Structures and energetics of Be_nC_n ($n = 1-5$) and Be_{2n}C_n ($n = 1-4$) clusters

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ABSTRACT

The structures and energies of Be_nC_n ($n = 1-5$) and Be_{2n}C_n ($n = 1-4$) clusters have been examined in theoretical electronic structure calculations. Cluster geometries were optimized in B3LYP/6-31G(2df) calculations and energies ordered in QCISD(T) calculations at the optimum geometries. Be and C bond to each other and to other atoms of their own kind, creating a great variety of low-energy clusters in a variety of structural types. Comparisons of the carbide clusters with previously explored silicide structures reveal some structural similarities, but the variety of carbide structures is much greater, owing primarily to the ability of carbon atoms to form multiple C–C bonds.

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1. Introduction

The carbides of beryllium are less well-characterized than are those of the other alkaline earths, partly because of the toxicity associated with beryllium compounds [1]. However, theoretical studies of BeC [2–8] and small clusters have been reported [9–14], motivated by prospects for developing new materials [10,14] and by the potential roles beryllium carbides may play in plasma physics [15] and cosmochemistry [11–13]. The present study is grounded in previous examinations of beryllium silicides [16,17] and motivated by the need to understand stability, bonding and structure in carbide clusters per se and in comparison to silicide clusters.

Beryllium is a component of stellar interiors [18] and therefore also of interstellar dust, where it may interact with small carbon clusters. Chen et al. [11,12] and Zhang [13] have examined the structures of singly and doubly charged anions of BeC_n (n as large as 14) in density functional theoretical (DFT) calculations. They found generally greater stability to be associated with linear ions in which an interior beryllium atom is flanked by two chains, each having an even number of carbon atoms.

Koch et al. [9] pioneered theoretical study of neutral carbides, examining the relative stabilities of linear and nonlinear isomers of Be_2C , BeC_2 and Be_2C_2 . Patrick et al. [10] have carefully examined the electronic state structures of C_nBe_m ($n = 1-3$, $m = 1-5$) clusters, with an eye to the structural effects of adding Be atoms and their implications for materials development. They concluded that regions of pure beryllium will form in clusters in which it exceeds

a threshold mole fraction. Ghouri et al. [14] have optimized geometries of a wide variety of neutral C_nBe_m ($n = 1-10$, $m = 1-11 - n$) clusters in B3PW91/6-31+G* DFT calculations, concentrating on planar structures of potential importance in the chemistry of interstellar dust.

There are well known differences among the compounds of carbon and of silicon, and how these manifest themselves in the formation of small clusters is of interest. Carbon atoms can form multiple bonds to each other, whereas silicon prefers single bonding and sp^3 hybridization [19]. Carbon can therefore form large stable cage clusters [20] that silicon cannot. On the other hand Be–Si and Be–Be bond lengths are about equal, leading to symmetric $\text{Be}_{2n}\text{Si}_n$ clusters [16]. Be_2Si , for example is nearly equilateral, and the low-energy isomer of Be_8Si_4 , which may be viewed as an icosahedron composed of twenty such triangles, has D_{2h} symmetry. In its silicide clusters beryllium does not behave as a typical alkaline earth, rather it accepts electrons from silicon, and stable cage clusters can form from a beryllium core structure face-capped by silicon atoms [17]. Carbon is more electronegative than silicon and may not perform the role of electron donor. To explore the stable geometries and relative energies of the carbide clusters in their low-lying electronic states cluster geometries have been determined in B3LYP/6-31G(2df) density functional calculations and the energy ordering in the clusters established in QCISD(T)/6-31G(2df) energies calculated at the optimized geometries.

The present study, though it examines structures found in previous studies, is focused upon Be_nC_n ($n = 1-5$) and Be_{2n}C_n clusters and aims to identify as many of the most stable isomers of each as possible. The analysis of a large fraction of the lowest-energy clusters may identify essential elements of stability and structural motifs useful in synthesizing larger clusters. In these goals the present study follows previous examinations of the beryllium

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Table 1Energies and minimum distances of BeC, Be₂C and Be₂C₂ clusters. Column contents are described in the text.

