Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPLEMENTARY INFORMATION

A Designer 32-Electron Superatomic CBe_8H_{12} Cluster: Core-Shell Geometry, Octacoordinate Carbon, and Cubic Aromaticity

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Table S1. Cartesian coordinates for optimized structures of CBe_8H_{12} (**1**), $Be_8H_{12}^{2+}$ (**2**), and $NBe_8H_{12}^{+}$ (**3**) clusters and their three lowest-lying isomers (***n*B**–***n*D**) at the PBE0-D3/def2-TZVPP level.

Table S2. Calculated Wiberg bond indices (WBIs), natural atomic charges (q, in |e|), and HOMO–LUMO energy gaps (Gap, in eV) of clusters **1–3** at the PBE0-D3/def2-TZVPP level. Nucleus independent chemical shifts (NICSs) are also presented at the PBE0/def2-TZVPP level.

Table S3. Composition analysis for occupied canonical molecular orbitals (CMOs) of neutral CBe_8H_{12} (**1**, O_h, $^1A_{1g}$) cluster. Main components greater than 20% are shown in **bold**.

Table S4. Composition analysis for occupied CMOs of $Be_8H_{12}^{2+}$ (**2**, O_h, $^1A_{1g}$) cluster. Main components greater than 20% are shown in **bold**.

Figure S1. Optimized global-minimum (GM) structures of a series of cubic clusters, CBe_8H_{12} (**1**), $Be_8H_{12}^{2+}$ (**2**), and $NBe_8H_{12}^{+}$ (**3**), at the PBE0-D3/def2-TZVPP level, along with their three lowest-lying isomers (***n*B**–***n*D**). Relative energies are listed in kcal mol^{-1} at the single-point CCSD(T) level, with zero-point energy (ZPE) corrections at PBE0-D3.

Figure S2. Calculated Wiberg bond indices (WBIs; blue color) and natural atomic charges (in |e|; red color) of neutral CBe_8H_{12} (**1**, O_h, $^1A_{1g}$) cluster at the PBE0-D3/def2-TZVPP level.

Figure S3. Root-mean-square deviations (RMSDs) of cluster CBe_8H_{12} (**1**) during the Born-Oppenheimer molecular dynamics (BOMD) simulations at selected temperatures of 300, 600, 900, and 1200 K.

Figure S4. Canonical molecular orbitals (CMOs) of $Be_8H_{12}^{2+}$ (**2**). (a) Twelve σ CMOs for 3c-2e Be–H–Be σ bonds. (b) One globally delocalized CMO, which is σ in nature as long as the complementary contributions from bridging H atoms are taken into account.

Figure S5. Optimized quasi-linear chain nanostructures of the $(CBe_8H_{12})_2$, $(CBe_8H_{12})_3$, and $(CBe_8H_{12})_4$ clusters at the PBE0/def2-TZVP level.

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Species	WBI[a]			q[a]			Gap	NICS(0)[b]	NICS(1)[b]	NICS[b]
	Be–X	Be–Be	Be–H	X	Be	H		Surface	1 Å above face	Center
CBe_8H_{12} (**1**)	0.38	0.19	0.47	–1.84	0.50	–0.18	7.44	–24.2	–4.1	-
$Be_8H_{12}^{2+}$ (**2**)	-	0.21	0.44	-	0.64	–0.26	5.28	–9.6	–1.1	–18.8
$NBe_8H_{12}^{+}$ (**3**)	0.25	0.18	0.47	–1.64	0.63	–0.20	9.10	–18.3	–2.8	-

[a] The central atom is denoted as "X", which represents C and N in clusters **1**/**3**, respectively.

[b] NICS(0) is calculated at the cluster surface (that is, the center of a Be_4 square), whereas NICS(1) is at 1 Å above the square. Also shown is NICS at cubic center of cluster **2**.

Table S3. Composition analysis for occupied canonical molecular orbitals (CMOs) of neutral CBe_8H_{12} (**1**, O_h, $^1A_{1g}$) cluster. Main components greater than 20% are shown in **bold**.

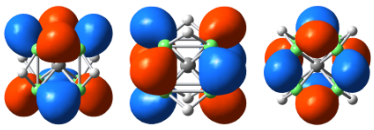
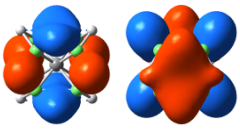
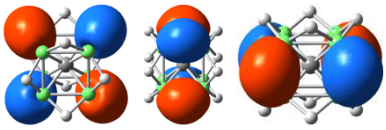
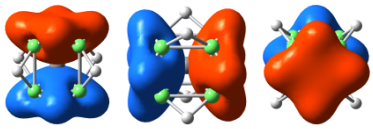
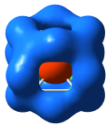
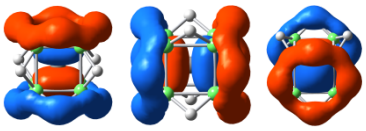
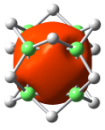
CMO		C (%)		Be_8 (%)		H_{12} (%)
		2s	2p	2s	2p	1s
2F^6	 HOMO–1	-	-	-	**36.7**	**63.3**
2D^{10}	 HOMO–2	-	-	13.6	**26.4**	**60.0**
	 HOMO–3	-	-	-	**49.3**	**50.7**
2P^6	 HOMO–5	**37.5**	-	15.5	18.8	**28.2**
2S^2	 HOMO–4	11.9	-	**22.7**	5.4	**60.0**
1P^6	 HOMO	-	**40.3**	6.0	**22.5**	**31.2**
1S^2	 HOMO–6	**47.4**	-	21.0	**28.5**	3.1

