Electronic Supplementary Information

Stabilization of beryllium-containing planar pentacoordinate carbon species through attaching hydrogen atoms

Xue-Feng Zhao,[a] Jian-Hong Bian,[a] Fang Huang,[c] Caixia Yuan,[a] Qiang Wang,[b]* Ping Liu,[b] Debao Li,[b] Xiaotai Wang[d,a] and Yan-Bo Wu[a,b]*

a. Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province, Institute of Molecular Science, Shanxi University, Taiyuan, 030006, China.
b. State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan, Shanxi, 030001, China.
c. College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, 88 East Culture Road, Jinan, Shandong, 250014, China.
d. Department of Chemistry, University of Colorado Denver, Campus Box 194, P.O. Box 173364, Denver, Colorado 80217-3364, United States.

*To whom correspondence should be address: wyb@sxu.edu.cn (Y.W.) and wqiang@sxicc.ac.cn (Q.W.)

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Fig. S1. Optimized structures CAl_4Be, $CAl_3Be_2^-$, $CAl_2Be_3^{2-}$, and $CAlBe_4^{3-}$ at the B3LYP/aug-cc-pVTZ level. Bond distances and NBO charges are given in black and italic blue fonts, respectively.

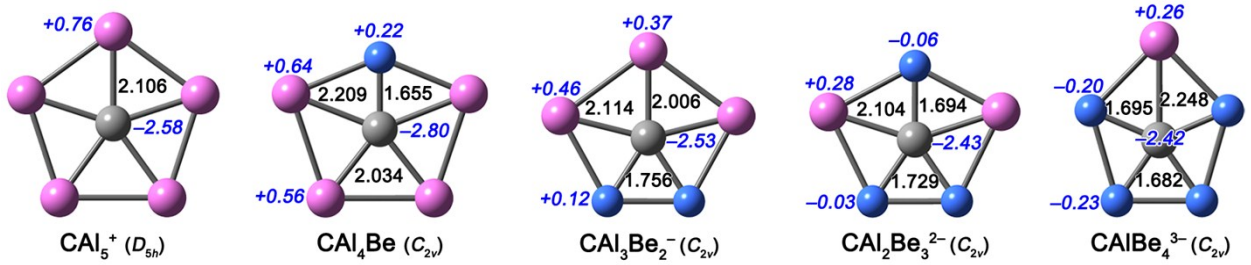


Fig. S2. AdNDP bonding patterns of **1a**–**3a** and **7a**–**9a** with occupation numbers (ONs).