Isomer	State	B3-LYP ^a	QCISD(T) ^a	d(C–C)	d(C–Be)	d(Be–Be)	E _{At} ^b	E _{At/(N–1)} ^b	ΔE _{Rel} ^b
<i>BeC</i>									
	³ Σ [–]	–52.59084	–52.45649	1.670			82.217	82.217	0.00
	⁵ Σ [–]	–52.59238	–52.44937	1.633			77.751	77.751	4.47
	¹ Σ ⁺	–52.54621	–52.41022	1.664			53.184	53.184	29.03
<i>Be₂C</i>									
A	¹ A ₁	–67.37879	–67.17451	1.565	2.094		147.480	73.740	0.00
B	⁵ Σ _u ⁺	–67.38059	–67.16092	1.655			138.950	69.475	8.53
A	³ B ₁	–67.37685	–67.15915	1.623	2.142		137.839	68.919	9.64
B	³ Π _g	–67.36986	–67.14175	1.566			126.923	63.461	20.56
C	³ Σ ⁺	–67.32448	–67.11367	1.652	2.117		109.300	54.650	38.18
C	⁵ Σ ⁺	–67.27555	–67.10896	1.661	1.961		106.345	53.172	41.14
A	⁵ B ₁	–67.30920	–67.09941	1.726	2.208		100.353	50.176	47.13
C	¹ Σ ⁺	–67.26137	–67.06475	1.658	2.063		78.600	39.300	68.88
A	⁷ B ₁	–67.20040	–66.99891	1.851	2.250		37.285	18.643	110.20
C	⁷ Σ	–67.15434	–66.98146	1.665	1.935		26.336	13.168	121.14
<i>Be₂C₂</i>									
A	¹ A'	–105.53700	–105.23951	1.262	1.645	1.958	369.333	123.111	0.00
B	¹ A	–105.51373	–105.20842	1.476	1.571	2.770	349.824	116.608	19.51
B	³ B	–105.50047	–105.18526	1.330	1.657	3.037	335.292	111.764	34.04
C	¹ Σ ⁺	–105.45888	–105.15968	1.268	1.539	2.101	319.236	106.412	30.59
C	³ Σ ⁺	–105.41677	–105.11640	1.228	1.623	1.954	292.081	97.360	77.25
D	⁵ Δ _g	–105.42936	–105.11633	1.328	1.635		292.035	97.345	77.30
B	⁵ B	–105.42668	–105.11533	1.357	1.762	3.252	291.409	97.136	77.92
D	³ Σ _g ⁺	–105.55612	–105.07212	1.230	1.638		264.294	88.098	105.04
D	¹ Σ _g ⁺	–105.50531	–105.07127	1.232	1.645		263.762	87.921	105.57
C	⁵ Σ	–105.33621	–105.00166	1.227	1.609	2.179	220.083	73.361	149.25
E	³ Σ _g ⁺	–105.20991	–104.93090	5.509	1.744	2.021	175.675	58.558	193.66

^a Energies in atomic units.^b Energies in kcal/mol. Distances in angstroms.**Table 2**Energies and minimum distances of Be₄C₂ clusters. Column contents are described in the text.

Isomer	State	B3-LYP ^a	QCISD(T) ^a	d(C–C)	d(C–Be)	d(Be–Be)	E _{At} ^b	E _{At/(N–1)} ^b	ΔE _{Rel} ^b
A	¹ A'	–135.01900	–134.59319	2.338	1.628	2.022	448.176	89.635	0.00
B	¹ A	–135.00981	–134.58259	1.416	1.656	1.916	441.525	88.305	6.65
C	¹ A ₁	–134.99682	–134.57149	1.382	1.559	2.055	434.559	86.912	13.62
B	³ A	–135.00180	–134.57070	1.382	1.661	1.921	434.063	86.813	14.11
D	¹ A	–135.00132	–134.56943	1.440	1.564	1.986	433.266	86.653	14.91
A	³ A''	–134.99499	–134.56546	2.780	1.578	1.885	430.775	86.155	17.40
B	⁵ A'	–134.99316	–134.55808	1.353	1.651	2.451	426.144	85.229	22.03
E	¹ A	–134.97137	–134.54828	1.366	1.691	2.020	419.990	83.998	28.19
F	³ A	–134.96575	–134.54623	1.728	1.587	2.020	418.705	83.741	29.47
G	⁵ A	–134.97904	–134.54095	1.483	1.606	2.166	415.393	83.079	32.78
H	³ A _g	–134.96293	–134.53976	2.070	1.719	1.940	414.647	82.929	33.53
I	¹ A	–134.96767	–134.53606	2.751	1.560	1.850	412.322	82.464	35.85
J	⁵ A	–134.96210	–134.52091	2.660	1.605	2.008	402.817	80.563	45.36
K	¹ A	–134.93720	–134.51471	1.978	1.679	1.919	398.929	79.786	49.25
G	³ A''	–135.01258	–134.51162	1.402	1.657	2.039	396.989	79.398	51.19
C	⁵ B ₂	–134.92243	–134.50734	1.277	1.713	2.125	394.301	78.860	53.87
L	⁵ A''	–134.88456	–134.45007	4.216	1.604	2.080	358.363	71.673	89.81

