

Supporting information

Hydrogenation of Dinitrogen to Ammonia in [WF(PH₂(CH₂)₂PH₂)₂N₂] Using H₂: Insights From DFT Calculations

Perumal Balu^b, Sambath Baskaran^a, Venu Kannappan^b and Chinnappan Sivasankar^{a*}

^aDepartment of Chemistry, School of Physical, Chemical and Applied Sciences Pondicherry

University, Puducherry 605 014, India

^bPostgraduate and Research Department of Chemistry, Presidency College,

Chennai 600 005. Tamil Nadu India.

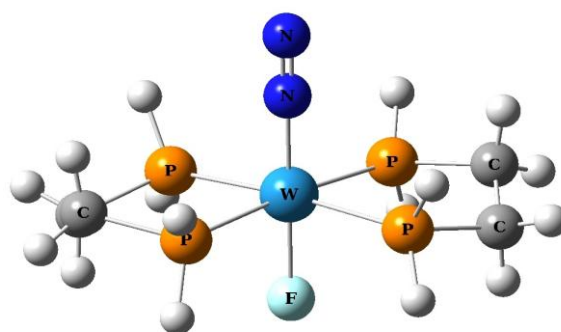
Table S1. Calculated energies for model systems **1-7**

S.No	Systems	Energy (Hartree)	ZPE (Hartree)	Entropy (cal/mol)	Solvation(kcal/mol)		
					Heptane	Toluene	THF
1	[F-W-N≡N] (1)	-465.174248	0.197567	141.281	-5.99	-7.71	-14.70
2	[F-W-N=N-H] ⁺ (2)	-465.5791775	0.209773	143.544	-22.67	-27.91	-44.19
3	[F-W-N-NH ₂] (3)	-466.3371628	0.219320	148.358	-5.28	-7.26	-13.42
4	[F-W≡N] ⁺ (4)	-410.2341221	0.195300	140.964	-25.41	-31.29	-50.51
5	[F-W=N-H] (5)	-411.0155501	0.202486	138.401	-5.00	-6.44	-12.52
6	[F-W-NH ₂] ⁺ (6)	-411.4746193	0.217546	141.403	-21.96	-26.80	-42.19
7	[F-W-NH ₃] (7)	-412.1906468	0.226509	142.949	-5.57	-7.51	-15.02
8	N ₂	-109.4808546	0.005165	45.885	-0.87	-0.48	-0.37
9	NH ₃	-56.54808390	0.033179	44.443	-3.05	-1.69	-1.32
10	[NH(ipr) ₂]	-292.3791170	0.206053	94.474	-2.20	-1.03	-0.76
11	[NH ₂ (ipr) ₂] ⁺	-292.7721990	0.221554	95.231	-45.02	-28.50	-23.20
12	[B(C ₆ F ₅) ₃]	-2208.2425824	0.151209	194.307	-10.23	-5.18	-3.85
13	[BH(C ₆ F ₅) ₃] ⁻	-2208.9745998	0.159494	195.337	-32.34	-20.56	-16.76

Cartesian coordinates of optimized geometries (in Å)

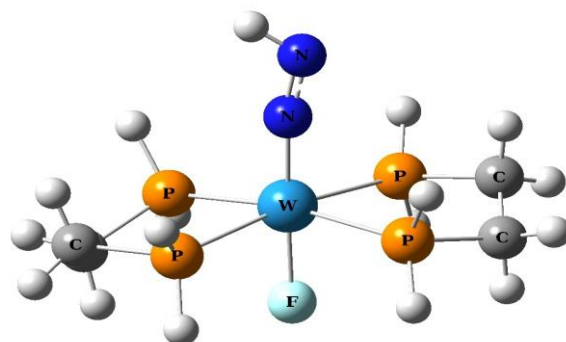
[F-W(PH₂(CH₂)₂PH₂)₂N₂] (1)

