Supporting Information

Nitrogen *versus* carbon in planar pentacoordinate environments supported by Be_5H_n rings

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Table of contents

Fig.S1 Optimized structures of the ppC analogue species $CBe_5H_n^{n-4}$ (n = 2–5) at the B3LYP/aug-cc-pVTZ level.

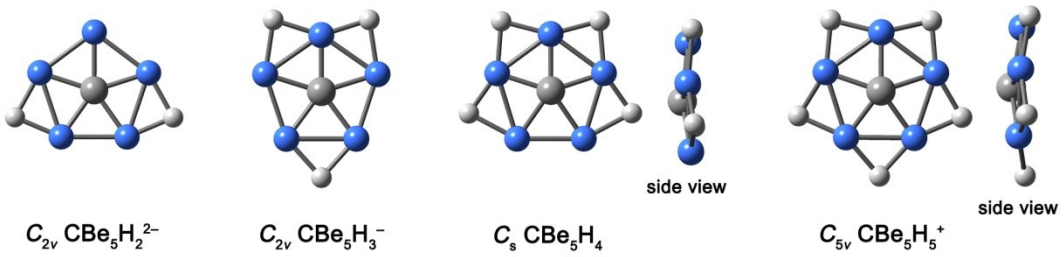


Fig.S2 The results of ELF analysis for **2A–5A** with the bifurcation values examined within NBe_5 moiety.

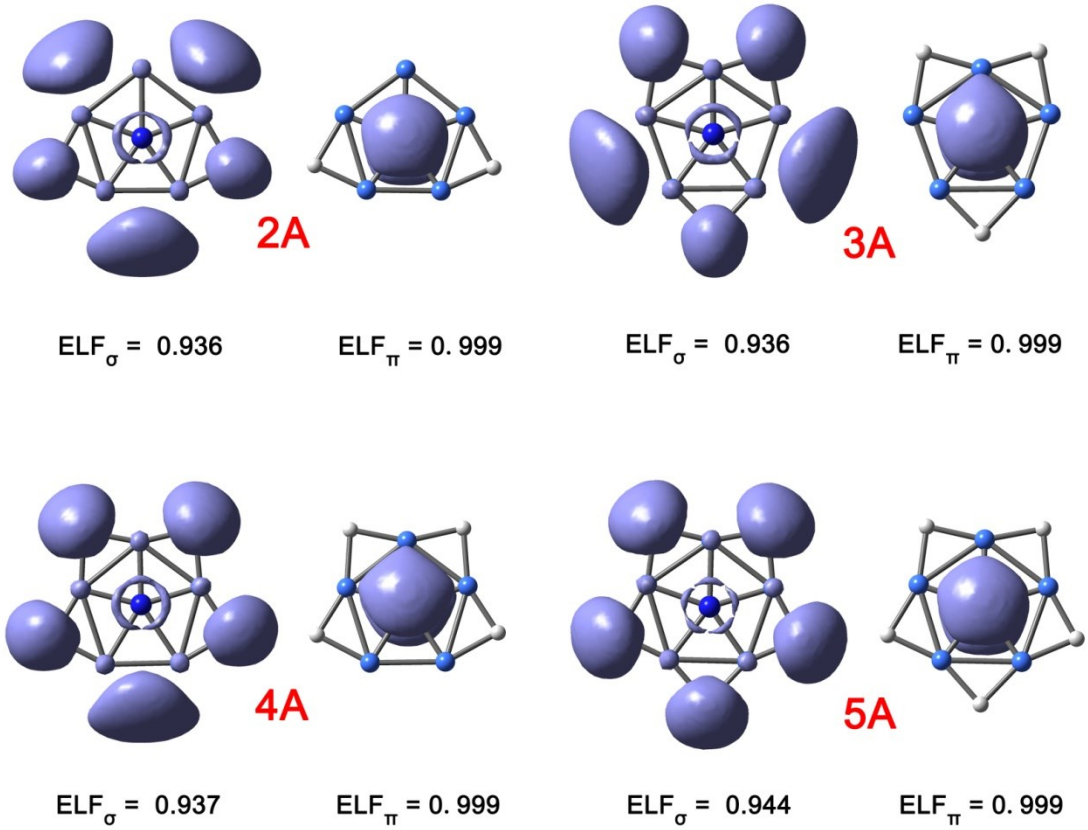


Fig.S3 Optimized structures of **1A–5A** and their four lowest isomers. The relative energies (kcal/mol) were calculated at the CCSD(T)//B3LYP level.