^a Energies in atomic units.^b Energies in kcal/mol. Distances in angstroms.

silicides [16,17], and comparison of the results of the present with the former studies may offer additional structural insight.

2. Methods

Starting geometries for optimization of the smaller clusters were taken from stable geometries of the individual atomic clusters [21,22], of beryllium carbides reported in previous studies [9–14], of Be_{*n*}Si_{*n*} and Be_{2*n*}Si_{*n*} clusters [16] and of variations on the foregoing. Final geometries and harmonic frequencies were obtained in B3LYP/6-31G(2df) optimizations. B3LYP contains Becke's [23] three-parameter exchange functional and the

correlation functional of Lee, Yang and Parr [24]. Calculations were done with Gaussian09 [25].

In previous work on beryllium silicide clusters [16] energies were ordered in G3XMP2 [26] calculations. The Gaussian-n [26,27] series of theoretical methods accurately reproduce thermochemical energies through a sequence of calculations that accounts for errors of basis set truncation and dynamic correlation energy. Gaussian-nX calculations are based on initial B3LYP/6-31G(2df) geometry optimizations. These have been applied to a test set of several hundred molecules and shown to produce consistently accurate results, and we have therefore employed this optimization method in the present study.

Table 3
Energies and minimum distances of Be₃C₃ clusters. Column contents are described in the text.

Isomer	State	B3-LYP ^a	QCISD(T) ^a	d(C–C)	d(C–Be)	d(Be–Be)	E _{At} ^b	E _{At} /(N – 1) ^b	ΔE _{Rel} ^b
A	³ A	–158.38312	–157.92731	1.258	1.634	2.035	596.697	119.339	0.00
B	¹ A	–158.36176	–157.91703	1.286	1.578	1.954	589.461	117.892	7.24
C	¹ A	–158.29500	–157.90202	1.325	1.598	3.230	580.830	116.166	15.87
D	¹ A	–158.35051	–157.89474	1.314	1.538	2.086	576.260	115.252	20.44
C	⁵ A	–158.34096	–157.87693	1.315	1.628	3.159	565.085	113.017	31.61
E	³ A	–158.33828	–157.87545	1.425	1.646	2.492	564.155	112.831	32.54
B	³ A	–158.32846	–157.87492	1.290	1.645	2.018	563.823	112.765	32.87
E	¹ A	–158.32949	–157.87377	1.454	1.531	2.851	563.099	112.620	33.60
C	³ A	–158.33861	–157.87274	1.315	1.627	3.154	562.453	112.491	34.24
F	³ A	–158.31349	–157.85316	1.438	2.114	1.605	550.168	110.034	46.53
G	¹ A ₁	–158.28548	–157.85115	1.577	1.652	2.063	548.908	109.782	47.79
H	¹ A	–158.29261	–157.84733	1.377	1.734	2.096	546.508	109.302	50.19
I	¹ A′	–158.28272	–157.84066	1.395	1.617	2.004	542.327	108.465	54.37
I	³ A′	–158.28760	–157.83573	1.387	1.639	2.035	539.232	107.846	57.46
J	⁵ A	–158.26665	–157.81281	1.434	1.706	3.412	524.846	104.969	71.85
K	⁵ A	–158.24592	–157.80941	1.425	1.718	2.010	522.715	104.543	73.98
B	⁵ A	–158.24980	–157.79979	1.288	1.659	2.116	516.678	103.336	80.02
G	³ B ₁	–158.19976	–157.79465	1.566	1.646	1.979	513.452	102.690	83.24
I	⁵ A	–158.22853	–157.78090	1.395	1.640	1.981	504.822	100.964	91.87
F	¹ A	–158.29874	–157.77624	1.428	1.667	2.016	501.898	100.380	94.80
L	³ A ₁	–158.21502	–157.74864	2.347	1.592	3.038	484.582	96.916	112.11
L	⁵ A ₂	–158.20290	–157.73960	2.095	1.604	2.351	478.911	95.782	117.79

^a Energies in atomic units.