W	0.00001600	-0.00002900	0.00959200
P	-1.91490800	1.59361400	0.13689100
H	-2.10499900	2.71311200	-0.74711400
P	-1.91784500	-1.59915000	0.12422200
H	-2.28985800	-2.35153100	-1.04500400
P	1.91448300	-1.59382500	0.13857100
H	2.10482100	-2.71379600	-0.74473400
P	1.91780700	1.59953900	0.12154000
C	-3.61265500	0.70104800	-0.10570300
C	-3.58041700	-0.69698500	0.53309800
H	-3.77595800	0.63322400	-1.18821700
H	-4.41153700	1.31476100	0.32493300
H	-4.42121200	-1.31042200	0.19143500
H	-3.62738300	-0.62602600	1.62664100
F	0.00091700	0.00194600	2.06173500
N	0.00021900	-0.00100200	-1.94205100
N	0.00098000	-0.00151500	-3.12834700
H	2.29079300	2.34829600	-1.04967100
H	-2.14507300	2.27677700	1.38488000
H	-1.99256500	-2.67186800	1.08261500
C	3.57940400	0.69723300	0.53389600
C	3.61238700	-0.70129000	-0.10360200
H	4.42104000	1.31002100	0.19316100
H	3.62437900	0.62717500	1.62756900
H	3.77658200	-0.63442800	-1.18603400
H	4.41102300	-1.31439900	0.32831200
H	1.99278200	2.67482400	1.07697800
H	2.14397800	-2.27617900	1.38709500



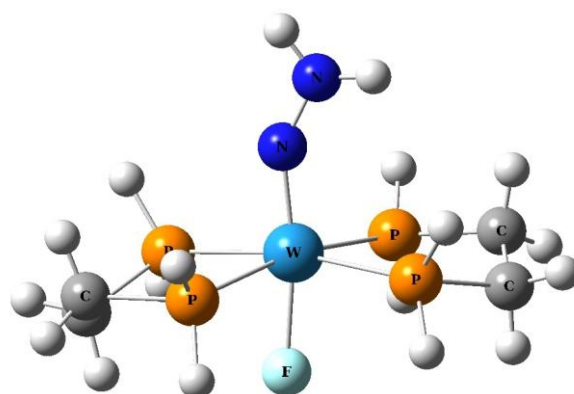
[F-W-N=NH(dpe)]⁺¹ (2)

W	-0.01527900	0.00315900	0.05048600
P	1.93392600	1.62912900	-0.23163400
H	2.13744400	2.74078000	0.64247300
P	1.91662300	-1.63814700	-0.28030300
H	2.33005500	-2.36807900	0.87615200
P	-1.98026500	-1.63261900	-0.08813600
H	-2.17818400	-2.69249000	0.84941800
P	-1.97739400	1.64378400	-0.08245400
C	3.59328100	0.67909300	-0.09535500
C	3.50658300	-0.69206700	-0.79417000
H	3.80263300	0.56405300	0.97458700
H	4.39477300	1.28241600	-0.53332800
H	4.38284800	-1.30202400	-0.55310700
H	3.46447900	-0.57680700	-1.88346900
F	-0.16419100	0.02841800	-1.92192600
N	0.19300900	-0.01981200	1.87244500
N	0.57048600	-0.04419400	3.09592400
H	-2.42070700	2.27165100	1.12268200
H	2.02909700	2.27095000	-1.50527500
H	1.85826100	-2.68945000	-1.24679000
C	-3.53311400	0.69700300	-0.68569700
C	-3.64824800	-0.68446100	-0.01115200
H	-4.42580500	1.29823100	-0.48657200
H	-3.42670500	0.59591500	-1.77194700
H	-3.91273700	-0.58456000	1.04836900
H	-4.42668900	-1.28239200	-0.49547900
H	-1.95272100	2.77158000	-0.96115500
H	-2.08297600	-2.35151300	-1.31953800
H	-0.21351900	-0.01935400	3.78192400