Table S4. Composition analysis for occupied CMOs of $Be_8H_{12}^{2+}$ (**2**, O_h, $^1A_{1g}$) cluster. Main components greater than 20% are shown in **bold**.

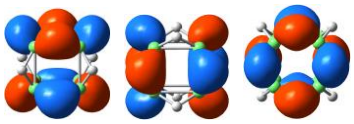
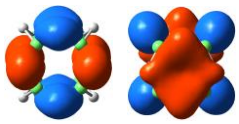
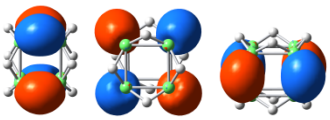
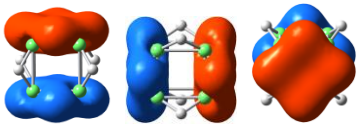
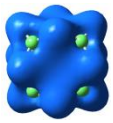
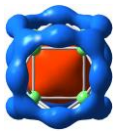
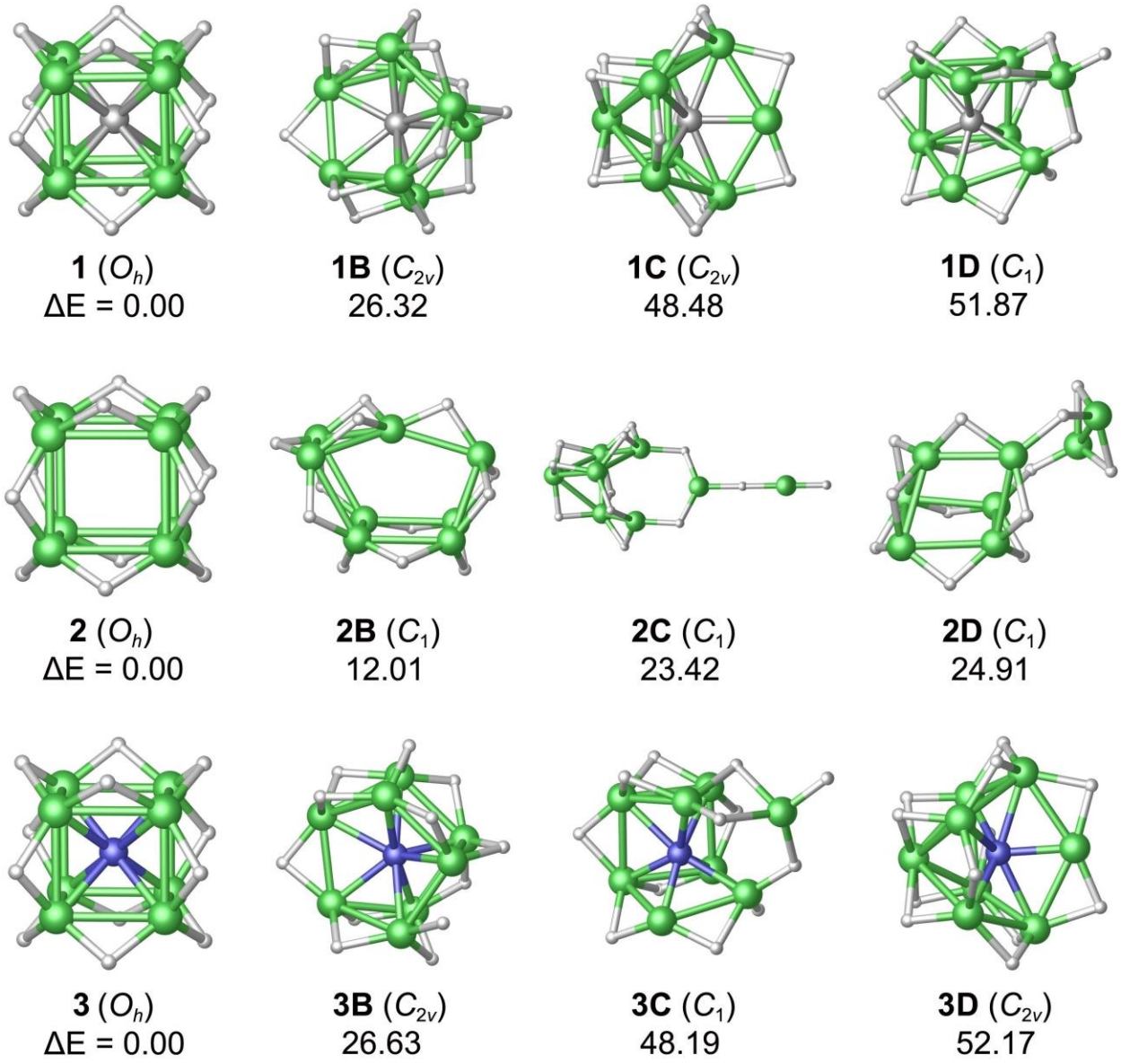
CMO		Be_8 (%)		H_{12} (%)
		2s	2p	1s
$2F^6$	 HOMO−1	-	**28.8**	**71.2**
$2D^{10}$	 HOMO−2	-	**39.8**	**60.2**
	 HOMO−3	15.8	19.2	**65.0**
$2P^6$	 HOMO−4	**29.6**	19.9	**50.5**
$2S^2$	 HOMO−5	**44.0**	17.8	**38.2**
$1S^2$	 HOMO	-	**66.3**	**33.7**

