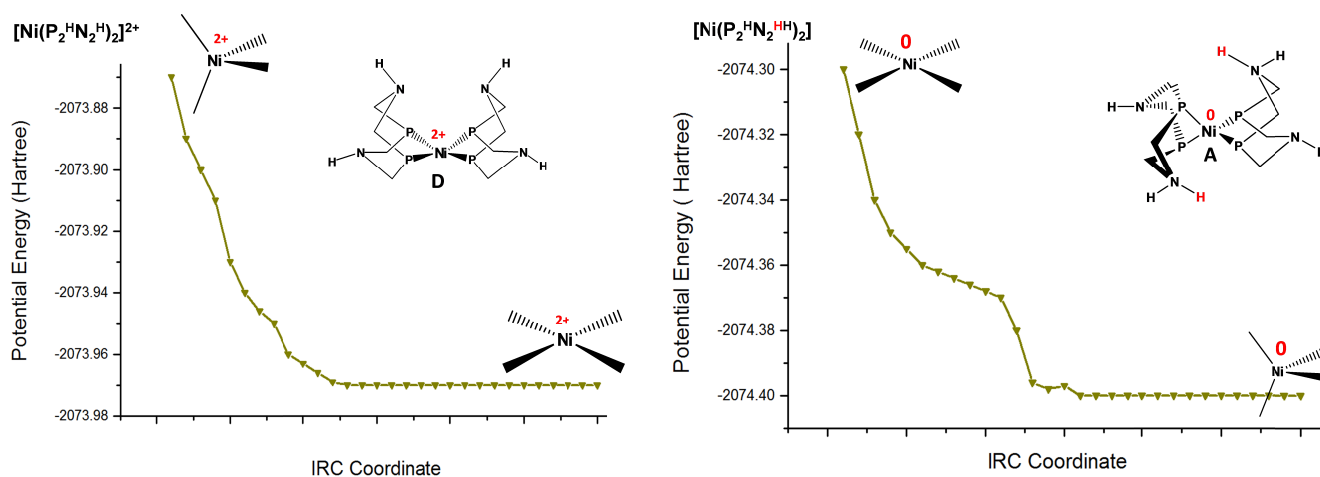


Supporting information

Efficient and Cyclic Hydrogen Evolution Reaction Mechanism on $[\text{Ni}(\text{P}^{\text{H}}_2\text{N}^{\text{H}}_2)_2]^{2+}$ Catalysts: A Theoretical and Multiscale Simulation Study

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S1. Schematic representation of potential energy profiles of $\text{Ni}(\text{P}_2^{\text{H}}\text{N}_2^{\text{H}})_2^{2+}$ (D) and $\text{Ni}(\text{P}_2^{\text{H}}\text{N}_2^{\text{HH}})_2^{2+}$ (A) along with the reaction coordinate change between square planar and tetrahedral for oxidation state +2(D) and 0 (A)



Cartesian coordinates of reactive species

A

Ni	-0.00146700	-0.11377500	0.02290300
P	-1.68857900	-0.67026100	1.41475300
P	-1.55312800	0.80965700	-1.37229500
N	-2.46525600	-1.82719600	-1.02986200
N	-3.51784900	1.27151600	0.55662700
C	-2.92183400	-1.77634600	0.43039800
H	-2.90556500	-2.79745700	0.81940500
H	-3.93189900	-1.36449400	0.46237000
C	-2.78888200	-0.57972000	-1.85922800
H	-3.81980900	-0.28798900	-1.65116000
H	-2.66812800	-0.84222900	-2.91338200
C	-2.84941800	0.84362100	1.78135800
H	-3.59874400	0.54021400	2.51817500
H	-2.20850200	1.61886600	2.22857800
C	-2.76523200	2.00759000	-0.45524900
H	-2.14581300	2.81907800	-0.04290000
H	-3.45881400	2.43595700	-1.18471800
P	1.54855500	1.41096300	0.73133400
P	1.69883300	-1.31774100	-0.85223300
N	3.53542400	0.78410300	-1.12704300
N	2.43948600	-1.01011500	1.84149000
C	2.77778000	1.94349600	-0.66377300
H	2.16784900	2.41727600	-1.44859300
H	3.46721300	2.69097000	-0.26049800
C	2.87454900	-0.22393300	-1.94989600
H	3.62805800	-0.87034000	-2.40882400
H	2.24341000	0.20053500	-2.74561400
C	2.76622200	0.48541800	1.89558800
H	3.80351200	0.62303000	1.58512200
H	2.62704600	0.81756400	2.92768700
C	2.91325600	-1.73939000	0.58204600
H	2.89139700	-2.81184000	0.79083000
H	3.92726800	-1.40911200	0.35064800
H	1.43698800	2.63717500	1.47326600
H	4.49726500	0.98171700	-1.38746600
H	1.79052300	-2.57368700	-1.55340600
H	-2.85641600	-2.66073300	-1.48926400
H	-1.44496700	1.45828500	-2.65050000
H	-1.77791900	-1.36845800	2.67313700
H	-4.47664500	1.58262700	0.68242500
H	2.81393300	-1.47818700	2.67777800
H	-1.41263600	-1.88389100	-0.99595900
H	1.38597100	-1.07101600	1.82227800