^b Energies in kcal/mol. Distances in angstroms.

Table 4
Energies and minimum distances of Be₆C₃ clusters. Column contents are described in the text.

Isomer	State	B3-LYP ^a	QCISD(T) ^a	d(C–C)	d(C–Be)	d(Be–Be)	E _{At} ^b	E _{At} /(N – 1) ^b	ΔE _{Rel} ^b
A	¹ A	–202.68001	–202.05519	1.303	1.585	1.963	776.056	97.007	0.00
B	³ A′′	–202.65999	–202.02897	2.698	1.712	1.927	759.604	94.950	16.45
C	¹ A	–202.65353	–202.02892	1.315	1.589	1.989	759.570	94.946	16.49
B	¹ A	–202.64122	–202.01611	2.221	1.631	1.904	751.530	93.941	24.53
A	³ A′′	–202.63945	–202.00879	1.380	1.586	1.953	746.938	93.367	29.12
D	³ A	–202.63220	–202.00222	1.297	1.592	1.979	742.813	92.852	33.24
E	¹ A	–202.62581	–201.99714	1.282	1.589	1.957	739.625	92.453	36.43
F	³ A	–202.62159	–201.99651	1.344	1.647	1.929	739.230	92.404	36.83
G	¹ A	–202.63231	–201.99112	1.444	1.557	1.916	735.850	91.981	40.21
G	³ A	–202.63389	–201.98662	1.444	1.557	2.065	733.026	91.628	43.03
H	¹ A	–202.59291	–201.97450	1.575	1.673	1.866	725.420	90.677	50.64
I	¹ A	–202.59412	–201.97289	13.212	1.633	1.938	724.413	90.552	51.64
J	³ A	–202.59898	–201.96923	1.463	1.623	1.939	722.117	90.265	53.94
B	¹ A′	–202.56697	–201.96644	2.626	1.742	2.000	720.366	90.046	55.69
K	³ A	–202.58354	–201.96176	1.435	1.648	1.918	717.427	89.678	58.63
D	⁵ A	–202.57562	–201.94307	1.369	1.621	2.031	705.698	88.212	70.36
L	³ A	–202.56377	–201.94259	1.352	1.662	1.939	705.394	88.174	70.66
B	⁵ A	–202.57497	–201.94174	2.713	1.705	1.862	704.862	88.108	71.19
E	⁵ A	–202.57185	–201.93660	1.321	1.653	2.018	701.637	87.705	74.42
L	¹ A	–202.55073	–201.93418	1.373	1.596	1.976	700.118	87.515	75.94
M	³ A	–202.55435	–201.92358	1.567	1.628	1.984	693.467	86.683	82.59
N	⁵ A	–202.55288	–201.92023	1.398	1.644	2.031	691.363	86.420	84.69
H	⁵ A	–202.54034	–201.91496	1.479	1.736	1.990	688.056	86.007	88.00
O	⁵ A	–202.53938	–201.91373	1.392	1.637	1.981	687.285	85.911	88.77
P	⁵ A	–202.56031	–201.88605	1.474	1.648	1.973	669.920	83.740	106.14

^a Energies in atomic units.

^b Energies in kcal/mol. Distances in angstroms.

Gaussian-n theory employs a QCISD(T)/6-31G* single-point calculation at the optimized geometry as the principal correlation energy correction. The present study replaces the multistep G3XMP2 process with a two-step estimation of the energy orderings via QCISD(T)/6-31G(2df) evaluated at the B3LYP/6-31G(2df) geometry. This is a time-saving approach, considering the more than 100 energy evaluations to be done, though it assumes that the 6-31G(2df) basis adequately describes the carbide clusters. For Be₂C and Be₂C₂ clusters in which the ground-state structures determined with the method disagree with the results of other studies QCISD/cc-pVTZ optimizations were performed, followed

by QCISD(T)/cc-pVTZ single-point energy calculations. This approach increases the degree of correlation energy correction in the optimization process, and uses the slightly larger cc-pVTZ correlation consistent basis sets [28] to probe possible basis-set effects on geometry and energy.