Figure S1. Optimized global-minimum (GM) structures of a series of cubic clusters, CBe_8H_{12} (**1**), $Be_8H_{12}^{2+}$ (**2**), and $NBe_8H_{12}^{+}$ (**3**), at the PBE0-D3/def2-TZVPP level, along with their three lowest-lying isomers (***n*B**–***n*D**). Relative energies are listed in kcal mol^{-1} at the single-point CCSD(T) level, with zero-point energy (ZPE) corrections at PBE0-D3.



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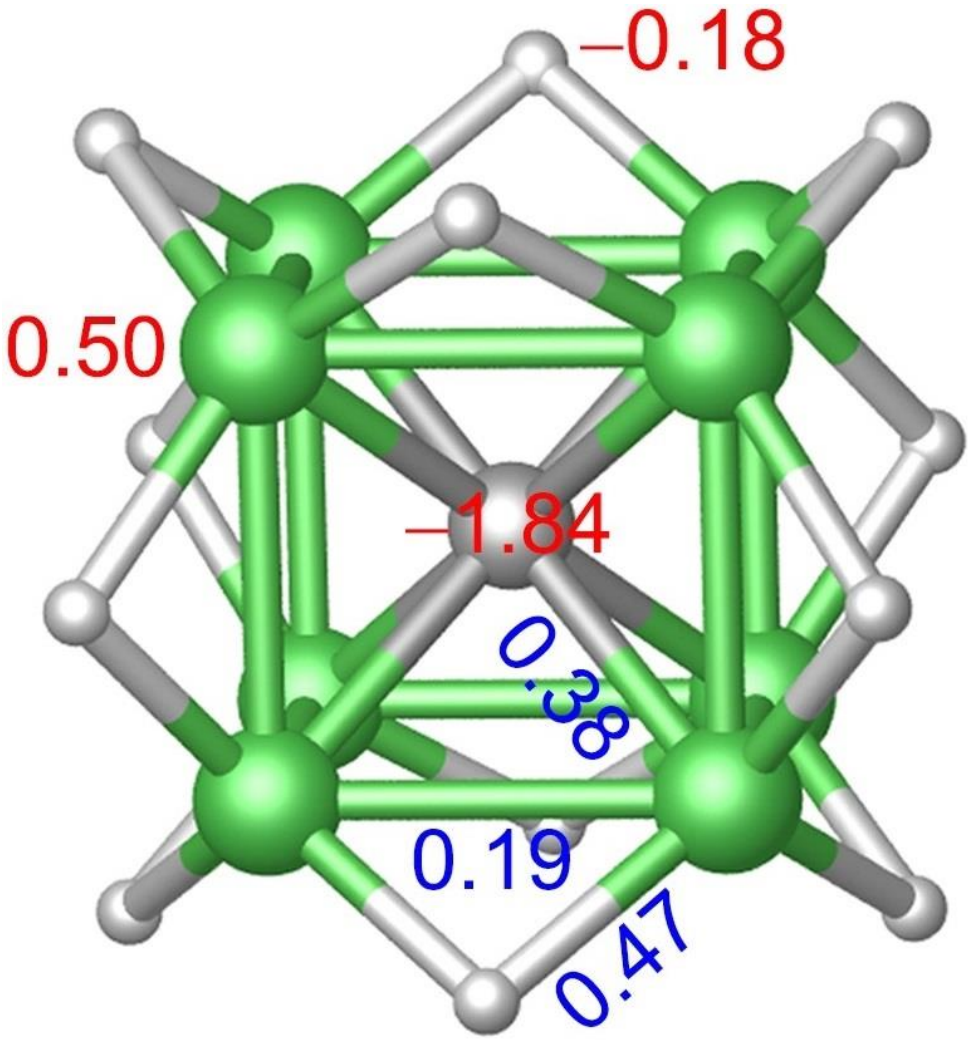