TS_{AB}

Ni	-0.02301500	0.08867400	0.18047300
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P	1.77020700	0.05713100	1.53043900
P	1.46224300	-0.23328900	-1.57781800
N	2.43529400	2.08717200	-0.29170100
N	3.51825100	-1.38990400	-0.08974800
C	2.95538000	1.47736800	1.01492200
H	2.95512800	2.26621600	1.77151500
H	3.96804200	1.10981000	0.84050300
C	2.68271800	1.24728000	-1.55149000
H	3.71902100	0.90498000	-1.53083500
H	2.51120200	1.89357300	-2.41624500
C	2.92970100	-1.46626600	1.24415600
H	3.72338000	-1.45159900	1.99662600
H	2.30785500	-2.35958800	1.40547600
C	2.69171300	-1.69155600	-1.25450400
H	2.07304300	-2.59415600	-1.13842800
H	3.33043600	-1.81655400	-2.13332600
P	-1.59989300	-1.62128000	0.22551900
P	-1.70392300	1.55700100	-0.37263500
N	-3.55026800	-0.33814600	-1.30512900
N	-2.27398700	0.35005900	2.03261900
C	-2.84240700	-1.60947800	-1.25501400
H	-2.25773700	-1.82268700	-2.16361400
H	-3.56146700	-2.42116900	-1.11097100
C	-2.87503300	0.86482100	-1.76006900
H	-3.61490500	1.63526300	-1.99553300
H	-2.24455300	0.70515200	-2.64833400
C	-2.71023100	-1.03549000	1.68573800
H	-3.76347300	-1.06693800	1.39461100
H	-2.54522700	-1.68897600	2.54576900
C	-2.82101500	1.45469500	1.19358700
H	-2.75572600	2.39559600	1.74490600
H	-3.85655700	1.26636200	0.89932300
H	-1.48475600	-3.02765300	0.48627000
H	-4.54197400	-0.39290900	-1.50958400
H	-1.74252600	2.96511300	-0.66566400
H	2.84218200	3.02434400	-0.42012200
H	1.25570800	-0.32829700	-2.99380000
H	1.81804700	0.20916300	2.95411600
H	4.47742700	-1.71908600	-0.15191100
H	-2.33654800	0.54494200	3.03441500
H	1.39356500	2.15966200	-0.18248600
H	-0.92465900	0.32060400	1.52527200

B

Ni	-0.02064100	-0.37490000	-0.38573300
P	1.35039600	1.42986100	-0.27321500
P	1.65992400	-1.53672000	0.32860700
N	2.73078700	-0.32726600	-1.93827400
N	3.15235800	0.41677300	1.51809900