3. Results and discussion

Tables 1–7 list the calculated ground-state B3LYP/6-31G(2df) and QCISD(T) energies of clusters and minimum interatomic

Table 5
Energies and minimum distances of Be₄C₄ clusters. Column contents are described in the text.

Isomer	State	B3-LYP ^a	QCISD(T) ^a	d(C–C)	d(C–Be)	d(Be–Be)	E _{At} ^b	E _{At} /(N – 1) ^b	ΔE _{Rel} ^b
A	¹ A	–211.30272	–210.70051	1.283	2.032	1.640	877.652	125.379	0.00
B	¹ A	–211.27517	–210.67637	1.241	1.638	2.047	862.504	123.215	15.15
A	³ A	–211.28107	–210.67293	1.287	1.643	1.989	860.349	122.907	17.30
C	¹ A	–211.25732	–210.66830	1.273	1.701	1.906	857.444	122.492	20.21
D	¹ A	–211.25546	–210.66213	1.373	1.649	1.973	853.571	121.939	24.08
E	³ A	–211.25175	–210.64601	1.258	1.632	2.124	843.451	120.493	34.20
D	³ A	–211.22731	–210.63005	1.328	1.649	2.290	833.438	119.063	44.21
F	¹ A	–211.23450	–210.62615	1.452	1.557	2.051	830.994	118.713	46.66
G	³ A	–211.20053	–210.60847	1.268	1.633	2.069	819.899	117.128	57.75
H	¹ A	–211.20180	–210.60697	1.397	1.673	1.963	818.959	116.994	58.69
I	⁵ A	–211.21639	–210.60142	1.279	1.616	2.173	815.474	116.496	62.18
J	¹ A	–211.18656	–210.59545	1.297	1.664	1.945	811.726	115.961	65.93
F	⁵ A	–211.19815	–210.59212	1.324	1.646	2.221	809.638	115.663	68.01
K	¹ A	–211.18062	–210.59047	1.294	1.693	1.940	808.603	115.515	69.05
L	¹ A	–211.14640	–210.56259	1.397	1.617	2.080	791.105	113.015	86.55
L	³ A	–211.15968	–210.56138	1.376	1.633	1.966	790.346	112.907	87.31
M	¹ A	–211.13704	–210.55357	1.643	1.620	1.964	785.443	112.206	92.21
N	¹ A	–211.11402	–210.53463	1.455	1.610	1.981	773.560	110.509	104.09
O	⁵ A	–211.12706	–210.52406	1.250	1.642	2.287	766.927	109.561	110.72
P	³ A	–211.10203	–210.51805	1.342	1.647	1.993	763.158	109.023	114.49
N	⁵ A	–211.10759	–210.50489	1.362	1.624	2.141	754.899	107.843	122.75
L	⁵ A	–211.09587	–210.50319	1.276	1.697	2.070	753.835	107.691	123.82
Q	⁵ A	–211.08364	–210.48891	1.394	1.572	2.122	744.869	106.410	132.78
H	⁵ A	–211.07894	–210.48012	1.334	1.650	2.124	739.353	105.622	138.30
R	¹ A	–211.08955	–210.44765	1.328	1.637	1.997	718.978	102.711	158.67
R	⁵ A	–211.03563	–210.44744	1.430	1.633	2.020	718.852	102.693	158.80

^a Energies in atomic units.

^b Energies in kcal/mol. Distances in angstroms.

Table 6
Energies and minimum distances of Be₈C₄ clusters. Column contents are described in the text.