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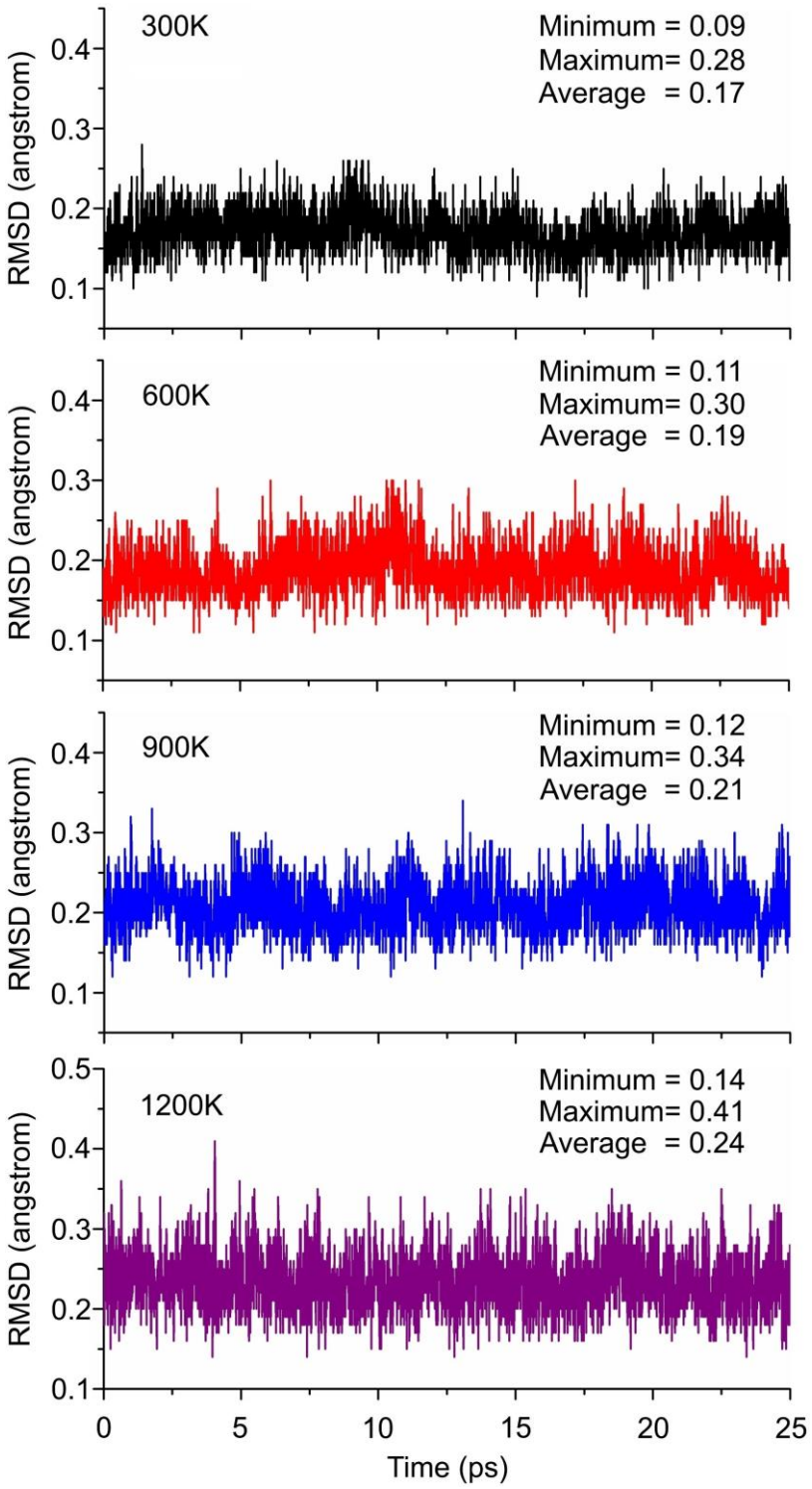