C	2.81546100	1.10355700	-1.43667700
H	2.75758200	1.75383000	-2.32251800
H	3.78564100	1.22819000	-0.93393600
C	3.05901900	-1.40888100	-0.93513900
H	4.00948500	-1.15171700	-0.44537100
H	3.15045100	-2.35450100	-1.49078700
C	2.29356800	1.58849400	1.35805900
H	2.92706700	2.48918800	1.33292100
H	1.54042600	1.71911700	2.16349300
C	2.50201000	-0.84032800	1.86576900
H	1.73074600	-0.76076700	2.66098200
H	3.26466100	-1.56115500	2.20309800
P	-1.38640200	-0.40338800	1.37406000
P	-1.81060100	0.20791600	-1.45677200
N	-3.68702500	-1.01415800	0.06648700
N	-1.88491200	2.14826100	0.51269300
C	-2.83588400	-1.57765000	1.10307000
H	-2.42110400	-2.58339700	0.87730800
H	-3.41202200	-1.64229300	2.04034600
C	-3.19115400	-1.05684200	-1.29937200
H	-4.00283100	-0.76510400	-1.98609300
H	-2.78692500	-2.03724800	-1.62980800
C	-2.21404300	1.26984800	1.63604500
H	-3.29941200	1.08385500	1.77159800
H	-1.80981800	1.70821600	2.56211500
C	-2.54051100	1.79972600	-0.74530100
H	-2.35889300	2.60095100	-1.47907400
H	-3.63429000	1.62888900	-0.66240200
H	0.12249000	-1.11646600	-1.69195900
H	1.71638800	-0.49282000	-2.19667100
H	3.92153700	0.61506100	2.16206500
H	1.10685700	2.79330100	-0.60536800
H	3.32111100	-0.44249200	-2.77847600
H	1.64752100	-2.94426800	0.56028800
H	-1.72368000	0.44479600	-2.85551800
H	-4.64603300	-1.35892500	0.13249200
H	-0.93684400	-0.77490100	2.67491300
H	-2.10117300	3.11999100	0.75494500

TS_{BC}

Ni	-0.03003000	-0.11674100	-0.40742600
P	-1.56074500	1.49092000	0.07865500
H	-1.15167700	2.85813200	0.13476500
P	1.69517700	1.27268200	-0.91703300
H	1.50091100	2.38327000	-1.79453200
P	1.74284400	-1.20825500	1.03165400
H	1.65273700	-2.35464200	1.88358000
P	-1.79008200	-1.50329500	-0.11790600
H	-1.51543400	-2.89545000	-0.25802000
C	2.65453200	2.00986300	0.59786500

N	3.45445400	0.98162500	1.22764100
H	4.41006200	1.23297800	1.45545300
C	3.02484500	0.19585100	-1.79324000
N	2.70473100	-1.23964200	-1.61027000
C	2.82788600	-0.01259400	2.08984500
C	3.01683600	-1.82812500	-0.27448100
C	-3.19047600	-1.07676200	-1.42930500
N	-3.78051200	0.22033100	-1.22566500
H	-4.57206500	0.24263600	-0.59402500
C	-2.58016500	-1.31968900	1.62755800
N	-3.21005200	-0.01571100	1.76097200
H	-4.07962500	0.01099700	2.28224900
C	-3.00059000	1.42413200	-1.28074300
C	-2.40765300	1.19616500	1.78940800
H	3.29955200	2.80774500	0.21865900
H	1.89980200	2.45900100	1.26042000
H	2.16964200	0.42226700	2.85750100
H	3.60470300	-0.59590000	2.59228300
H	3.02008000	0.43485700	-2.85941300
H	3.99424500	0.45651400	-1.35478300
H	4.02758800	-1.56188500	0.05558200
H	2.93811800	-2.91590700	-0.34716200
H	-3.63881800	2.29783000	-1.12578500
H	-2.47623400	1.52795500	-2.23627300
H	-2.69130700	-1.15025500	-2.40145300
H	-3.95717600	-1.85348800	-1.36703500
H	-1.59544800	1.17882900	2.53420000
H	-3.05053900	2.05557400	2.00274500
H	-3.33316400	-2.10468000	1.74731700
H	-1.77153000	-1.50474900	2.35335200
H	0.31820800	-1.08091500	-1.73012700
H	1.21071400	-1.20904200	-1.68652000
H	3.06794100	-1.81298100	-2.37575400

C

Ni	0.00008300	-0.21974400	-0.00041900
P	1.64301300	0.04770900	-1.45709200
P	1.64278900	0.04383000	1.45728100
N	2.69957500	-2.02102000	-0.00250000
N	3.32441200	1.58942300	0.00204500
C	2.96104800	-1.29112800	-1.23200900
H	2.88430100	-1.98010400	-2.08766300
H	3.94236300	-0.77416800	-1.26734200
C	2.96075200	-1.29455500	1.22908000
H	3.94211300	-0.77779900	1.26620400
H	2.88361300	-1.98584800	2.08283100
C	2.57166500	1.66890300	-1.23674700
H	3.27408700	1.77099000	-2.08047100
H	1.83702100	2.50068800	-1.29536400
C	2.57152600	1.66557200	1.24095800