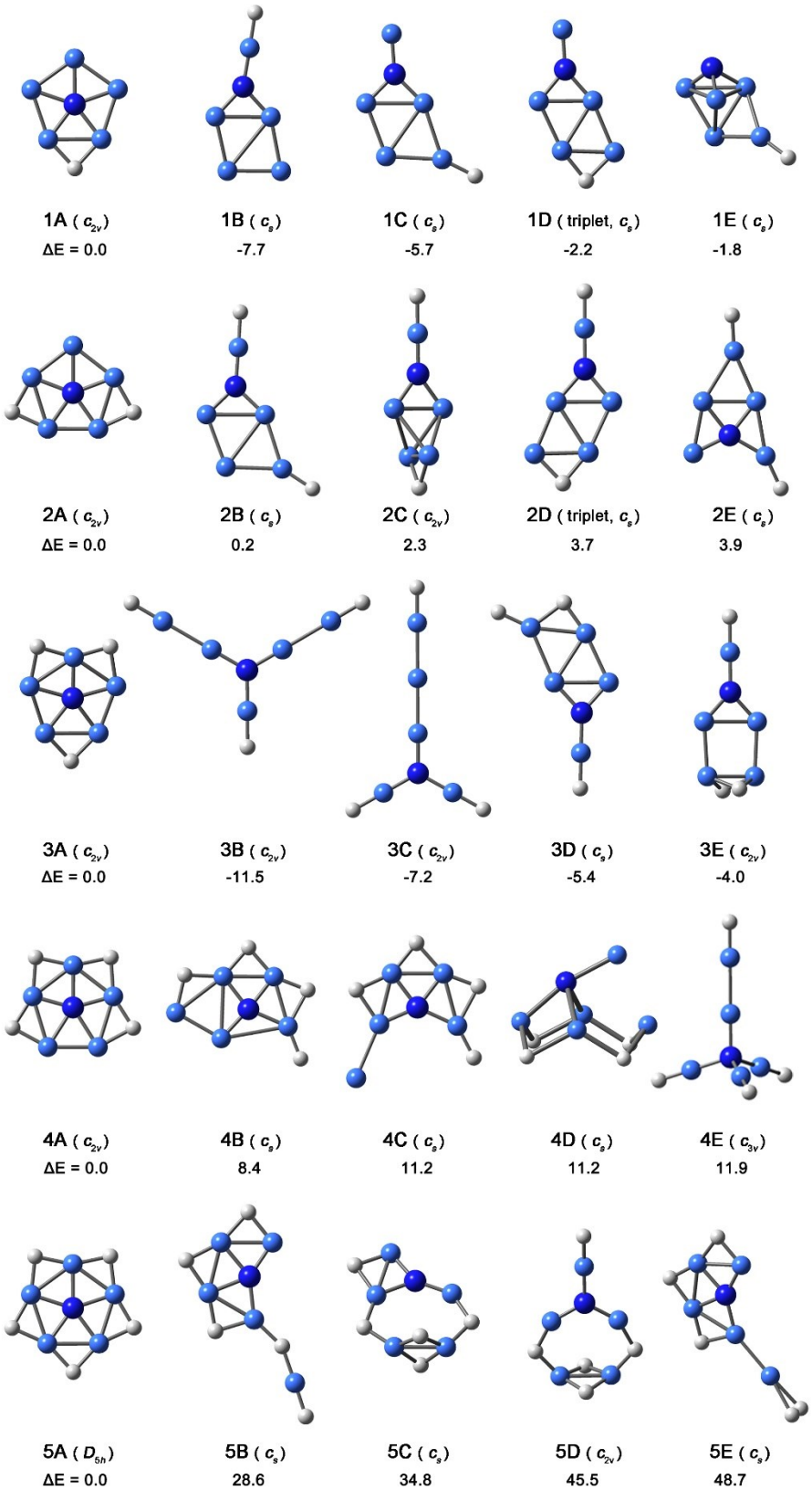


Fig.S4 The five independent 20 ps BOMD simulations of **2A–5A** at 500 K.