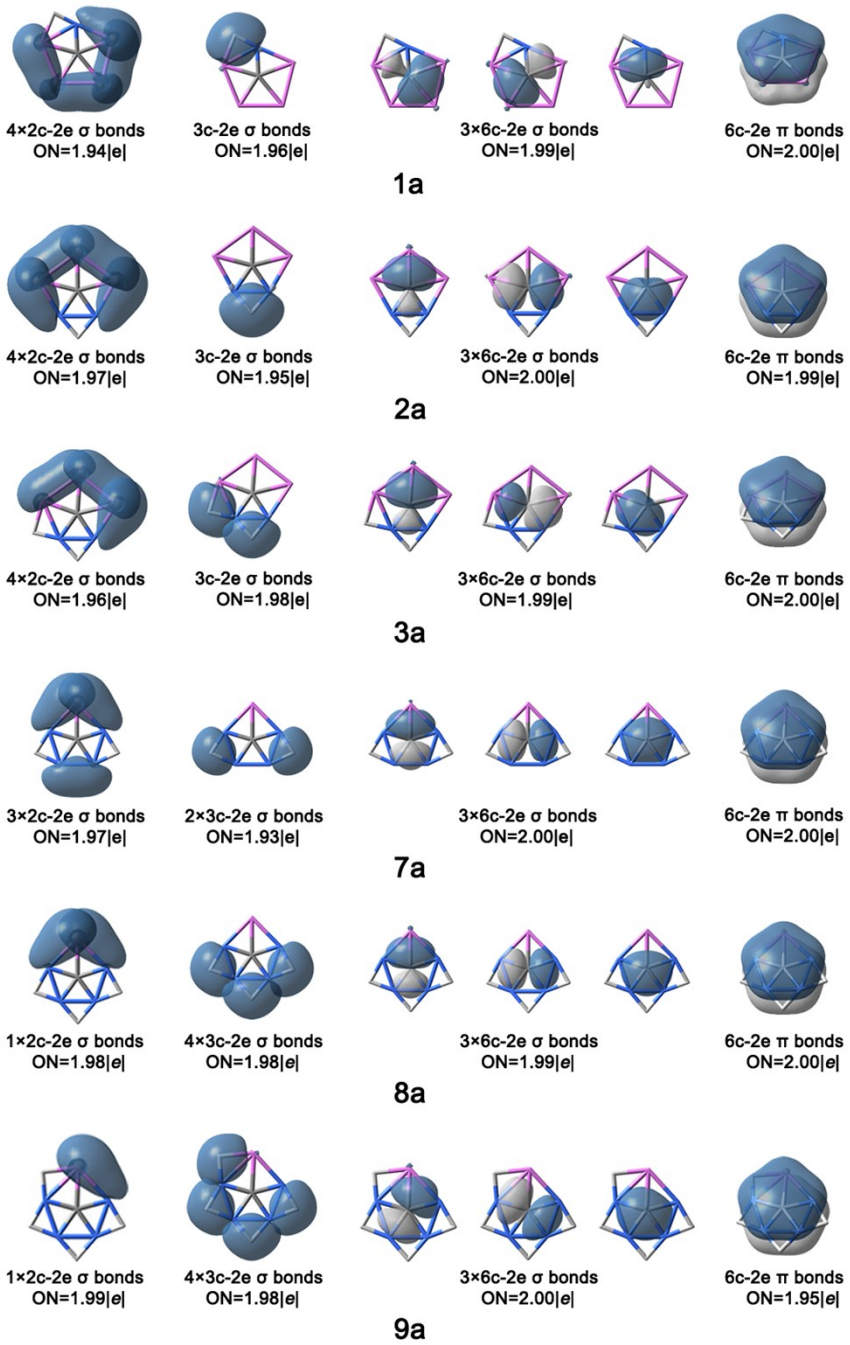


Fig. S3. NICS of CAl_4Be, $CAl_3Be_2^-$, **1a–3a**, and **7a–9a**. Points with negative NICS values (shown in red balls) are aromatic.