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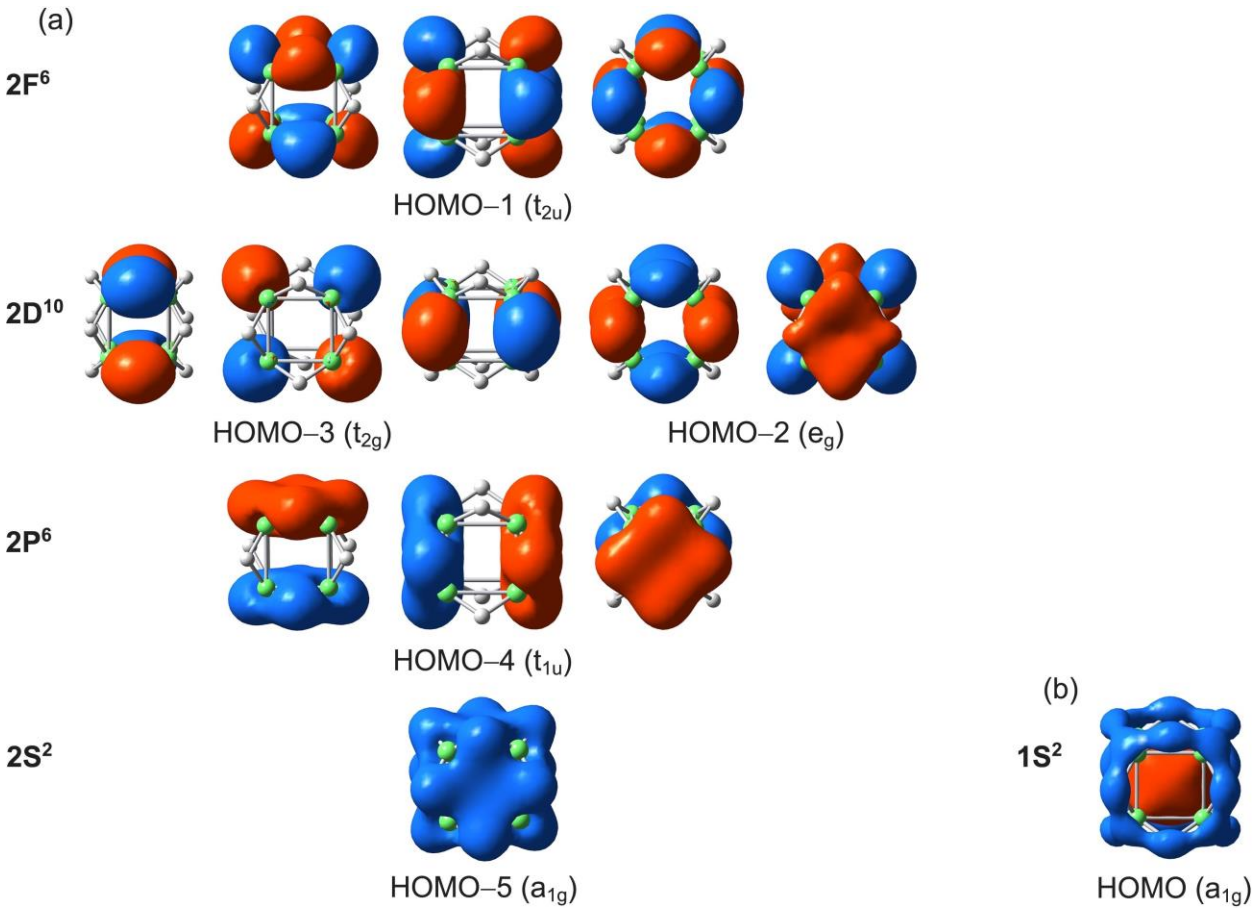

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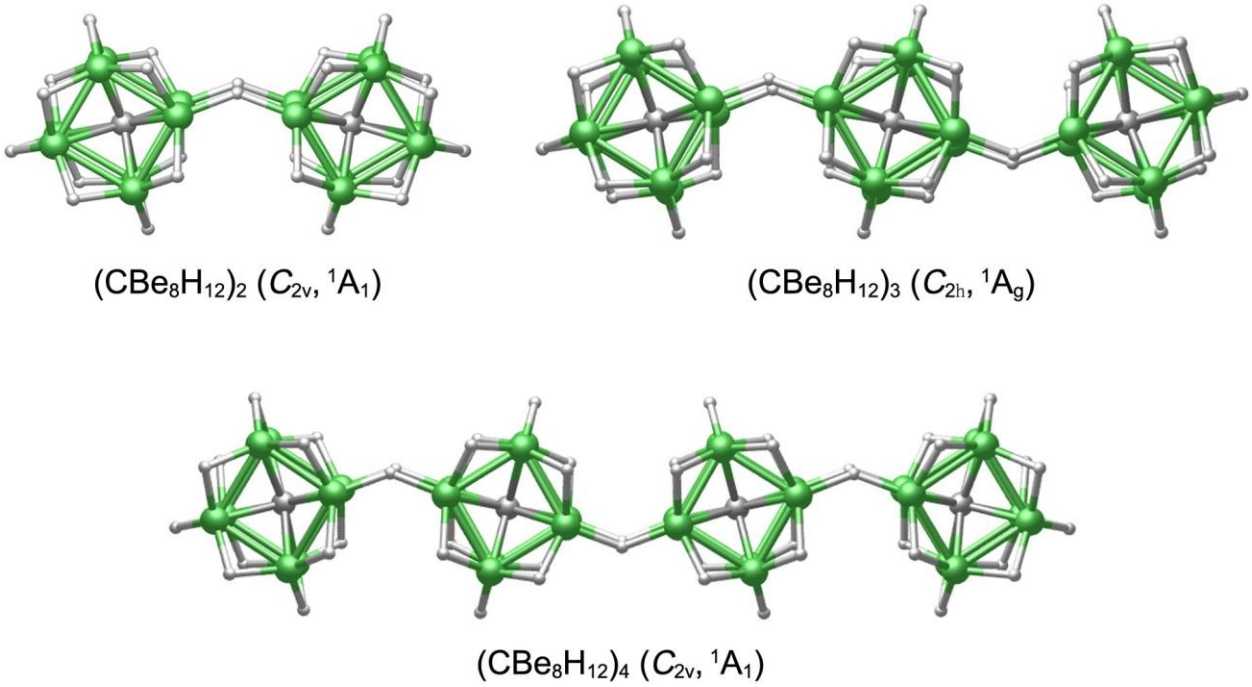