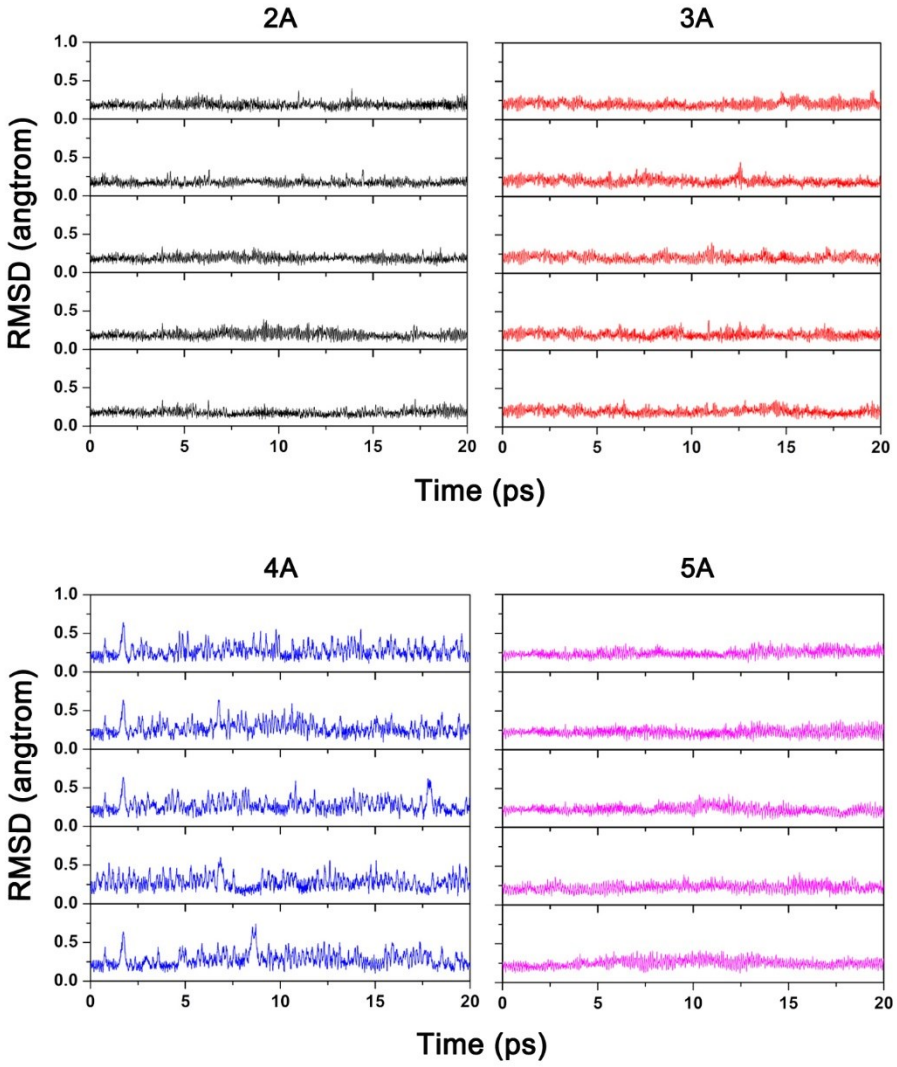
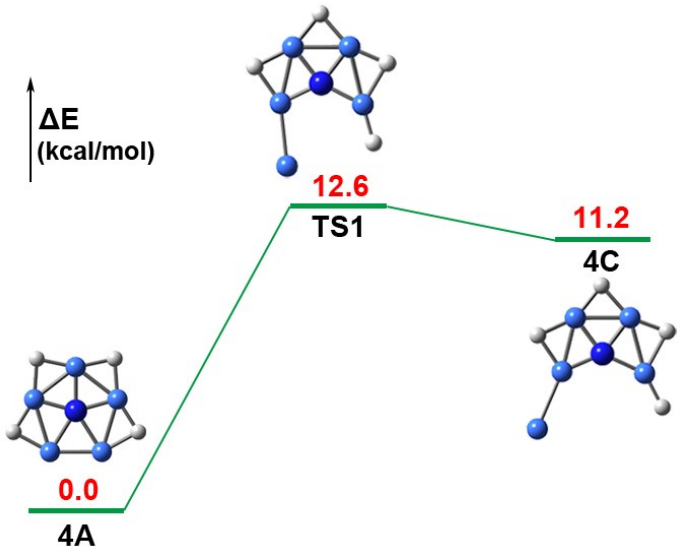