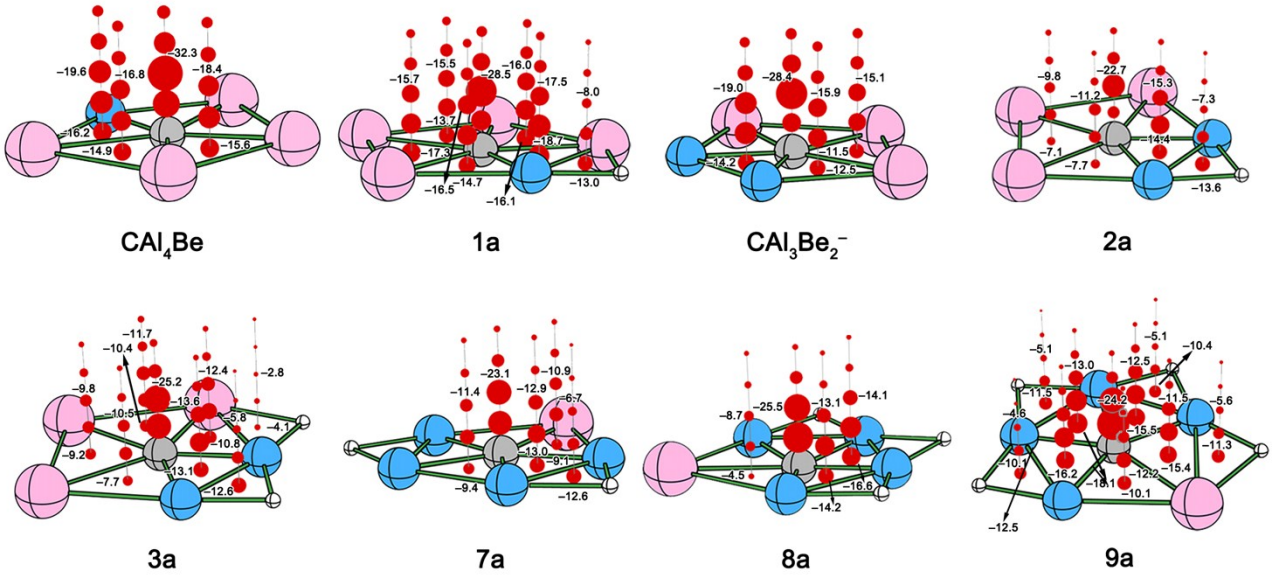
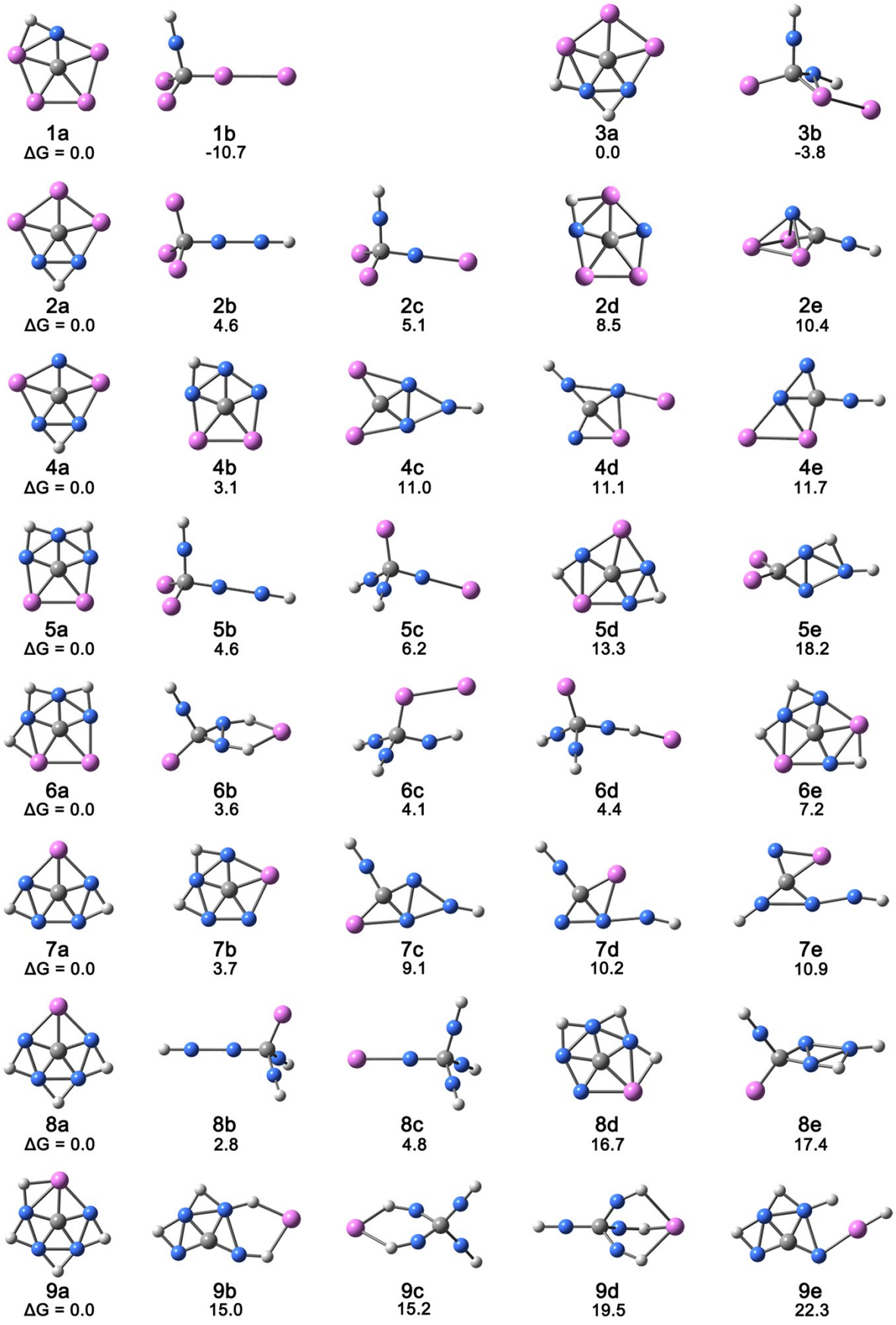