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1 O_h CBe_8H_{12}

Be	1.02990200	-1.02990200	1.02990200
Be	-1.02990200	-1.02990200	1.02990200
Be	-1.02990200	-1.02990200	-1.02990200
Be	-1.02990200	1.02990200	-1.02990200
Be	-1.02990200	1.02990200	1.02990200
Be	1.02990200	1.02990200	1.02990200
Be	1.02990200	1.02990200	-1.02990200
Be	1.02990200	-1.02990200	-1.02990200
H	1.77914600	0.00000000	1.77914600
H	1.77914600	0.00000000	-1.77914600
H	-1.77914600	0.00000000	1.77914600
H	-1.77914600	0.00000000	-1.77914600
H	1.77914600	1.77914600	0.00000000
H	1.77914600	-1.77914600	0.00000000
H	-1.77914600	-1.77914600	0.00000000
H	-1.77914600	1.77914600	0.00000000
C	0.00000000	0.00000000	0.00000000
H	0.00000000	1.77914600	1.77914600
H	0.00000000	-1.77914600	1.77914600
H	0.00000000	-1.77914600	-1.77914600
H	0.00000000	1.77914600	-1.77914600

1B C_{2v} CBe_8H_{12}

Be	-1.05898000	0.00000000	-1.40650900
Be	1.05898000	0.00000000	-1.40650900
Be	1.01723200	1.52910400	-0.08530500
Be	-1.01723200	1.52910400	-0.08530500
H	0.00000000	0.00000000	-2.46454900
H	0.00000000	2.48992300	-0.52004700
H	1.87206000	1.22636900	-1.22450300
H	-1.87206000	1.22636900	-1.22450300

C	0.00000000	0.00000000	0.05064400
Be	1.01723200	-1.52910400	-0.08530500
Be	-1.01723200	-1.52910400	-0.08530500
Be	0.00000000	1.01017000	1.58336000
H	0.00000000	-2.48992300	-0.52004700
H	1.25353400	-1.79227100	1.35373900
H	-1.25353400	-1.79227100	1.35373900
H	1.87206000	-1.22636900	-1.22450300
H	-1.87206000	-1.22636900	-1.22450300
H	-1.25353400	1.79227100	1.35373900
H	1.25353400	1.79227100	1.35373900
Be	0.00000000	-1.01017000	1.58336000
H	0.00000000	0.00000000	2.63391200

1C C_{2v} CBe_8H_{12}

Be	-1.43657200	1.00788400	-0.45416900
Be	0.00000000	0.00000000	1.87553000
Be	1.43657200	1.00788400	-0.45416900
Be	1.43657200	-1.00788400	-0.45416900
Be	0.00000000	-1.68651100	0.86316100
Be	-1.43657200	-1.00788400	-0.45416900
Be	0.00000000	0.00000000	-1.65346900
Be	0.00000000	1.68651100	0.86316100
H	-2.51306400	0.00000000	-0.24355000
H	1.11628400	1.16476100	-1.83378600
H	0.00000000	-1.34668400	2.35390800
H	2.51306400	0.00000000	-0.24355000
H	-1.11628400	-1.16476100	-1.83378600
H	-1.11628400	1.16476100	-1.83378600
H	0.00000000	1.34668400	2.35390800
H	1.26930800	-2.22128800	0.38472100
C	0.00000000	0.00000000	0.17478600
H	-1.26930800	-2.22128800	0.38472100
H	-1.26930800	2.22128800	0.38472100
H	1.26930800	2.22128800	0.38472100
H	1.11628400	-1.16476100	-1.83378600

1D C_1 CBe_8H_{12}

C	0.29711700	0.01474300	-0.22300200
Be	-0.53074100	-1.55552700	-0.03289200
Be	-0.83119700	0.90760000	-1.12615600
Be	0.71200200	1.74409600	-0.15612700
Be	1.05335900	-1.12816900	-1.19499700
Be	-0.55061400	0.77682600	1.17018000
Be	0.80618300	-0.75636000	1.31406100
H	-2.16403000	0.58080300	-1.34610600
H	-1.97409400	0.73529600	1.08399300
H	0.08420000	0.06289400	2.27992900
H	0.20770000	-2.07985900	1.19775800
H	-1.93680100	-1.57357100	-0.02586000
H	2.26982500	-0.51193900	1.24742100
H	2.46829700	-0.79430300	-1.17175500
H	-0.15869000	2.22411100	-1.28187300
H	0.04592900	2.14931600	1.08891400
H	0.27013200	-2.31391600	-1.19000600
Be	-2.52105700	-0.16274000	-0.02155300
H	-3.87246200	-0.24416500	0.03314800
Be	2.05488000	0.18056900	-0.05617900
H	2.20603500	1.65169600	-0.16289800