Fig.S5 The energy profile for the generation of **4C** from **4A**. The relative energies (ΔE, in kcal/mol) were calculated at the CCSD(T)//B3LYP level.



Cartesian coordinates of optimized structures of the species reported in the text.

Cartesian coordinates of structures optimized at the B3LYP/aug-cc-pVTZ level. The total energies (E) were reported at the CCSD(T)//B3LYP level.

0A

Be	0.000000	0.000000	-1.690428
Be	0.000000	0.993611	1.367588
Be	0.000000	1.607698	-0.522372
Be	0.000000	-1.607698	-0.522372
Be	0.000000	-0.993611	1.367588
N	0.000000	0.000000	-0.000002

1A

E= -128.62767750 a.u.

N	0.000000	0.000000	0.054021
Be	0.000000	0.998018	-1.246199
Be	0.000000	0.000000	1.760136
Be	0.000000	-0.998018	-1.246199
Be	0.000000	1.615438	0.610520
Be	0.000000	-1.615438	0.610520
H	0.000000	0.000000	-2.333261

2A

E= -129.34549172 a.u.

N	0.000000	0.000000	0.016433
Be	0.000000	0.945386	-1.320171
Be	0.000000	0.000000	1.777703
Be	0.000000	1.537444	0.594143
Be	0.000000	-1.537444	0.594143
Be	0.000000	-0.945386	-1.320171
H	0.000000	-2.272401	-0.708813
H	0.000000	2.272401	-0.708813

3A

E= -129.91326948 a.u.

N	0.000000	0.000000	0.024093
Be	0.000000	1.629721	-0.428588
Be	0.000000	-1.008066	1.355316
Be	0.000000	-1.629721	-0.428588
Be	0.000000	1.008066	1.355316
Be	0.000000	0.000000	-1.533220
H	0.000000	1.371047	-1.934579
H	0.000000	-1.371047	-1.934579
H	0.000000	0.000000	2.419563

4A

E= -130.31261006 a.u.

N	0.000000	0.000000	0.000953
Be	0.000000	0.949031	-1.505749
Be	0.000000	-1.526521	0.421957
Be	0.000000	-0.949031	-1.505749
Be	0.000000	0.000000	1.602171
Be	0.000000	1.526521	0.421957
H	0.000000	-2.283018	-0.777526
H	0.000000	-1.426655	1.905014
H	0.000000	1.426655	1.905014
H	0.000000	2.283018	-0.777526

5A

E= -130.55159375 a.u.

N	-0.000005	0.000000	0.000000
Be	-1.662397	0.000000	0.000000
Be	1.344910	-0.977133	0.000000
Be	-0.513709	-1.581039	0.000000
Be	1.344910	0.977133	0.000000
Be	-0.513709	1.581039	0.000000
H	0.747697	-2.301176	0.000000
H	2.419600	0.000000	0.000000
H	0.747697	2.301176	0.000000
H	-1.957494	1.422206	0.000000
H	-1.957494	-1.422206	0.000000

1B

E= -128.63996627 a.u.

N	0.849959	-0.394741	0.000000
Be	-1.874525	1.793212	0.000000
Be	0.000000	0.904360	0.000000
Be	-2.359597	-0.189205	0.000000
Be	2.325575	-0.519065	0.000000
Be	-0.494227	-1.136724	0.000000
H	3.661382	-0.647126	0.000000

1C

E= -128.63679569 a.u.