Fig. S4. B3LYP/aug-cc-pvtz-optimized structures for **1a**–**9a** and their isomers. The relative free energies (kcal/mol) were calculated using CCSD(T)/ aug-cc-pvtz electronic energies plus B2PLYP-D3/aug-cc-pvtz Gibbs free energy corrections.



Coordinates. The Cartesian coordinates of structures shown in Fig. 1 optimized at the B3LYP/aug-cc-pVTZ level and those shown in Fig. S4 optimized at the B3LYP/aug-cc-pVTZ level. The energies for structures shown in Fig. S4 were obtained using CCSD(T)/aug-cc-pVTZ electronic energies plus B2PLYP-D3/aug-cc-pVTZ Gibbs free energy corrections.

1a

Free energy = -1021.066317 a.u.

Al	1.87238525	1.22975310	0.00000000
Al	1.49143450	-1.28104745	0.00000000
Al	-0.99351044	-1.53265379	0.00000000
Al	-2.12956619	0.67341815	0.00000000
Be	-0.28496333	1.92875431	0.00000000
C	-0.06148973	0.28128860	0.00000000
H	-1.62086891	2.43414102	0.00000000

1b

Free energy = -1021.083382 a.u.

Be	1.91309368	-1.25199636	0.00000000
C	0.26879006	-1.00189168	0.00000000
H	3.21924002	-1.44389613	0.00000000
Al	-0.45377568	-1.92513524	1.72942900
Al	0.10567503	0.88476095	0.00000000
Al	-0.45377568	-1.92513524	-1.72942900
Al	-0.15845868	3.92421966	0.00000000

2a

Free energy = -793.9898113 a.u.

C	0.00000000	0.00000000	-0.48015985
Al	0.00000000	2.03696600	0.03274715
Be	0.00000000	0.95319500	-1.89056185
Be	0.00000000	-0.95319500	-1.89056185
H	0.00000000	0.00000000	-3.02079085
Al	0.00000000	-2.03696600	0.03274715
Al	0.00000000	0.00000000	1.55190915

2b

Free energy = -793.9825208 a.u.

Be	0.00000000	0.00000000	1.54944677
Be	0.00000000	0.00000000	3.62711677
C	-0.00000000	0.00000000	-0.09673823
H	0.00000000	0.00000000	4.96276177
Al	0.00000000	1.92999989	-0.64329709
Al	1.67142893	-0.96499994	-0.64329709

Al	-1.67142893	-0.96499994	-0.64329709

2c

Free energy = -793.9816207 a.u.

Be	-1.91915445	0.86894054	0.00000000
Be	-0.12347921	-0.89085824	0.00000000
C	-0.28654550	0.74792783	0.00000000
H	-3.24267339	0.99235411	0.00000000
Al	0.43600357	1.48249244	-1.70407908
Al	0.13818371	-3.37977336	0.00000000
Al	0.43600357	1.48249244	1.70407908

2d

Free energy = -793.976209 a.u.

Be	-0.56910784	-1.64898580	0.00000000
Be	-0.81340283	1.54864721	0.00000000
C	-0.22334783	-0.01261080	0.00000000
H	-2.24314983	1.64243521	0.00000000
Al	1.60101616	-1.21429480	0.00000000
Al	-2.30356283	-0.20137579	0.00000000
Al	1.40356817	1.32602320	0.00000000

2e

Free energy = -793.9732032 a.u.

Be	-1.49263384	0.00429805	0.00000000
Be	0.12195300	2.72788279	0.00000000
C	-0.35393678	1.17791156	0.00000000
H	0.52159444	3.99629770	0.00000000
Al	0.23890136	0.13200350	1.64471693
Al	0.23890136	0.13200350	-1.64471693
Al	0.06717801	-1.95573704	0.00000000

3a

Free energy = -794.3609493 a.u.

