.52073
Pt 1.85470 -0.04031 -0.56461

TS1 (Isomer_2): Triplet State:

Zr 0.00010 -0.76670 1.26738
Zr -0.00004 1.37925 -0.41915

H -0.00186 -0.470793 2.28556
H -0.001270 6.1116 2.83807
N 0.00057 1.28890 1.77358
N -0.000822 5.1545 1.43444
Pt -1.98156 -0.32872 -0.40072
Pt 1.98159 -0.32862 -0.40068

TS1, III : Singlet State

Zr -0.00256 -0.69700 1.42439
Zr -0.02420 1.47972 -0.42618
N -0.04636 1.20019 1.76970
N 0.08386 2.46546 1.43110
Pt -1.82287 -0.42823 -0.40120
Pt 1.85299 -0.38472 -0.39853
H -0.71271 3.09000 0.53843
H -0.82865 3.35145 -0.49309

Structure, IV_Isomer_2: Singlet State:

Zr 0.02008 -1.13147 1.02610
Zr -0.05056 1.61546 -0.03254
H 0.14939 -2.78321 1.97510
H 0.92991 0.87231 2.62205
N 0.07006 0.72975 2.07987
N -0.53938 1.95806 1.78429
Pt -1.86210 -0.27197 -0.47007
Pt 1.90601 -0.19295 -0.44516

Structure, IV_Isomer_2: Quintet State:

Zr -0.00345 1.49338 -1.06159
Zr -0.00053 0.10524 1.80230
H -0.00404 2.03871 -2.88170
H -0.01263 3.96016 0.88766
N -0.00846 3.01345 0.50641
N -0.00580 2.05286 1.38417
Pt 1.36768 -0.67234 -0.26174
Pt -1.36415 -0.67904 -0.26221

Structure, IV: Singlet State:

Zr 0.00219 -1.23935 1.08833
Zr -0.00242 1.60666 0.06420
N -0.00009 0.30315 2.15679
N -0.00258 1.67381 2.12709
Pt -1.79427 -0.21839 -0.50092
Pt 1.79480 -0.21595 -0.50110
H -0.00415 2.12899 3.03296
H -0.00932 3.21803 -0.96411

TS2 (Isomer_2): Singlet State:

Zr 0.03304 -1.00594 1.14818
Zr -0.05880 1.56752 -0.22229
H 0.17160 -2.56358 2.22959

H 0.94541 1.24748 2.52466
N 0.12179 1.00261 1.96872
N -0.64012 2.13913 1.63058
Pt -1.86005 -0.36732 -0.44290
Pt 1.90462 -0.27283 -0.42677
H 0.10206 3.59481 -0.03849
H -0.03753 3.19786 0.88754

TS2 (Isomer_2): Triplet State:

Zr 0.00023 1.49502 -0.08693
Zr -0.00020 -1.19703 0.91219
H -0.00001 2.82252 -1.45153
H 0.00040 2.45824 2.89424
N 0.00036 1.93465 2.02198
N 0.00038 0.61186 2.14027
Pt 1.97103 -0.21278 -0.44538
Pt -1.97105 -0.21255 -0.44545
H -0.00293 -1.47196 2.96297
H -0.00233 -0.37762 2.93330

TS2, V; Singlet State:

Zr 0.08908 -1.43654 0.73802
Zr -0.06027 1.53875 0.35634
N -0.03800 -0.13312 2.16294
N 0.05117 1.20696 2.43712
Pt -1.85126 -0.12469 -0.51783
Pt 1.82258 -0.04074 -0.55915
H -0.38243 1.46835 3.31832
H -0.16155 3.30628 -0.33519
H 0.69063 -1.18798 2.60915
H 0.84600 -2.28873 2.43723

Structure VI: Singlet State:

Zr -0.05353 -1.52871 0.49822
Zr 0.05348 1.53003 0.49461
H 0.03115 -3.40134 0.24080
H 0.80463 -0.92979 3.12493
N 0.14910 -0.69759 2.38107
N -0.15057 0.70615 2.38015
Pt -1.84805 0.01086 -0.51142
Pt 1.84820 -0.01244 -0.51117
H -0.03108 3.40149 0.22938
H -0.80413 0.94009 3.12512

Structure VI: Triplet State:

Zr -0.19707 -1.69323 0.76514
Zr 0.19656 1.69632 0.75934
H -0.27124 -3.57908 0.65984
H 0.34172 -1.06818 3.45746
N 0.00721 -0.70694 2.56612
N -0.00985 0.71732 2.56408
Pt -1.39773 0.12612 -0.67447

Pt 1.39827 -0.12884 -0.67308
H 0.27104 3.58163 0.64615
H -0.345191.08114 3.45404

TS3, Structure, VII: Singlet State:

Zr -0.08964 -1.530000.43654
Zr 0.08643 1.56226 0.40965
H 0.19916 -3.28033 -0.17010
H 0.98206 -0.706863.02404
N 0.18959 -0.481842.42344
N -0.051300.92803 2.36486
Pt -1.869490.03220 -0.50044
Pt 1.86957 -0.04649 -0.49956
H 0.08247 3.39652 -0.03145
H -0.519671.26123 3.20289
H -0.93622 -2.435742.11874
H -0.65384 -1.533772.49019

TS3, Structure, VII: Triplet State:

Zr -0.40025 -0.797171.60149
Zr 0.20994 1.81830 -0.44142
H -0.18703 -2.411432.54025
H 0.00380 1.51070 3.35464
N -0.348251.24370 2.43584
N -0.335182.32320 1.51080
Pt -1.23607 -0.41029 -0.82783
Pt 1.45078 -0.50920 -0.25825
H 0.49048 3.13022 -1.77057
H -0.855893.12047 1.87000
H -2.22945 -0.105262.20981
H -1.572950.66240 2.48154