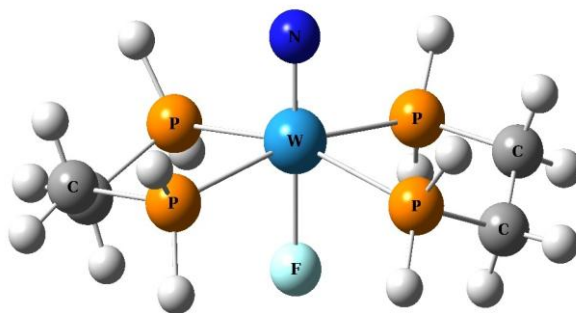
[F-W-N-NH₂(dpe)] (3)

W	-0.00333300	-0.00051400	0.05577600
P	1.85708900	1.61910400	-0.22065700
H	2.15328100	2.69126100	0.69449500
P	1.85126000	-1.57797500	-0.38341200
H	2.38523900	-2.47917800	0.62007900
P	-1.92619600	-1.61306400	-0.18023700
H	-2.18674100	-2.75126400	0.65883000
P	-1.95589400	1.62275800	0.04717400
C	3.57605000	0.72445500	-0.22496200
C	3.47293900	-0.64657900	-0.91368500
H	3.87072900	0.61525400	0.82625300
H	4.31448200	1.36274600	-0.72330300
H	4.34123400	-1.27438200	-0.68346700
H	3.41311700	-0.52871700	-2.00248900
F	-0.36224600	0.16034100	-2.01074400
N	0.03741600	-0.04482200	1.91894300
N	0.74303800	-0.24927600	3.06677300
H	-2.45135200	2.16914800	1.28182600
H	1.94785400	2.36922300	-1.44859700
H	1.79740100	-2.54605000	-1.45480500
C	-3.52638600	0.72053200	-0.61986300
C	-3.62723300	-0.70341700	-0.04149200
H	-4.42032500	1.30643800	-0.37885500
H	-3.41215400	0.68938300	-1.70970400
H	-3.88317200	-0.67309100	1.02541800
H	-4.39684300	-1.28462300	-0.56161100
H	-2.02261700	2.81622800	-0.75334100
H	-2.07878800	-2.24490500	-1.46103500
H	0.25579100	-0.20015200	3.95282000
H	1.65046400	-0.71597500	3.04376800



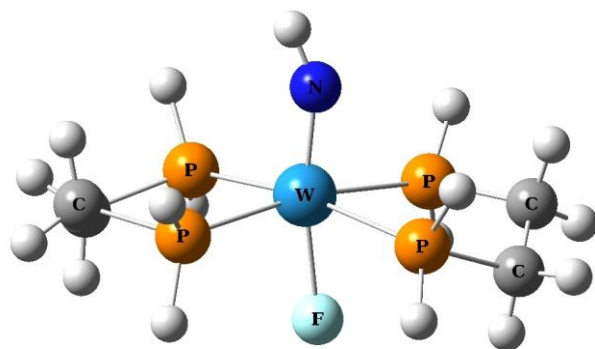
[F-W≡N (dpe)]⁺¹ (4)

W	0.00007900	-0.00005500	0.31320700
P	1.98398200	1.65100800	-0.01518800
H	2.28807000	2.65388000	0.95038100
P	1.94120100	-1.68237100	-0.08232400
H	2.54616700	-2.33906200	1.02900400
P	-1.98412300	-1.65103200	-0.01403300
H	-2.28910500	-2.65295400	0.95224600
P	-1.94107900	1.68244600	-0.08103200
C	3.60012000	0.63962700	-0.15543200
C	3.35956300	-0.69639900	-0.89050600
H	3.96112900	0.47372000	0.86585800
H	4.35172600	1.23339800	-0.68498700
H	4.27281700	-1.29968800	-0.88919400
H	3.05816000	-0.52845800	-1.92983700
F	-0.00254700	0.00006700	-1.80960000
N	0.00104900	-0.00011200	2.04036900
H	-2.54697500	2.33814000	1.03039400
H	1.95157500	2.40832000	-1.22345600
H	1.73877100	-2.76980000	-0.98225300
C	-3.35846700	0.69663000	-0.89097700
C	-3.59995800	-0.63940200	-0.15621600
H	-4.27172500	1.29991400	-0.89075400
H	-3.05565500	0.52873600	-1.92989400
H	-3.96220000	-0.47348700	0.86463900
H	-4.35097600	-1.23310800	-0.68667500
H	-1.73827600	2.77062600	-0.97996100
H	-1.95104400	-2.40941900	-1.22158700