2 O_h $Be_8H_{12}^{2+}$

Be	1.10085000	-1.10085000	1.10085000
Be	-1.10085000	-1.10085000	1.10085000
Be	-1.10085000	-1.10085000	-1.10085000
Be	-1.10085000	1.10085000	-1.10085000
Be	-1.10085000	1.10085000	1.10085000
Be	1.10085000	1.10085000	1.10085000
Be	1.10085000	1.10085000	-1.10085000
Be	1.10085000	-1.10085000	-1.10085000
H	1.74371400	0.00000000	1.74371400
H	1.74371400	0.00000000	-1.74371400
H	-1.74371400	0.00000000	1.74371400
H	-1.74371400	0.00000000	-1.74371400
H	1.74371400	1.74371400	0.00000000
H	1.74371400	-1.74371400	0.00000000
H	-1.74371400	-1.74371400	0.00000000
H	-1.74371400	1.74371400	0.00000000

H	0.00000000	1.74371400	1.74371400
H	0.00000000	-1.74371400	1.74371400
H	0.00000000	-1.74371400	-1.74371400
H	0.00000000	1.74371400	-1.74371400

2B C_1 $Be_8H_{12}^{2+}$

Be	1.99837000	0.09719100	-1.14636100
Be	1.98637300	0.49790800	1.06078700
H	2.86777800	0.09777900	-0.00167100
Be	0.34286400	-0.94091600	1.24445500
Be	0.36546700	-1.33802800	-0.84214000
H	0.46034700	-2.09297900	0.38284400
H	-0.79797100	-0.76899400	2.10378700
H	-0.77380600	-1.46300500	-1.71059100
H	1.55004300	-0.54262300	1.92278300
H	1.58097400	-1.18365400	-1.59857900
Be	-1.69489900	-0.66141600	-0.99258100
Be	-1.73715000	1.39237300	-0.25938600
Be	-1.72485200	-0.27485300	1.15458100
Be	0.43304800	1.28886300	-0.23033900
H	1.23286800	1.26179400	-1.44697000
H	1.22419000	1.69446000	0.92340500
H	-2.16602300	0.63593200	-1.40625100
H	-2.24976900	-1.21144000	0.20709600
H	-2.19419200	1.08543400	1.07084500
H	-0.61132500	2.24280600	-0.40276300

2C C_1 $Be_8H_{12}^{2+}$

Be	0.07597100	0.87904700	-0.65324600
Be	-4.83882200	0.21810800	0.05264200
Be	1.44324200	-0.29014900	1.30377100
Be	1.04831100	-0.82179700	-1.25719300
Be	-1.98976500	-0.03221100	0.04462100
Be	2.83107000	-0.16594900	-0.29511200
Be	-0.08984900	-1.34759100	0.42585000
Be	1.74369200	1.57081800	0.42042300
H	0.69852300	2.14642700	-0.38431800
H	0.51109800	-1.30134800	1.73675600

H	-3.41713900	0.09554100	0.05997200
H	0.25101600	0.20053400	-1.92796700
H	-6.14839200	0.33310900	0.05627600
H	1.53912900	1.09072300	1.77342700
H	0.38721000	-2.01693200	-0.76004600
H	2.72819100	-0.86012700	0.95394000
H	-1.54490600	-1.28832800	0.47398100
H	2.97500000	1.26717600	-0.26617000
H	2.45900600	-0.83670400	-1.51054000
H	-1.33413600	1.12882200	-0.37233100

2D C_1 $Be_8H_{12}^{2+}$

Be	1.75979400	1.23183200	-0.73676500
Be	-2.40594700	1.21513000	0.00237700
Be	1.04655700	-0.67987500	-1.13166700
Be	0.56249300	-0.45461200	1.33682500
Be	-0.62455400	-1.46869500	-0.13579500
Be	-2.87224800	-0.63852400	-0.17843400
Be	-0.04234100	1.26517900	0.39177700
Be	2.49920100	-0.44131600	0.42326000
H	-2.03945800	-1.72633300	-0.40105800
H	-0.24049300	-1.66247500	1.24414700
H	1.41895000	0.48298500	-1.93426700
H	-1.24254100	1.95495000	-0.07974300
H	1.93215500	-0.64380600	1.72292100
H	2.20613400	-1.38290800	-0.61048200
H	-2.66758300	0.18660600	1.01035900
H	0.05408200	-1.68052300	-1.39287200
H	0.92125800	2.21066800	-0.11363100
H	-0.01554600	0.80869400	1.77278500
H	-2.94366400	0.46196400	-1.13527600
H	2.92488800	0.87369800	0.03080700