C	-0.10445760	0.50437565	0.00000000
Al	-1.90773588	-0.34023382	0.00000000
Be	-1.21810934	1.79518028	0.00000000
Be	0.66149198	1.98016216	0.00000000
H	-0.36669329	3.01010061	0.00000000
Al	2.09162999	0.19712838	0.00000000
Al	0.26323240	-1.58512523	0.00000000
H	-2.59273624	1.32927439	0.00000000

3b

Free energy = -794.3670515 a.u.

Be	1.39649400	1.57324500	1.12758300
Be	-0.14913600	-0.51220100	1.24886300
C	0.90698800	0.24120100	0.27290200
H	1.77038000	2.64074400	1.80460800
H	-1.36390200	-1.01209100	1.61783300
Al	2.62357900	-0.84119600	-0.21596100
Al	-3.03150700	-0.40643300	0.16730500
Al	-0.42575200	0.68455000	-1.07177800

4a

Free energy = -566.7256483 a.u.

C	0.00000000	0.00000000	0.20592091
Al	0.00000000	2.01017500	-0.41336009
Be	0.00000000	0.00000000	-1.46876009
Be	0.00000000	0.96987000	1.58384591
Be	0.00000000	-0.96987000	1.58384591
H	0.00000000	0.00000000	2.71610991
Al	0.00000000	-2.01017500	-0.41336009

4b

Free energy= -566.7207172 a.u.

Be	2.02082686	0.48467141	0.00000000
Be	-0.86875921	1.74952891	0.00000000
Be	1.05270763	2.13691274	0.00000000
C	0.29182560	0.52866984	0.00000000
H	-0.16278967	3.02667531	0.00000000
Al	0.77170136	-1.46055433	0.00000000
Al	-1.57226021	-0.36122618	0.00000000

4c

Free energy= -566.7081363 a.u.

Be	0.00000000	0.00000000	3.31349431
Be	0.00000000	0.97651200	1.37111031
Be	0.00000000	-0.97651200	1.37111031
C	0.00000000	0.00000000	0.03807031
H	0.00000000	0.00000000	4.66886631
Al	0.00000000	-1.56630800	-1.12000569
Al	-0.00000000	1.56630800	-1.12000569

4d

Free energy= -566.7078896 a.u.

Be	-2.48913992	1.45137242	0.00000000
Be	-2.18682033	-1.20325189	0.00000000
Be	-0.05080056	1.10947492	0.00000000
C	-1.44879344	0.23025770	0.00000000
H	-3.42564670	2.41758898	0.00000000
Al	0.06835784	-1.22504614	0.00000000
Al	2.31821528	0.51508330	0.00000000

4e

Free energy= -566.7070337 a.u.

Be	2.72992796	0.44944532	0.00000000
Be	-0.13825039	-1.18537043	0.00000000
Be	1.66959630	-2.00971579	0.00000000
C	1.37809776	-0.41992296	0.00000000
H	3.93830072	1.04296248	0.00000000
Al	-2.37897404	-0.17232405	0.00000000
Al	0.12882151	1.13071935	0.00000000

5a

Free energy= -567.2843333 a.u.

C	0.00000000	0.00000000	0.58504317
Al	0.00000000	1.28956500	-1.04832483
Be	0.00000000	1.57695600	1.17139417
Be	0.00000000	-1.57695600	1.17139417
Be	0.00000000	0.00000000	2.25898417
H	0.00000000	1.40145900	2.66954817
H	0.00000000	-1.40145900	2.66954817
Al	0.00000000	-1.28956500	-1.04832483

5b

Free energy= -567.2770239 a.u.

Be	3.55207943	-0.33289053	0.00000000
Be	1.50408904	0.01225214	0.00000000
Be	-0.16830836	1.90532327	0.00000000
C	-0.11701128	0.26923325	0.00000000
H	-0.23883490	3.23187604	0.00000000
H	4.86863252	-0.55473331	0.00000000
Al	-0.90304501	-0.40889545	1.70203900
Al	-0.90304501	-0.40889545	-1.70203900

5c

Free energy= -567.2745174 a.u.