Structure VIII: Singlet State:

Zr -0.00008 -1.524020.61910
Zr -0.000111.57721 -0.08609
H 0.00020 -3.22734 -0.16995
H 0.83606 0.32203 2.93521
N 0.00335 0.53440 2.38967
N -0.000911.90316 1.94100
Pt -1.93468 -0.12912 -0.39202
Pt 1.93443 -0.12907 -0.39248
H 0.00031 3.04246 -1.26778
H -0.005142.58150 2.69455
H 0.00058 -2.090402.41971
H -0.822530.31960 2.94453

Structure VIII: Triplet State:

Zr 0.96501 1.66226 0.49348
Zr -0.78954 -1.439660.82054
H 0.34013 3.04068 -0.62007
H -0.341231.40652 3.10702
N 0.25697 0.71831 2.64805

N -0.37955 -0.578532.66801
Pt 1.23240 -0.71480 -0.64361
Pt -1.324340.54158 -0.65823
H -1.68054 -3.097500.67624
H -0.52782 -0.898073.62230
H 2.08519 2.47974 1.81684
H 1.13531 0.69735 3.16819

TS4, IX; Singlet State:

Zr -0.05075 -1.586220.48530
Zr 0.07123 1.58815 -0.06544
H -0.08587 -3.23147 -0.41770
H 0.47807 -0.125763.21496
N -0.188460.10113 2.47863
N -0.168311.50778 2.16753
Pt -1.93261 -0.06494 -0.42100
Pt 1.94664 -0.13360 -0.36819
H -0.085982.99414 -1.28091
H -0.593582.08726 2.88639
H -0.12581 -2.446322.16530
H -1.11893 -0.157772.80565
H 1.26396 2.85040 1.06125
H 0.85197 2.17614 1.80472

Structure X: Singlet State:

Zr 0.03271 1.63381 0.06095
Zr -0.03264 -1.633820.06117
H 0.02544 2.99464 -1.22815
H -0.232291.20709 3.17631
N 0.17915 0.70371 2.39126
N -0.17999 -0.703052.39143
Pt 1.99895 -0.02749 -0.31961
Pt -1.998880.02742 -0.31974
H -0.02581 -2.99454 -1.22803
H 0.23107 -1.206133.17688
H 0.18704 3.02193 1.32635
H 1.19353 0.75376 2.47789
H -0.18643 -3.021871.32671
H -1.19442 -0.753032.47752

Structure XI: Singlet State:

Zr -0.000081.66329 0.00069
Zr 0.00008 -1.663290.00070
H -0.000262.73389 -1.51916
Pt 1.97674 0.00004 -0.00041
Pt -1.97675 -0.00004 -0.00038
H 0.00024 -2.73390 -1.51915
H -0.000182.73176 1.52203
H 0.00021 -2.731761.52204

Table 2S. The energies (in a.u.) of the reactants, intermediates, transition states and products studied in this paper.

Molecules	State	E _{tot}	E + ZPC	H	G
H ₂		-1.179571	-1.169509	-1.166205	-1.181001
N ₂		-109.559694	-109.554124	-109.550819	-109.572557
N ₂ H ₄		-111.910575	-111.857293	-111.853089	-111.879886
Zr ₂ Pt ₂ , I	S	-332.884720	-332.882359	-332.874871	-332.919523
	T	-332.885943	-332.883681	-332.876146	-332.921775
	Q	-332.673782	-332.672103	-332.664118	-332.712376
I + N ₂	S	-442.444414	-442.436483	-442.425690	-442.492080
	T	-442.445637	-442.437805	-442.426965	-442.494332
II	S	-442.488862	-442.479204	-442.469903	-442.517830
	T	-442.487018	-442.477427	-442.467931	-442.517305
	Q	-442.450828	-442.442217	-442.432109	-442.483272
II + H ₂	S	-443.668433	-443.648713	-443.636108	-443.698831
TS1, (Isomer_2)	S	-443.647512	-443.626354	-443.616389	-443.665416
	T	-443.633232	-443.612712	-443.602074	-443.653986
TS1, III	S	-443.656918	-443.634910	-443.625002	-443.674036
IV, Isomer_2	S	-443.693694	-443.667382	-443.657079	-443.706575
	Q	-443.650421	-443.624981	-443.613852	-443.666862
IV	S	-443.719807	-443.693934	-443.683295	-443.733320
IV, Isom_2 + H ₂	S	-444.873265	-444.836891	-444.823284	-444.887576
IV + H ₂	S	-444.899378	-444.863443	-444.849500	-444.914321
TS2, (Isomer_2)	S	-444.869540	-444.829949	-444.819180	-444.869463
	T	-444.842978	-444.805495	-444.793652	-444.847547
V, TS2	S	-444.882180	-444.843819	-444.832677	-444.883547
VI	S	-444.942069	-444.898963	-444.887251	-444.939933
	T	-444.893399	-444.850876	-444.838855	-444.892693
VI + H ₂	S	-446.121640	-446.068472	-446.053456	-446.120934
TS3, VII	S	-446.093279	-446.036462	-446.024249	-446.077325
	T	-446.047349	-445.990786	-445.978436	-446.032671
VIII	S	-446.132123	-446.069832	-446.057152	-446.111361
VIII + H ₂	S	-447.311694	-447.239341	-447.223357	-447.292362
TS4, IX	S	-447.271648	-447.195436	-447.182283	-447.237261
X	S	-447.300073	-447.218667	-447.204971	-447.261108
XI	S	-335.356142	-335.331560	-335.321305	-335.370837
	T	-335.282298	-335.258913	-335.247970	-335.300292
XI + N ₂ H ₄	S	-447.266717	-447.188853	-447.174394	-447.250723