H	1.83680600	2.49714700	1.30169500
H	3.27386600	1.76555400	2.08500100
P	-1.64286100	0.04803300	-1.45709400
P	-1.64294800	0.04356800	1.45712600
N	-3.32484900	1.58906100	0.00235600
N	-2.69914200	-2.02125600	-0.00318900
C	-2.57182500	1.66906800	-1.23621700
H	-1.83724000	2.50093700	-1.29432000
H	-3.27402800	1.77141500	-2.08008500
C	-2.57217700	1.66505800	1.24139900
H	-3.27464700	1.76436500	2.08541600
H	-1.83783100	2.49693000	1.30255200
C	-2.96073600	-1.29098500	-1.23249300
H	-3.94209400	-0.77409700	-1.26762700
H	-2.88395800	-1.97971300	-2.08834600
C	-2.96047900	-1.29510400	1.22859400
H	-2.88305900	-1.98659200	2.08216800
H	-3.94204600	-0.77874800	1.26590100
H	-1.31966000	0.02641200	2.84399900
H	1.31973500	0.03394700	-2.84400700
H	3.14714000	-2.94035900	-0.00373900
H	-1.31969900	0.03514300	-2.84404900
H	4.13510300	2.21052700	0.00293100
H	-4.13571300	2.20993900	0.00324800
H	-3.14697500	-2.94048100	-0.00468400
H	1.31946500	0.02734900	2.84415900
H	-0.39847900	-2.11115000	-0.00330600
H	0.39898200	-2.11097000	-0.00306600

TS_{cc}

Ni	-0.00000048	-0.34316500	-0.00002168
P	-1.64077707	-0.00028289	1.45329395
P	-1.64076792	-0.00009600	-1.45330354
N	-2.88450675	-1.96118394	-0.00013480
N	-3.17563211	1.69192796	0.00009918
C	-3.07372307	-1.21379168	1.22871141
H	-3.05358874	-1.90728871	2.08414389
H	-4.00329786	-0.60749539	1.27556322
C	-3.07371533	-1.21363366	-1.22888608
H	-4.00328983	-0.60733135	-1.27566577
H	-3.05357561	-1.90702068	-2.08440760
C	-2.42096376	1.69926021	1.23943102
H	-3.11285668	1.86015296	2.08266269
H	-1.61577238	2.46310003	1.30241742
C	-2.42095595	1.69941958	-1.23922697
H	-1.61576418	2.46326750	-1.30211007
H	-3.11284357	1.86042077	-2.08244229
P	1.64076793	-0.00028750	1.45330428
P	1.64077708	-0.00010061	-1.45329321
N	3.17563689	1.69191903	0.00011917

N	2.88450125	-1.96119205	-0.00011663
C	2.42096074	1.69925340	1.23944627
H	1.61577112	2.46309548	1.30242760
H	3.11284882	1.86014421	2.08268229
C	2.42096855	1.69941278	-1.23921172
H	3.11286193	1.86041202	-2.08242269
H	1.61577932	2.46326295	-1.30209989
C	3.07371193	-1.21380033	1.22873077
H	4.00328814	-0.60750665	1.27558843
H	3.05357026	-1.90729730	2.08416311
C	3.07371967	-1.21364231	-1.22886672
H	3.05358339	-1.90702927	-2.08438837
H	4.00329617	-0.60734261	-1.27564056
H	1.31691538	-0.04629103	-2.83939470
H	-1.31691550	-0.04665247	2.83938949
H	-3.41318098	-2.83595069	-0.00019271
H	1.31689750	-0.04665617	2.83939778
H	-3.93085765	2.37918702	0.00014099
H	3.93086435	2.37917596	0.00016574
H	3.41317302	-2.83596029	-0.00017122
H	-1.31689762	-0.04628733	-2.83940299
H	-0.00000186	-2.20054838	-0.39069911
H	-0.00000432	-2.20059860	0.39041689

TS_{CD}

Ni	0.02020672	-0.12178762	-0.00026964
P	1.66313672	0.14566538	-1.45694264
P	1.66291272	0.14178638	1.45743036
N	2.71969872	-1.92306362	-0.00235064
N	3.34453572	1.68737938	0.00219436
C	2.98117172	-1.19317162	-1.23185964
H	2.90442472	-1.88214762	-2.08751364
H	3.96248672	-0.67621162	-1.26719264
C	2.98087572	-1.19659862	1.22922936
H	3.96223672	-0.67984262	1.26635336
H	2.90373672	-1.88789162	2.08298036
C	2.59178872	1.76685938	-1.23659764
H	3.29421072	1.86894638	-2.08032164
H	1.85714472	2.59864438	-1.29521464
C	2.59164972	1.76352838	1.24110736
H	1.85692972	2.59510338	1.30184436
H	3.29398972	1.86351038	2.08515036
P	-1.62273728	0.14598938	-1.45694464
P	-1.62282428	0.14152438	1.45727536
N	-3.30472528	1.68701738	0.00250536
N	-2.67901828	-1.92329962	-0.00303964
C	-2.55170128	1.76702438	-1.23606764
H	-1.81711628	2.59889338	-1.29417064
H	-3.25390428	1.86937138	-2.07993564
C	-2.55205328	1.76301438	1.24154836