Isomer	State	B3-LYP ^a	QCISD(T) ^a	d(C–C)	d(C–Be)	d(Be–Be)	E _{At} ^b	E _{At} /(N – 1) ^b	ΔE _{Rel} ^b
A	¹ A	–270.36260	–269.52892	1.289	1.598	2.079	1111.298	101.027	0.00
B	¹ A	–270.33538	–269.50291	1.323	1.578	1.956	1094.976	99.543	16.32
C	¹ A	–270.32200	–269.49335	1.392	1.604	2.044	1088.977	98.998	22.32
D	³ A	–270.32161	–269.48211	2.589	1.610	1.925	1081.920	98.356	29.38
E	³ A	–270.31543	–269.47750	1.352	1.582	1.932	1079.030	98.094	32.27
F	³ A	–270.30554	–269.47110	2.701	1.653	1.867	1075.011	97.728	36.29
G	¹ A	–270.29759	–269.47030	1.337	1.681	1.954	1074.510	97.683	36.79
H	¹ A	–270.29104	–269.46435	2.554	2.080	2.082	1070.776	97.343	40.52
I	³ A	–270.25847	–269.43022	1.379	1.646	1.930	1049.361	95.396	61.94
J	¹ A	–270.25232	–269.42491	1.363	1.631	1.939	1046.028	95.093	65.27
J	³ A	–270.25123	–269.41809	1.674	1.588	1.915	1041.748	94.704	69.55
K	¹ A	–270.24565	–269.41179	2.773	1.639	2.008	1037.795	94.345	73.50
E	⁵ A	–270.24785	–269.40980	1.359	1.624	1.929	1036.548	94.232	74.75
L	⁵ A	–270.24018	–269.40024	2.562	1.618	1.907	1030.548	93.686	80.75
M	³ A	–270.22054	–269.39357	1.524	1.719	1.996	1026.361	93.306	84.94
M	¹ A	–270.22004	–269.39226	1.554	1.690	1.858	1025.538	93.231	85.76
N	³ A'	–270.22066	–269.39099	1.522	1.719	1.930	1024.743	93.158	86.56
I	⁵ A	–270.18958	–269.35765	1.395	1.649	1.944	1003.820	91.256	107.48
O	¹ A	–270.14882	–269.33032	1.416	1.611	1.965	986.671	89.697	124.63
P	¹ A	–270.13407	–269.31807	1.371	1.644	1.957	978.982	88.998	132.32
Q	⁵ A	–270.09951	–269.26990	1.652	1.631	2.065	948.760	86.251	162.54

^a Energies in atomic units.

^b Energies in kcal/mol. Distances in angstroms.

distances, while Figs. 1–7 depict the structures of low-energy structures for each cluster. The three rightmost columns of Table 1 show, respectively, the cluster atomization energies, the atomization energies divided by the number of atoms in the cluster less one, and the energy of each cluster relative to the most stable member of its kind calculated from the QCISD(T) energies. In each Figure carbon atoms are depicted as larger and darker in color; beryllium atoms are smaller and lighter. The size difference is used to make identification of the atoms easier; the covalent radii of the two are not very different. We shall discuss the clusters ordered by *n*, the number of carbon atoms.

BeC and Be₂C. BeC has a spin triplet ground state (see Table 1) at the QCISD(T)/6-31G(2df) level. The bond length is 1.67 Å. A quintet lies 0.19 eV (4.47 kcal/mol) above the ground state and a singlet somewhat higher. These findings agree closely with those obtained by Ghouri et al. [14] in B3PW91/6-31+G* calculations and by Patrick et al. [10] in B3PW91 calculations with a larger (8s, 7p, 1d) basis. Patrick et al. checked the B3PW91 results in CI and CASSCF calculations that confirmed the DFT result. Heaven et al. [7] have established the ground state of BeC both spectroscopically and in extensive computations and confirm the results of the purely computational studies. The ground state of BeSi is also ³Σ⁻.

Table 7
Energies and minimum distances of Be_5C_5 clusters. Column contents are described in the text.