Be	-1.15389441	1.40452798	1.30065200
Be	-1.15389441	1.40452798	-1.30065200
Be	0.69604299	0.17310717	0.00000000
C	-0.92427541	0.44616915	0.00000000
H	-1.35461545	2.15798328	2.37587600
H	-1.35461545	2.15798328	-2.37587600
Al	3.16325885	-0.26133150	0.00000000
Al	-2.03234603	-1.19417881	0.00000000

5d

Free energy= -567.2631765 a.u.

Be	0.88507054	1.65495137	0.00000000
Be	-1.03151470	1.57212645	0.00000000
Be	-0.02597413	-1.43066842	0.00000000
C	0.03766548	0.23520634	0.00000000
H	1.31798115	-1.99859642	0.00000000
H	-0.07872791	2.74746645	0.00000000
Al	1.97679864	-0.30199739	0.00000000
Al	-2.03645810	-0.41690612	0.00000000

5e

Free energy= -567.2553243 a.u.

Be	-0.14250409	-3.19438917	0.00000000
Be	-1.07529672	-1.23798131	0.00000000
Be	0.85304826	-1.32834682	0.00000000
C	-0.08353625	0.07851823	0.00000000
H	1.46091547	-2.57354016	0.00000000
H	-0.10862414	-4.53054334	0.00000000
Al	0.02338217	1.14137859	1.66659500
Al	0.02338217	1.14137859	-1.66659500

6a

Free energy= -567.6598771 a.u.

C	-0.28148420	0.53889916	0.00000000
Al	-0.63832648	-1.65954991	0.00000000
Be	-1.90386833	0.24405930	0.00000000
Be	0.75962013	1.85175793	0.00000000
Be	-1.15215721	1.99040897	0.00000000
H	-2.56675428	1.55156035	0.00000000
H	-0.12678778	3.03904835	0.00000000
Al	1.51693423	-0.30324183	0.00000000

H	2.14616816	1.34738432	0.00000000

6b

Free energy= -567.6541602 a.u.

Be	0.24253787	0.17323757	-1.11944544
Be	0.24253787	0.17323757	1.11944544
Be	-1.34193096	1.95986069	0.00000000
C	-0.90063884	0.37310499	0.00000000
H	1.51883126	-0.09487258	1.52565405
H	-1.67775087	3.23442642	0.00000000
H	1.51883126	-0.09487258	-1.52565405
Al	3.13181161	-0.25941416	0.00000000
Al	-2.55709297	-0.85663619	0.00000000

6c

Free energy= -567.6532896 a.u.

Be	-2.37313714	-0.33265326	1.31555637
Be	-2.37313714	-0.33265326	-1.31555637
Be	-0.28907034	-1.43397281	0.00000000
C	-1.37060661	-0.22179040	0.00000000
H	0.97900690	-1.92700076	0.00000000
H	-3.11535423	-0.40303627	2.40032646
H	-3.11535423	-0.40303627	-2.40032646
Al	-0.07872304	1.22326172	0.00000000
Al	2.66462456	-0.26472841	0.00000000

6d

Free energy= -567.6528696 a.u.

Be	-1.34577508	1.40433662	-1.31520497
Be	-1.34577508	1.40433662	1.31520497
Be	0.39752889	0.12203142	0.00000000
C	-1.16240344	0.43124161	0.00000000
H	-1.45300460	2.13796932	2.40746910
H	-1.45300460	2.13796932	-2.40746910
H	1.75627481	-0.14879593	0.00000000
Al	-2.44424126	-1.16275121	0.00000000
Al	3.77502896	-0.25551118	0.00000000

6e

Free energy= -567.6483568 a.u.

Be	-0.90215300	1.63407315	0.00000000
Be	-0.06907200	-1.43407085	0.00000000

Be	0.99518500	1.56359515	0.00000000
C	-0.00100600	0.21588415	0.00000000
H	0.07659301	2.71729715	0.00000000
H	2.39558100	1.20204214	0.00000000
H	-1.42043500	-1.94026485	0.00000000
Al	-2.05397300	-0.26294285	0.00000000
Al	1.96616200	-0.53157785	0.00000000

7a

Free energy= -340.0087218 a.u.