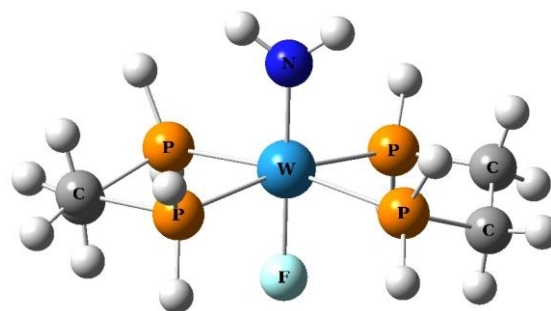
[F-W=NH (dpe)] (5)

W	-0.03057000	0.00181400	0.17987900
P	-1.92003700	-1.58817900	-0.08686800
H	-2.18333900	-2.69340200	0.80517200
P	-1.90473000	1.59377000	-0.09336700
H	-2.36704500	2.38793100	1.02974700
P	1.92135000	1.62403000	-0.03067300
H	2.19014300	2.69986600	0.88188200
P	1.92864600	-1.62889000	0.02210100
C	-3.62997800	-0.69376600	0.01812500
C	-3.55046400	0.71025000	-0.60269800
H	-3.87971000	-0.63497300	1.08520200
H	-4.39107000	-1.30583000	-0.47853600
H	-4.40137800	1.32900000	-0.29499800
H	-3.54423400	0.65213600	-1.69762700
F	0.29343800	-0.06015500	-1.88965600
N	0.03640100	0.02377300	2.01673400
H	2.44565500	-2.24078400	1.21439300
H	-2.04551600	-2.30607000	-1.33017200
H	-1.90207000	2.65203100	-1.07290000
C	3.48370200	-0.69564100	-0.62819800
C	3.60673100	0.68810800	0.03703700
H	4.38009800	-1.29824200	-0.44511900
H	3.34471000	-0.59653900	-1.71103100
H	3.86719000	0.58786900	1.09827000
H	4.38158400	1.28993200	-0.45052400
H	1.96285000	-2.77508800	-0.84561000
H	2.06155100	2.33316200	-1.26985700
H	-0.39134200	0.09508200	2.94695800



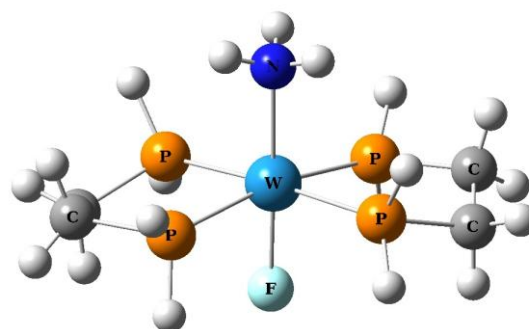
[F-W-NH₂(dpe)]⁺ (6)