Isomer	State	B3-LYP ^a	QCISD(T) ^a	$d(\text{C}-\text{C})$	$d(\text{C}-\text{Be})$	$d(\text{Be}-\text{Be})$	E_{At}^{b}	$E_{\text{At}}/(N-1)^{\text{b}}$	$\Delta E_{\text{Rel}}^{\text{b}}$
A	¹ A	-264.13882	-263.39902	1.263	1.596	1.970	1111.736	123.526	0.00
B	¹ A	-264.13182	-263.38496	1.275	1.572	1.886	1102.917	122.546	8.82
A	³ A	-264.12553	-263.37883	1.263	1.601	1.970	1099.072	122.119	12.66
C	³ A	-264.11953	-263.36701	1.254	1.584	2.041	1091.653	121.295	20.08
D	¹ A	-264.05737	-263.32859	1.314	1.661	2.001	1067.543	118.616	44.19
E	¹ A	-264.06519	-263.32101	1.286	1.644	2.049	1062.786	118.087	48.95
F	¹ A	-264.03910	-263.30933	1.261	1.629	1.971	1055.456	117.273	56.28
G	⁵ A	-264.04377	-263.29560	1.257	1.602	2.059	1046.843	116.316	64.89
E	³ A	-264.02056	-263.28500	1.269	1.635	2.039	1040.189	115.577	71.55
H	³ A	-264.02391	-263.28437	1.357	1.627	2.017	1039.798	115.533	71.94
C	⁵ A	-264.03714	-263.27904	1.262	1.653	2.031	1036.449	115.161	75.29
I	⁵ A	-263.99317	-263.25206	1.384	1.657	2.082	1019.518	113.280	92.22
H	⁵ A	-263.98986	-263.24953	1.354	1.673	2.000	1017.933	113.104	93.80
J	¹ A	-263.97767	-263.24145	1.412	1.613	1.980	1012.860	112.540	98.88
K	⁵ A'	-263.97627	-263.21173	1.413	1.645	2.699	994.216	110.468	117.52
L	⁵ A	-264.01878	-263.21056	1.263	1.636	2.028	993.480	110.387	118.26
M	¹ A	-263.92692	-263.19944	1.520	1.616	1.999	986.502	109.611	125.23
N	⁵ A	-263.92387	-263.18652	1.392	1.598	2.008	978.396	108.711	133.34
K	³ A	-263.97785	-263.11433	1.403	1.637	2.643	933.092	103.677	178.64

^a Energies in atomic units.

^b Energies in kcal/mol. Distances in angstroms.

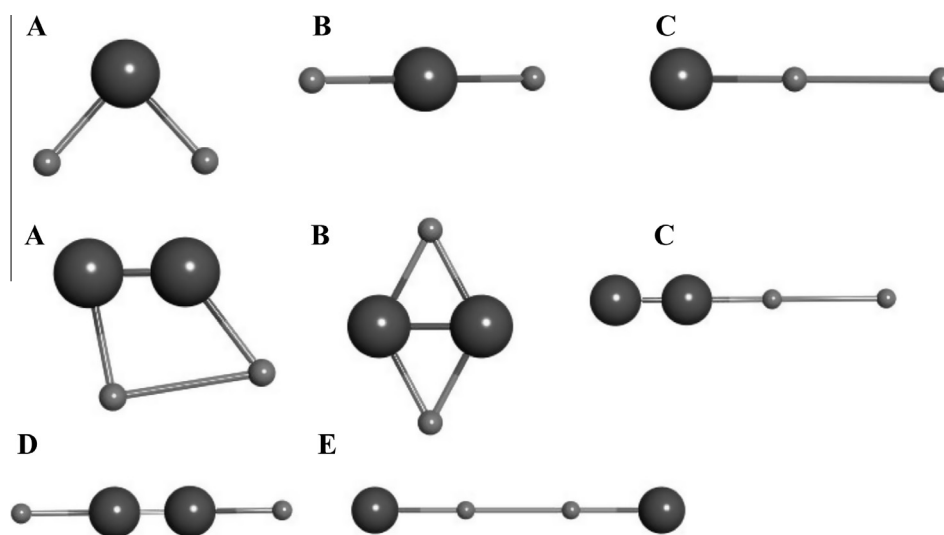


Fig. 1. B3LYP/6-31G(2df) optimized structures of Be_2C and Be_2C_2 . Carbons atoms are larger and darker in color; beryllium atoms are smaller and lighter.

Three low-lying structures of Be_2C were found. For each the singlet, triplet and quintet states lie relatively close in energy (Table 1). QCISD(T) places a bent ¹A₁ structure (Fig. 1, isomer A) lowest in energy and linear ⁵Σ_u⁺ isomer B 0.37 eV (8.53 kcal/mol) higher. The triplets of both these structures are also relatively low-lying, with all states of structure C, linear C–Be–Be, higher. These results agree with those obtained by Koch et al. [9], except that that work did not explore the quintet or septet states, and therefore reported the ³B₁ state of structure A to be second-lowest in energy. Ghouri et al. [14] found the bent triplet to be the global minimum. It should be noted that the B3 functional [23] employed in all the DFT calculations under discussion admixes Hartree–Fock exchange, and therefore possesses the tendency of the HF method to favor higher multiplicities. It is a tendency that can be corrected by accounting for dynamic (pairwise) electron correlation, which QCISD(T) does well. Although the singlet is the lower energy multiplicity (Table 1) in B3LYP calculations, the B3LYP energy of the ³B₁ state is much nearer that of the ¹A₁ than is the QCISD(T).