N	-1.139410	-0.241855	0.000000
Be	0.000000	0.782234	0.000000
Be	-2.655152	-0.269564	0.000000
Be	-0.112213	-1.364263	0.000000
Be	1.913372	-0.728919	0.000000
Be	2.141265	1.363972	0.000000
H	2.826789	2.559143	0.000000

1D

E= -128.63120848 a.u.

N	-1.130274	-0.303907	0.000000
Be	1.886797	1.630933	0.000000
Be	1.886269	-0.324943	0.000000
Be	-2.613745	-0.448204	0.000000
Be	0.000000	0.766514	0.000000
Be	0.074433	-1.246218	0.000000
H	2.976902	0.615020	0.000000

1E

E= -128.63050766 a.u.

N	-1.217657	0.464273	0.000000
Be	1.223555	-1.588738	0.000000
Be	-0.328660	-0.341027	1.008391
Be	-0.328660	-0.341027	-1.008391
Be	-0.328660	1.679508	0.000000
Be	1.417893	0.474875	0.000000
H	1.901730	-2.784276	0.000000

2B

E= -129.34524040 a.u.

N	0.937586	-0.428169	0.000000
Be	0.000000	0.805658	0.000000
Be	-1.969364	1.690383	0.000000
Be	2.417765	-0.497130	0.000000
Be	-0.243098	-1.396814	0.000000
Be	-2.138743	-0.434990	0.000000
H	-2.586609	2.910807	0.000000
H	3.757270	-0.582052	0.000000

2C

E= -129.34185529 a.u.

N	0.000000	0.000000	1.004694
Be	0.000000	0.951753	-0.242891
Be	0.939855	0.000000	-1.960378
Be	-0.939855	0.000000	-1.960378
Be	0.000000	0.000000	2.469983
Be	0.000000	-0.951753	-0.242891
H	0.000000	0.000000	3.818475
H	0.000000	0.000000	-3.105105

2D

E= -129.33965449 a.u.

N	0.921936	-0.487195	0.000000
Be	2.358805	-0.805532	0.000000
Be	-1.653961	1.967122	0.000000
Be	0.000000	0.782266	0.000000
Be	-2.050016	0.060677	0.000000
Be	-0.453147	-1.176508	0.000000
H	-2.929502	1.206555	0.000000
H	3.669227	-1.108292	0.000000

2E

E= -129.33936278 a.u.

N	0.000000	0.685741	0.000000
Be	-0.261095	-2.490313	0.000000
Be	-1.266340	1.526024	0.000000
Be	-1.161911	-0.458569	0.000000
Be	0.822220	-0.714853	0.000000
Be	1.451508	1.286591	0.000000
H	2.180081	2.427157	0.000000
H	-0.517606	-3.822859	0.000000

3B

E= -129.93162451 a.u.

N	0.000000	0.549965	0.000000
Be	0.005801	2.052580	0.000000
Be	-3.091748	-1.242242	0.000000
Be	-1.305014	-0.202305	0.000000
Be	1.301432	-0.207498	0.000000
Be	3.087959	-1.247962	0.000000
H	-4.242907	-1.916726	0.000000
H	0.010411	3.379141	0.000000
H	4.238778	-1.922467	0.000000

3C

E= -129.92470516 a.u.

N	0.007587	-1.387093	0.000000
Be	-0.011772	2.211305	0.000000
Be	-1.297616	-2.130023	0.000000
Be	1.320726	-2.116083	0.000000
Be	-0.024095	4.311931	0.000000
Be	0.000000	0.122639	0.000000
H	-2.452757	-2.782182	0.000000
H	2.482572	-2.756303	0.000000
H	-0.031894	5.649062	0.000000

3D

E= -129.92194698 a.u.

N	1.065938	-0.436330	0.000000
Be	-1.906562	-0.404737	0.000000
Be	2.564943	-0.493823	0.000000
Be	-0.126909	-1.370896	0.000000
Be	-1.995186	1.664702	0.000000
Be	0.000000	0.660406	0.000000
H	-3.003369	0.477013	0.000000
H	3.890836	-0.549126	0.000000
H	-2.494177	2.903807	0.000000

3E

E= -129.91958283 a.u.