C	0.00000000	0.00000000	-0.48306586
Al	0.00000000	0.00000000	1.59750114
Be	0.00000000	1.58941200	-0.02061086
Be	0.00000000	-1.58941200	-0.02061086
Be	0.00000000	0.97200800	-1.89735086
Be	0.00000000	-0.97200800	-1.89735086
H	0.00000000	2.36329800	-1.26271286
H	0.00000000	-2.36329800	-1.26271286

7b

Free energy= -340.0027631 a.u.

Be	-1.17995879	1.78044597	0.00000000
Be	-1.70637226	-0.09848833	0.00000000
Be	1.55141572	0.06099435	0.00000000
Be	0.78946891	1.83291550	0.00000000
C	-0.08734810	0.43964592	0.00000000
H	-0.12399748	2.94506484	0.00000000
H	2.19981920	1.45208644	0.00000000
Al	0.04846558	-1.64142283	0.00000000

7c

Free energy= -339.9942838 a.u.

Be	0.90510757	-0.90982773	0.00000000
Be	3.05140510	-0.46702294	0.00000000
Be	1.44507308	0.97046201	0.00000000
Be	-0.73278114	1.88408953	0.00000000
C	-0.09607441	0.40101593	0.00000000
H	-1.38592398	3.06138280	0.00000000
H	4.35401455	-0.84652433	0.00000000
Al	-1.62052789	-0.81013520	0.00000000

7d

Free energy= -339.9924432 a.u.

Be	0.49992616	-2.49086571	0.00000000
Be	1.91756805	1.34565658	0.00000000
Be	1.30565893	-0.53932132	0.00000000
Be	-0.62701114	2.14782060	0.00000000
C	0.36304437	0.88810555	0.00000000
H	0.42640007	-3.84573705	0.00000000
H	-1.33444175	3.29438170	0.00000000
Al	-1.05036865	-0.51003373	0.00000000

7e

Free energy= -339.9913434 a.u.

Be	-1.52853220	1.29061957	0.00000000
Be	0.94074890	2.32531524	0.00000000
Be	1.26681723	-2.15405564	0.00000000
Be	1.32456472	-0.07392590	0.00000000
C	0.05895477	0.98698490	0.00000000
H	1.66555880	-3.45241404	0.00000000
H	1.58003042	3.51050517	0.00000000
Al	-0.89336250	-0.88706259	0.00000000

8a

Free energy= -340.5741621 a.u.

C	0.11665320	0.44145958	0.00000000
Al	-0.03300362	-1.67549471	0.00000000
Be	0.03185825	-0.06450859	1.59263600
Be	0.03185825	-0.06450859	-1.59263600
Be	-0.02624185	1.77320721	0.96006200
Be	-0.02624185	1.77320721	-0.96006200
H	-0.08571352	1.27497212	2.32968400
H	-0.08571352	1.27497212	-2.32968400
H	-0.14437629	2.91314049	0.00000000

8b

Free energy= -340.5697316 a.u.

Be	0.29552957	1.39868634	1.29812700
Be	-1.38943881	-0.06949447	0.00000000
Be	0.29552957	1.39868634	-1.29812700
Be	-3.36562880	-0.70727841	0.00000000
C	0.17406271	0.41688363	0.00000000
H	0.41510726	2.17374167	2.36894100
H	-4.63561239	-1.11704862	0.00000000

H	0.41510726	2.17374167	-2.36894100
Al	1.49361966	-1.06262582	0.00000000

8c

Free energy= -340.5664802 a.u.

Be	0.00000000	1.54110250	1.87502232
Be	-1.33463391	-0.77055125	1.87502232
Be	-0.00000000	0.00000000	-0.28619559
Be	1.33463391	-0.77055125	1.87502232
C	0.00000000	0.00000000	1.35365741
H	0.00000000	2.80281469	2.28661324
H	-2.42730873	-1.40140735	2.28661324
H	2.42730873	-1.40140735	2.28661324
Al	-0.00000000	0.00000000	-2.79517459

8d

Free energy= -340.5475499 a.u.