W	0.00001900	-0.00002000	0.16970400
P	-1.96373700	-1.62347600	-0.07647100
H	-2.20306000	-2.71652000	0.81386600
P	-1.95387600	1.63176700	-0.03695000
H	-2.43765900	2.27010600	1.15082900
P	1.96365700	1.62351200	-0.07593200
H	2.20308700	2.71570700	0.81541300
P	1.95382800	-1.63174600	-0.03653700
C	-3.64012800	-0.68571900	-0.04439600
C	-3.50360000	0.70681700	-0.69066300
H	-3.94499200	-0.60531800	1.00618400
H	-4.39721800	-1.27898000	-0.56669300
H	-4.39621300	1.31073600	-0.49947000
H	-3.37585600	0.62395400	-1.77609300
F	0.00065600	0.00008900	-1.82556900
N	-0.00041300	-0.00016100	2.12428100
H	2.43770700	-2.27035700	1.15104200
H	-2.01126700	-2.30138000	-1.33442000
H	-1.89758100	2.76314700	-0.91096800
C	3.50343900	-0.70687400	-0.69069000
C	3.64019100	0.68581700	-0.04486300
H	4.39607000	-1.31078800	-0.49954900
H	3.37540700	-0.62431300	-1.77610600
H	3.94582000	0.60575100	1.00550800
H	4.39676900	1.27908200	-0.56789400
H	1.89715700	-2.76291700	-0.91079900
H	2.01095400	2.30264300	-1.33321800
H	-0.82386200	0.11835000	2.72306300
H	0.82285700	-0.11819900	2.72340300



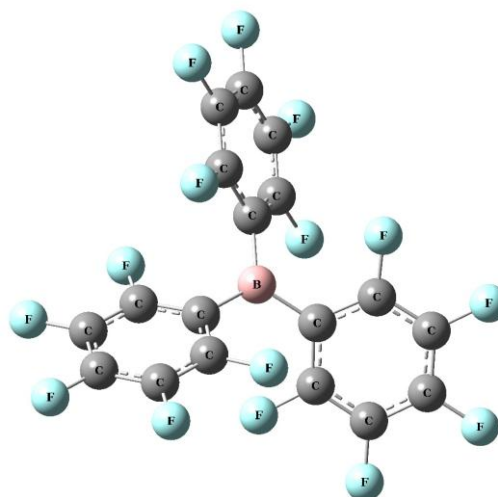
[F-W-NH₃(dpe)] (7)

W	0.00277400	-0.01074300	0.11780100
P	1.86031700	1.58337800	-0.09115800
H	2.18826200	2.73064300	0.73802700
P	1.90247600	-1.55778300	-0.08606200
H	2.38434400	-2.28346600	1.08964000
P	-1.87985600	-1.56781500	-0.21832000
H	-2.20660100	-2.77782400	0.51348500
P	-1.89643100	1.58044300	0.13167200
C	3.61778400	0.74901900	-0.06980800
C	3.54322600	-0.67473000	-0.63747000
H	3.95447000	0.74149000	0.97503400
H	4.31039800	1.37239200	-0.64682300
H	4.40249500	-1.28137400	-0.32929600
H	3.50958400	-0.65292900	-1.73347200
F	-0.12154700	0.19428000	-1.96741400
N	0.08715500	-0.25977300	2.43804700
H	-2.41721300	2.23955500	1.31761000
H	1.92757100	2.28216200	-1.36136900
H	1.97809800	-2.69430000	-0.98336700
C	-3.51888200	0.75512800	-0.54640600
C	-3.62126900	-0.71007100	-0.10155300
H	-4.38778500	1.33922300	-0.22277300
H	-3.44069000	0.82133900	-1.63803500
H	-3.94957400	-0.78511200	0.94347000
H	-4.33193400	-1.26598700	-0.72374200
H	-1.90977200	2.75911700	-0.70833900
H	-1.97651300	-2.14274600	-1.54357800
H	0.88897800	-0.83524000	2.70640200
H	0.20081700	0.68334600	2.81457500
H	-0.76912300	-0.67483700	2.80514500



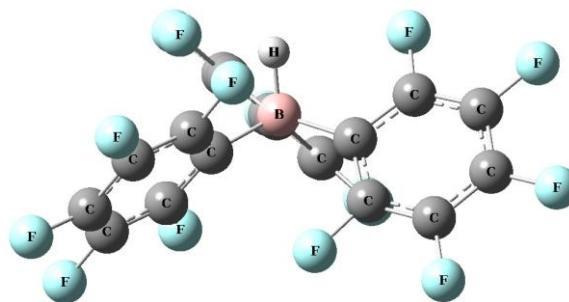
[C₆F₅B]