N	0.000000	0.000000	1.089076
Be	0.000000	0.000000	2.582876
Be	0.000000	0.930683	-2.072882
Be	0.000000	1.040366	-0.017178
Be	0.000000	-1.040366	-0.017178
Be	0.000000	-0.930683	-2.072882
H	-1.035095	0.000000	-2.573053
H	0.000000	0.000000	3.911556
H	1.035095	0.000000	-2.573053

4B

E= -130.29920352 a.u.

N	0.000000	0.283030	0.000000
Be	-0.511663	-1.208648	0.000000
Be	1.510182	0.039065	0.000000
Be	-0.289455	1.905067	0.000000
Be	-1.579866	0.399470	0.000000
Be	1.649404	-1.946095	0.000000
H	-1.873140	1.761466	0.000000
H	0.473385	2.987726	0.000000
H	-1.971613	-1.018152	0.000000
H	0.256957	-2.467692	0.000000

4C

E= -130.29469695 a.u.

N	0.000000	0.244035	0.000000
Be	-0.659964	1.686751	0.000000
Be	-0.118888	-1.286879	0.000000
Be	-1.553338	0.000991	0.000000
Be	1.290210	1.225635	0.000000
Be	1.234240	-2.981939	0.000000
H	-2.118018	1.338111	0.000000
H	-1.637319	-1.441974	0.000000
H	2.615988	1.211703	0.000000
H	0.370311	2.605675	0.000000

4D

E= -130.29470579 a.u.

N	0.181189	0.788641	0.000000
Be	-1.463304	-0.944035	0.000000
Be	-1.308160	1.042793	0.000000
Be	0.181189	-0.326741	1.215160
Be	1.635015	0.179236	0.000000
Be	0.181189	-0.326741	-1.215160
H	-0.722393	-1.431898	-1.173116
H	-0.722393	-1.431898	1.173116
H	1.636367	-0.577371	-1.258868
H	1.636367	-0.577371	1.258868

4E

E= -130.29363838 a.u.

N	0.000000	0.000000	0.556992
Be	0.000000	0.000000	-3.133136
Be	0.000000	1.506884	1.068911
Be	-1.305000	-0.753442	1.068911
Be	0.000000	0.000000	-1.051304
Be	1.305000	-0.753442	1.068911
H	-2.377295	-1.372532	1.486833
H	0.000000	2.745064	1.486833
H	0.000000	0.000000	-4.448612
H	2.377295	-1.372532	1.486833

5B

E= -130.50604376 a.u.

N	0.000000	0.659418	0.000000
Be	-0.851916	1.914620	0.000000
Be	-0.159882	-0.922407	0.000000
Be	1.049343	1.925582	0.000000
Be	-1.656696	-3.266675	0.000000
Be	1.517923	0.060320	0.000000
H	0.038567	3.034582	0.000000
H	2.339726	1.272007	0.000000
H	-1.190345	-1.913203	0.000000
H	1.269647	-1.347518	0.000000
H	-2.052680	-4.507560	0.000000

5C

E= -130.49618227 a.u.

N	0.000000	0.999095	0.000000
Be	1.510727	-1.678690	0.000000
Be	-1.059397	2.065760	0.000000
Be	-1.357984	0.207354	0.000000
Be	1.429351	0.628182	0.000000
Be	-0.408918	-1.913220	0.000000
H	-2.314214	1.385921	0.000000
H	0.585244	-1.950534	1.074075
H	2.314502	-0.492429	0.000000
H	-1.625892	-1.223635	0.000000
H	0.585244	-1.950534	-1.074075

5D

E= -130.47915721 a.u.

N	0.000000	0.000000	1.019407
Be	0.000000	0.971527	-2.112327
Be	0.000000	0.000000	2.590547
Be	0.000000	-1.272781	0.259006
Be	0.000000	1.272781	0.259006
Be	0.000000	-0.971527	-2.112327
H	1.073588	0.000000	-2.255461
H	-1.073588	0.000000	-2.255461
H	0.000000	1.899532	-1.029474
H	0.000000	-1.899532	-1.029474
H	0.000000	0.000000	3.898399

5E

E= -130.47405822 a.u.