Be	0.85613494	1.80664369	0.00000000
Be	1.52443193	0.03718497	0.00000000
Be	-1.76695424	0.14988301	0.00000000
Be	-1.08689063	1.90621487	0.00000000
C	-0.09188329	0.43227444	0.00000000
H	1.76184169	-1.35139771	0.00000000
H	0.00538576	2.95808072	0.00000000
H	2.24214634	1.33451755	0.00000000
Al	-0.12038170	-1.62573487	0.00000000

8e

Free energy= -340.5464202 a.u.

Be	1.15212100	-0.04129200	0.87919700
Be	-0.53842200	1.93051500	0.05484000
Be	2.97126800	-0.50512100	-0.16698600
Be	1.09320800	0.07592200	-1.06827100
C	-0.17450700	0.35212600	-0.06576200
H	4.25696200	-0.86286400	-0.11101800
H	-0.84485100	3.21970500	0.14367900
H	2.34144400	-0.43235400	1.46515400
Al	-1.80147800	-0.75979500	0.00781800

9a

Free energy= -340.96418 a.u.

Be	-0.92072256	1.84334120	0.00000000
Be	1.00263428	1.78413330	0.00000000

Be	-1.62521053	0.06294564	0.00000000
Be	1.57879568	-0.05581999	0.00000000
C	-0.00854362	0.43424712	0.00000000
H	1.65221500	-1.50617639	0.00000000
H	0.07301322	2.93252783	0.00000000
H	2.35356744	1.20715701	0.00000000
H	-2.31883137	1.36219275	0.00000000
Al	-0.14236078	-1.62612189	0.00000000

9b

Free energy= -340.9402214 a.u.

Be	-2.35285539	0.96785703	0.00000000
Be	-2.93930466	-0.79540827	0.00000000
Be	-0.06459115	-1.28576398	0.00000000
Be	-0.42924205	0.95916924	0.00000000
C	-1.40496480	-0.41973281	0.00000000
H	-1.46204026	2.07405597	0.00000000
H	0.95344981	1.13847756	0.00000000
H	-3.75792978	0.38437203	0.00000000
H	1.27268105	-1.55307149	0.00000000
Al	2.65904623	0.08393437	0.00000000

9c

Free energy= -340.9398834 a.u.

Be	0.00000000	1.14263300	-0.30651200
Be	-1.33656100	0.00000000	-2.41264800
Be	0.00000000	-1.14263300	-0.30651200
Be	1.33656100	0.00000000	-2.41264800
C	0.00000000	0.00000000	-1.44373600
H	-2.43554600	0.00000000	-3.13674500
H	2.43554600	0.00000000	-3.13674500
H	0.00000000	-1.53505900	0.99919500
H	0.00000000	1.53505900	0.99919500
Al	0.00000000	0.00000000	2.66852200

9d

Free energy= -340.9330466

Be	0.00000000	1.37219951	0.53701228
Be	-0.00000000	0.00000000	3.06071026
Be	-1.18835963	-0.68609975	0.53701228
Be	1.18835963	-0.68609975	0.53701228
C	-0.00000000	0.00000000	1.40883126
H	0.00000000	0.00000000	4.37639826
H	1.70509837	-0.98443901	-0.67356788
H	-1.70509837	-0.98443901	-0.67356788
H	-0.00000000	1.96887801	-0.67356788

Al	0.00000000	0.00000000	-2.26889774

9e

Free energy=-340.9287044

Be	2.72149735	-0.88771659	0.00000000
Be	2.23439241	0.90844602	0.00000000
Be	-0.19650143	-1.20906871	0.00000000
Be	0.30910028	1.01390241	0.00000000
C	1.20372021	-0.42743555	0.00000000
H	-1.05739511	1.40847813	0.00000000
H	3.60483866	0.24369655	0.00000000
H	-3.56206244	0.58013940	0.00000000
H	1.40288595	2.06160412	0.00000000
Al	-2.14496483	-0.07935057	0.00000000