B	-0.00128400	0.00029500	0.00286000
C	1.48009800	-0.51423700	0.00192400
C	2.49295600	0.10004100	0.76439300
C	1.89295300	-1.62364800	-0.76173300
C	3.81645100	-0.34839900	0.78565100
C	3.20960300	-2.09150200	-0.78618000
C	4.17663300	-1.45008900	-0.00116800
C	-1.18733500	-1.02576500	0.00271800
C	-2.36265900	-0.82205300	-0.74749200
C	-1.15339400	-2.21864400	0.75212600
C	-3.42541800	-1.72929400	-0.77088000
C	-2.20230400	-3.14194400	0.77366800
C	-3.34451000	-2.89573200	0.00087700
C	-0.29550300	1.54089100	0.00054100
C	-1.34365000	2.11122200	0.75010500
C	0.47010000	2.45403700	-0.75124300
C	-1.61467800	3.48206200	0.77131800
C	0.21950000	3.82868100	-0.77557000
C	-0.82850100	4.34537200	-0.00274600
F	-4.54405200	-1.48848600	-1.53871200
F	-2.48167800	0.31403600	-1.53783200
F	-4.38238000	-3.79590400	-0.00019700
F	-2.12332000	-4.28416000	1.54043000
F	-0.04671200	-2.49800900	1.54388300
F	0.96976000	-2.28203300	-1.56429100
F	3.56240400	-3.17030300	-1.56766000
F	5.47470000	-1.90024500	-0.00300900
F	4.76322600	0.27909300	1.56591600
F	2.17789800	1.18771000	1.56918000
F	1.51027800	1.98499400	-1.54344900
F	0.98861300	4.67422700	-1.54521600
F	-1.08458000	5.69519100	-0.00420400
F	-2.64157600	3.98823100	1.53824800
F	-2.14209600	1.29482700	1.54111700



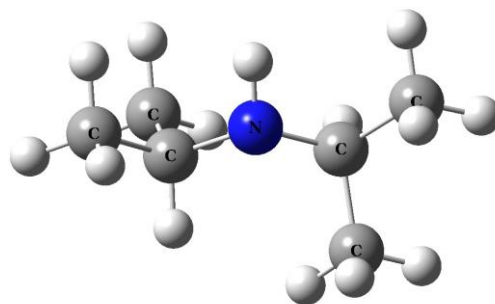
[C₆F₅BH]⁻

B	-0.00202700	-0.00182000	0.76041800
C	0.36126700	1.53319600	0.32972900
C	1.27715200	1.92764000	-0.65888400
C	-0.23216000	2.60875500	1.01605000
C	1.59518300	3.26234800	-0.94725200
C	0.04651300	3.95636200	0.76164000
C	0.97560000	4.28762200	-0.22946100
C	-1.51240300	-0.45560300	0.32815900
C	-2.14803800	-1.50540800	1.01660800
C	-2.31126500	0.13885200	-0.66196200
C	-3.45447500	-1.93777400	0.76270400
C	-3.62634000	-0.25306200	-0.94988600
C	-4.20512300	-1.30064400	-0.23022900
C	1.14776700	-1.08216300	0.33038600
C	1.03619600	-2.07048000	-0.66090100
C	2.37441500	-1.10468000	1.01945900
C	2.03589600	-3.01031500	-0.94907500
C	3.40472900	-2.01698600	0.76549500
C	3.23180500	-2.98531900	-0.22830600
F	-4.01716400	-2.98509200	1.48325100
F	-1.45381400	-2.19094200	2.01584700
F	-5.50613900	-1.70656200	-0.49863300
F	-4.35956300	0.38201100	-1.94556400
F	-1.80313400	1.17593200	-1.45128000
F	-1.17607000	2.35123300	2.01255100
F	-0.58128200	4.96750100	1.48008800
F	1.27418700	5.61724500	-0.49853600
F	2.51314300	3.57943000	-1.94177700
F	1.92264000	0.96903000	-1.44696200
F	2.61849000	-0.15950800	2.01815600
F	4.59257100	-1.97763200	1.48665300
F	4.23696200	-3.90558200	-0.49722300
F	1.85611400	-3.96147400	-1.94672000
F	-0.11323500	-2.14921800	-1.45393800
H	-0.00352800	-0.00227400	1.96903400