H	-3.25452328	1.86232138	2.08556536
H	-1.81770728	2.59488638	1.30270136
C	-2.94061228	-1.19302862	-1.23234364
H	-3.92197028	-0.67614062	-1.26747764
H	-2.86383428	-1.88175662	-2.08819664
C	-2.94035528	-1.19714762	1.22874336
H	-2.86293528	-1.88863562	2.08231736
H	-3.92192228	-0.68079162	1.26605036
H	-1.29953628	0.12436838	2.84414836
H	1.33985872	0.13190338	-2.84385764
H	3.16726372	-2.84240262	-0.00358964
H	-1.29957528	0.13309938	-2.84389964
H	4.15522672	2.30848338	0.00308036
H	-4.11558928	2.30789538	0.00339736
H	-3.12685128	-2.84252462	-0.00453464
H	1.33958872	0.12530538	2.84430836
H	-0.40860219	-2.20910413	-0.00345235
H	0.36885775	-2.20892864	-0.00321837

D

Ni	-0.02143286	-0.00811898	-0.24560427
P	2.20250576	-0.15025195	-0.36263480
P	0.48402010	2.15068790	-0.04421859
N	1.97230114	1.14953837	2.02460890
N	2.82441898	2.27308840	-1.41791223
C	2.99165589	0.48548999	1.22053897
H	3.36620721	-0.39145236	1.76707656
H	3.85022149	1.12023947	0.92489791
C	1.51063383	2.43230968	1.50672040
H	2.31097906	3.15007038	1.23770639
H	0.84596837	2.89989260	2.24680960
C	2.94792104	0.86539906	-1.75558241
H	4.01402611	0.60036445	-1.81126511
H	2.46582168	0.55542484	-2.70479588
C	1.49130973	2.84920269	-1.46542130
H	0.92736145	2.67625691	-2.40439769
H	1.56318364	3.93509771	-1.30536602
P	-0.51702105	-2.17741869	-0.33757170
P	-2.24913962	0.13161015	-0.24557022
N	-2.91098321	-2.11684323	-1.61784679
N	-1.91789245	-1.50016025	1.91451268
C	-1.57985198	-2.66861583	-1.80436436
H	-1.05554998	-2.35455496	-2.72959128
H	-1.64221564	-3.76680286	-1.80299472
C	-3.05099644	-0.67582043	-1.73988794
H	-4.11891252	-0.41387573	-1.71138030
H	-2.61024322	-0.22644165	-2.65274817
C	-1.47903386	-2.69032804	1.19536006
H	-2.29046063	-3.36446957	0.85620262
H	-0.78499841	-3.25839097	1.83074804

C	-2.97047878	-0.73235377	1.25951092
H	-3.32088131	0.05382221	1.94297510
H	-3.84114389	-1.32237826	0.91128134
H	-2.84634899	1.42838500	-0.24315581
H	2.78820265	-1.43491934	-0.57423258
H	2.28295746	1.24374778	2.99411255
H	0.55771890	-3.11324926	-0.41910943
H	3.50407324	2.84535530	-1.91976627
H	-3.60965500	-2.61478246	-2.17027199
H	-2.18690796	-1.73697424	2.87200546
H	-0.58538201	3.09075337	0.05531797