N	-0.592581	-0.239382	0.000096
Be	-0.684981	1.377238	-0.001679
Be	-2.170782	0.168291	-0.000243
Be	0.954682	0.267168	-0.000240
Be	3.004071	-0.194231	-0.000233
Be	-1.354909	-1.536424	0.002205
H	-2.750155	-1.225004	0.002186
H	4.750686	-0.035790	0.044538
H	4.650299	-0.793090	-0.042819
H	0.648044	1.794045	-0.001889
H	-2.143131	1.607348	-0.001927

2A'

E= -129.32806008 a.u.

N	0.000000	0.000000	0.059536
Be	0.000000	1.600020	-0.347340
Be	0.000000	-0.984574	1.518608
Be	0.000000	-1.600020	-0.347340
Be	0.000000	0.984574	1.518608
Be	0.000000	0.000000	-1.492043
H	0.000000	1.358590	-1.909361
H	0.000000	-1.358590	-1.909361

3 A'

E= -129.89819251 a.u.

N	-0.360635	-0.132530	0.000000
Be	0.358253	2.278302	0.000000
Be	0.012645	-1.280000	0.969105
Be	0.012645	0.728386	1.310697
Be	0.012645	-1.280000	-0.969105
Be	0.012645	0.728386	-1.310697
H	0.286373	-0.691201	2.220148
H	0.316370	-2.390189	0.000000
H	0.286373	-0.691201	-2.220148

TS1

E= -130.29247475 a.u.

N	0.191324	0.007876	-0.000076
Be	-2.834169	0.127107	0.000000
Be	0.902963	-1.381535	0.000086
Be	-1.000405	-0.968379	-0.000097
Be	1.720357	0.369053	0.000051
Be	0.136647	1.602676	-0.000005
H	-0.241195	-2.290722	0.000034
H	2.324417	-1.011975	0.000183
H	1.761078	1.773421	0.000116

H	-0.885138	2.478454	0.000061

MP2/aug-cc-pVTZ-optimized structures (in Cartesian coordinates) for **1A**–**5A**

1A

N	0.000000	0.000000	0.057252
Be	0.000000	1.010793	-1.265677
Be	0.000000	0.000000	1.785949
Be	0.000000	-1.010793	-1.265677
Be	0.000000	1.643002	0.616494
Be	0.000000	-1.643002	0.616494
H	0.000000	0.000000	-2.351097

2A

N	0.000000	0.000000	0.017846
Be	0.000000	0.957574	-1.335332
Be	0.000000	0.000000	1.798236
Be	0.000000	1.556911	0.598909
Be	0.000000	-1.556911	0.598909
Be	0.000000	-0.957574	-1.335332
H	0.000000	-2.287325	-0.713243
H	0.000000	2.287325	-0.713243

3A

N	0.000000	0.000000	0.025470
Be	0.000000	1.647530	-0.434964
Be	0.000000	-1.019418	1.369606
Be	0.000000	-1.647530	-0.434964
Be	0.000000	1.019418	1.369606
Be	0.000000	0.000000	-1.549058
H	0.000000	1.378673	-1.946593
H	0.000000	-1.378673	-1.946593
H	0.000000	0.000000	2.433991

4A

N	0.000000	0.000000	-0.000939
Be	0.000000	0.959120	-1.518475
Be	0.000000	-1.541826	0.426852
Be	0.000000	-0.959120	-1.518475
Be	0.000000	0.000000	1.617272
Be	0.000000	1.541826	0.426852
H	0.000000	-2.296739	-0.780205
H	0.000000	-1.434752	1.915441
H	0.000000	1.434752	1.915441
H	0.000000	2.296739	-0.780205

5A

N	0.000000	0.000000	0.000002
Be	0.000000	0.000000	1.678342
Be	0.000000	0.986504	-1.357806
Be	0.000000	1.596201	0.518634
Be	0.000000	-0.986504	-1.357806
Be	0.000000	-1.596201	0.518634
H	0.000000	2.313735	-0.751784
H	0.000000	0.000000	-2.432805
H	0.000000	-2.313735	-0.751784
H	0.000000	-1.429968	1.968183
H	0.000000	1.429968	1.968183