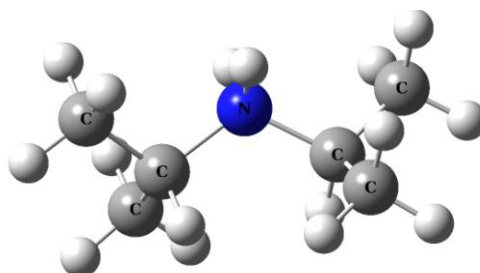
[(ⁱPr)₂NH]

N	0.01503200	-0.59740800	-0.04678400
H	-0.10789400	-1.38061200	0.59829700
C	-1.25328600	0.14929800	-0.22462500
C	-1.70072100	0.95747300	1.02466100
H	-1.10067600	0.85725500	-1.05076800
H	-2.61922900	1.52264900	0.81480500
H	-1.90258300	0.28253700	1.86921400
H	-0.93124300	1.67440600	1.33858700
C	1.26583800	0.14642200	0.23792400
C	2.37583300	-0.87780800	0.54748700
H	1.16011300	0.80449000	1.12518500
H	3.32146300	-0.37040700	0.77618200
H	2.11101200	-1.50149000	1.41386600
H	2.53072000	-1.53847800	-0.31493900
C	-2.34801000	-0.84749400	-0.65424300
C	1.66133800	1.03391000	-0.96116700
H	-2.04311200	-1.37779300	-1.56352400
H	-3.29799800	-0.33212100	-0.84547700
H	-2.52580300	-1.59489500	0.13396500
H	1.76650600	0.41713900	-1.86250500
H	2.61607300	1.53911100	-0.76320800
H	0.91147600	1.80924900	-1.16241000



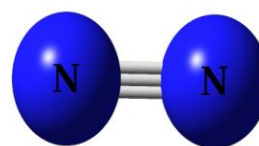
$[(i\text{Pr})_2\text{NH}_2]^+$

N	0.00000800	-0.00015500	-0.58134600
H	-0.10794500	-0.82285700	-1.19166700
C	-1.31442200	0.15758600	0.23785500
C	-1.75298100	-1.21832200	0.76322900
H	-1.05407700	0.81918700	1.07002800
H	-2.64061200	-1.09129000	1.39156800
H	-2.02890700	-1.89353900	-0.05798900
H	-0.98834900	-1.70360700	1.38018000
C	1.31445100	-0.15762300	0.23791000
C	2.36943000	-0.82657300	-0.65759300
H	1.05419700	-0.81928100	1.07007300
H	3.28928500	-0.97346400	-0.08218900
H	2.04639300	-1.81483400	-1.01064500
H	2.62313400	-0.20386400	-1.52542200
C	-2.36927100	0.82672400	-0.65765700
C	1.75278300	1.21836000	0.76326700
H	-2.04602400	1.81489700	-1.01076400
H	-3.28907900	0.97385000	-0.08223900
H	-2.62313800	0.20403400	-1.52545200
H	2.02857400	1.89361600	-0.05796300
H	2.64045600	1.09147300	1.39157700
H	0.98810400	1.70353700	1.38023700
H	0.10798600	0.82231400	-1.19197700



N₂

N	0.00000000	0.00000000	0.56666800
N	0.00000000	0.00000000	-0.56666800



NH₃

N	0.00000000	0.00000000	0.00000000
H	0.00000000	1.00522200	0.00000000
H	0.87054800	-0.50261100	0.00000000
H	-0.87054800	-0.50261100	0.00000000