3 O_h $NBe_8H_{12}^{+}$

Be	1.04035600	-1.04035600	1.04035600
Be	-1.04035600	-1.04035600	1.04035600
Be	-1.04035600	-1.04035600	-1.04035600
Be	-1.04035600	1.04035600	-1.04035600

Be	−1.04035600	1.04035600	1.04035600
Be	1.04035600	1.04035600	1.04035600
Be	1.04035600	1.04035600	−1.04035600
Be	1.04035600	−1.04035600	−1.04035600
H	1.75191400	0.00000000	1.75191400
H	1.75191400	0.00000000	−1.75191400
H	−1.75191400	0.00000000	1.75191400
H	−1.75191400	0.00000000	−1.75191400
H	1.75191400	1.75191400	0.00000000
H	1.75191400	−1.75191400	0.00000000
H	−1.75191400	−1.75191400	0.00000000
H	−1.75191400	1.75191400	0.00000000
N	0.00000000	0.00000000	0.00000000
H	0.00000000	1.75191400	1.75191400
H	0.00000000	−1.75191400	1.75191400
H	0.00000000	−1.75191400	−1.75191400
H	0.00000000	1.75191400	−1.75191400

3B C_{2v} $NBe_8H_{12}^{+}$

Be	−1.06224900	0.00000000	−1.39751800
Be	1.06224900	0.00000000	−1.39751800
Be	1.03607600	1.56500600	−0.08736600
Be	−1.03607600	1.56500600	−0.08736600
H	0.00000000	0.00000000	−2.41332000
H	0.00000000	2.45219200	−0.54811000
H	1.87474300	1.19043600	−1.18040900
H	−1.87474300	1.19043600	−1.18040900
Be	1.03607600	−1.56500600	−0.08736600
Be	−1.03607600	−1.56500600	−0.08736600
Be	0.00000000	1.01483900	1.58264400
H	0.00000000	−2.45219200	−0.54811000
H	1.26394600	−1.71332400	1.33683200
H	−1.26394600	−1.71332400	1.33683200
H	1.87474300	−1.19043600	−1.18040900
H	−1.87474300	−1.19043600	−1.18040900
H	−1.26394600	1.71332400	1.33683200
H	1.26394600	1.71332400	1.33683200
Be	0.00000000	−1.01483900	1.58264400
H	0.00000000	0.00000000	2.59038400

N	0.00000000	0.00000000	0.03004500

3C C_1 $NBe_8H_{12}^+$

N	0.31661900	-0.02635200	-0.16234600
Be	-0.66682200	-1.49508400	0.12049000
Be	-0.97751600	0.99473200	-0.74434400
Be	0.91549900	1.66510800	-0.35323300
Be	0.75683100	-1.15932900	-1.26398600
Be	-0.22996300	0.97500500	1.20743200
Be	0.85059900	-0.77510400	1.34588000
H	-2.06043300	0.37217100	-1.37533400
H	-1.59448000	1.19521900	0.65954500
H	0.20889400	0.14660000	2.29286100
H	0.13094100	-2.02099400	1.25618300
H	-2.03989900	-1.35332000	0.34860700
H	2.29854600	-0.67460800	1.09607500
H	2.17685600	-1.04343200	-1.35478300
H	-0.14203100	2.09593000	-1.27390800
H	0.62146400	2.12628100	0.99115200
H	-0.16886300	-2.21617200	-1.12649200
Be	-2.71623000	-0.12113700	-0.11053600
H	-3.97442700	0.11715600	0.24159500
Be	2.06800400	-0.05919500	-0.21900500
H	2.32548200	1.33965500	-0.54988100

3D C_{2v} $NBe_8H_{12}^+$

Be	-1.47852600	1.02299000	-0.46195800
Be	0.00000000	0.00000000	1.83682200
Be	1.47852600	1.02299000	-0.46195800
Be	1.47852600	-1.02299000	-0.46195800
Be	0.00000000	-1.71450100	0.84996300
Be	-1.47852600	-1.02299000	-0.46195800
Be	0.00000000	0.00000000	-1.65775600
Be	0.00000000	1.71450100	0.84996300
H	-2.47960400	0.00000000	-0.16955000
H	1.08294300	1.15029800	-1.79974000
H	0.00000000	-1.33384400	2.29076500
H	2.47960400	0.00000000	-0.16955000

H	-1.08294300	-1.15029800	-1.79974000
H	-1.08294300	1.15029800	-1.79974000
H	0.00000000	1.33384400	2.29076500
H	1.26990600	-2.18531700	0.38686900
N	0.00000000	0.00000000	0.18348800
H	-1.26990600	-2.18531700	0.38686900
H	-1.26990600	2.18531700	0.38686900
H	1.26990600	2.18531700	0.38686900
H	1.08294300	-1.15029800	-1.79974000