TS_{DE}

Ni	0.00000000	0.00000000	0.00000000
P	2.28510830	0.00000000	0.00000000
H	2.97041416	1.25340531	0.00000000
P	-0.24291890	2.20775813	-0.53084911
H	0.88716950	3.07076614	-0.39655937
P	-2.21640784	-0.05590692	-0.54662404
H	-2.91748850	-1.29461955	-0.42804858
P	0.31167320	-2.26412239	-0.02133665
H	-0.83639159	-3.11387239	-0.04164154
C	-0.81599523	2.39657419	-2.40530625
N	-2.13709859	1.88179923	-2.65640254
H	-2.89049873	2.53804560	-2.48848115
C	-1.60360988	3.07278259	0.52414936
N	-2.91928607	2.54303207	0.19760825
H	-3.68409064	3.20894529	0.21509716
C	-2.46988423	0.50120655	-2.41796706
C	-3.26509377	1.16481415	0.51268857
C	1.35753688	-2.86649727	1.53131761
N	2.71268142	-2.37951802	1.54403023
H	3.37596203	-2.95108531	1.03393132
C	1.31584422	-2.81096179	-1.57516107
N	2.68588674	-2.32770706	-1.48804491
H	3.39836514	-2.94547730	-1.86198802
C	3.00755937	-0.97006990	1.55098479
C	2.97959579	-0.90384401	-1.55623774
H	-0.77362974	3.45827874	-2.66222957
H	-0.05709549	1.86408705	-2.98865979
H	-1.83636910	-0.17418624	-3.00301025
H	-3.51461552	0.31788969	-2.68247281
H	-1.30791315	2.92884333	1.57504857
H	-1.57753772	4.14407943	0.30247116
H	-4.32158488	0.99364692	0.28485235
H	-3.08657457	0.88408294	1.56235479
H	4.08953032	-0.81419989	1.56388691
H	2.56669010	-0.46723701	2.41690944
H	0.79042232	-2.51119864	2.39685639
H	1.35295059	-3.95962995	1.52922417

H	2.54178012	-0.39610218	-2.43113315
H	4.06368266	-0.75733612	-1.58377058
H	1.31811264	-3.90439895	-1.61585535
H	0.76169332	-2.43551902	-2.45090589
N	-0.26342045	0.20900190	2.22473097
C	-0.42311664	0.33618302	3.57943466
C	-0.59437525	0.47249236	5.02798519
H	0.35509512	0.25561332	5.54936171
H	-0.90725183	1.50047400	5.28312498
H	-1.36295494	-0.23263163	5.39166404

E

Ni	0.18246986	0.27164198	0.43497931
P	2.32135913	0.07001823	-0.12470323
H	2.84327263	1.36011747	-0.24400804
P	-0.03031972	2.23643974	-0.57333143
H	1.22938087	2.84673821	-0.56129910
P	-1.96954669	0.07107494	-0.06754672
H	-2.38142956	-1.19205457	0.37040049
P	0.21474424	-1.94724996	0.33958991
H	-1.08692188	-2.39578127	0.60361064
C	-0.60854875	2.05730667	-2.34141416
N	-2.00565070	1.57181595	-2.42939245
H	-2.58049855	2.20318038	-1.90945478
C	-1.27077981	3.28457201	0.36094554
N	-2.66724646	2.76774547	0.23112843
H	-3.26085054	3.41138614	0.71971738
C	-2.26402507	0.20640729	-1.91012712
C	-2.94287870	1.41560271	0.80258001
C	1.40324184	-2.60532935	1.62347759
N	2.82860482	-2.30667901	1.28649234
H	3.01070024	-2.70507458	0.38461425
C	0.74148158	-2.56535891	-1.35154906
N	2.16552538	-2.26970921	-1.64908624
H	2.36811391	-2.67837361	-2.53852859
C	3.22768458	-0.86881090	1.22136703
C	2.54014103	-0.83698276	-1.74817837
H	-0.57481158	3.02309850	-2.80047279
H	0.04426571	1.38338434	-2.85989873
H	-1.63886315	-0.49514905	-2.41837676
H	-3.29360518	-0.01831646	-2.09933975
H	-0.99230847	3.31768249	1.39436271
H	-1.25086072	4.27037506	-0.05442322
H	-3.98530235	1.21982703	0.66590928
H	-2.70086398	1.40361558	1.84680041
H	4.27505412	-0.83654700	1.00313160
H	3.03432967	-0.39814002	2.16122459
H	1.15546516	-2.18056892	2.57631048
H	1.29855927	-3.67034219	1.66315285
H	1.94974108	-0.35561669	-2.49714907

H	3.57572540	-0.79789436	-2.01657923
H	0.62203337	-3.62803671	-1.36364088
H	0.11887290	-2.11915380	-2.10050706
N	0.36803994	0.81673321	2.19115200
C	-0.35850497	0.19305260	3.17496149
C	-1.02195826	-0.36652872	4.42240336
H	-0.28676671	-0.85918187	5.02566929
H	-1.46540889	0.43255845	4.97800649
H	-1.77830538	-1.06981412	4.14204654