In Be_2Si B3LYP finds the ³B₁ state to be lowest in energy, whereas G3XMP2 theory establishes the singlet as ground state [16].

Patrick et al. [10] found the ground state of Be_2C to be the ⁵Σ_u⁺ state of the linear isomer B (Fig. 1), 0.12 eV (2.76 kcal/mol) lower in energy than the singlet of bent structure A. Four studies of Be_2C thus arrive at three different ground states. Calculations on the singlet, triplet and quintet states of isomers A and B were carried out using QCISD/cc-pVTZ geometry optimizations to test the accuracy of the B3LYP geometries, followed by QCISD(T) energy evaluation. The geometries calculated differed very slightly from the B3LYP/6-31G(2df) optimized geometries, which in turn differ little from the geometries reported in any of the studies cited. The global minimum was found to be the ¹A₁ state of structure A, 0.41 eV (9.43 kcal/mol) below the ³B₁ state of the same structure, which lay 0.02 eV below the ⁵Σ_u⁺ state of structure B. Thus the larger-scale calculations reverse the order of the second- and third-lowest energy species. That the two studies which agree on the ground state, this one and that of Koch et al. [9], both employ

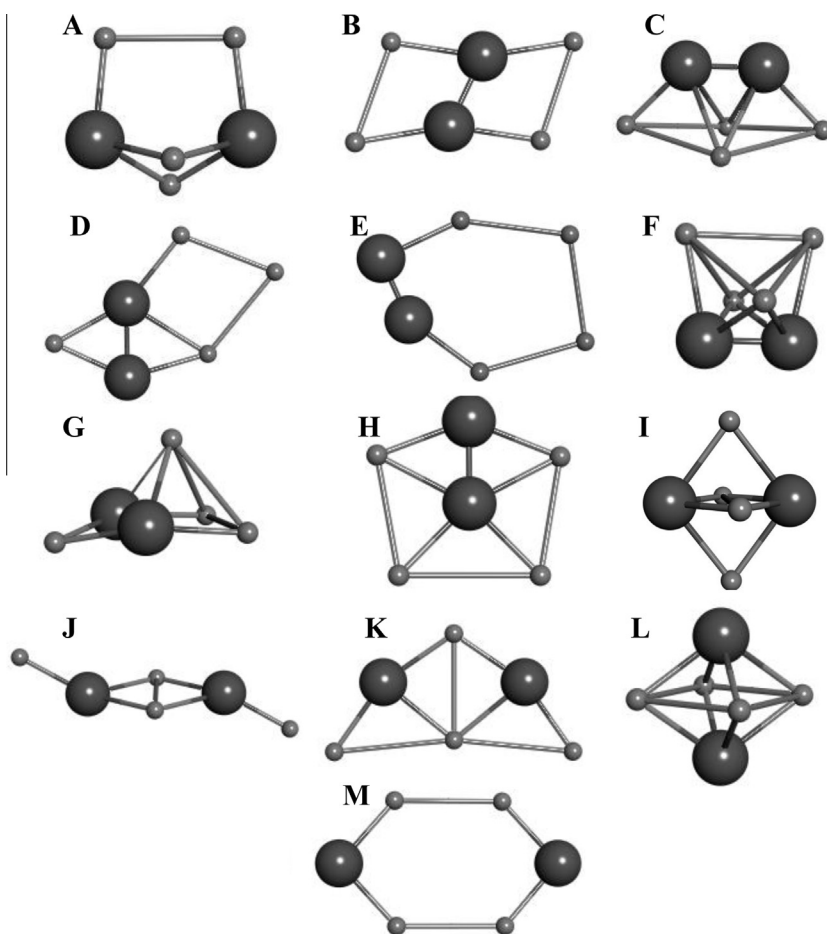


Fig. 2. Optimized structures of low-energy Be_4C_2 clusters labeled from A to M in order of decreasing stability.

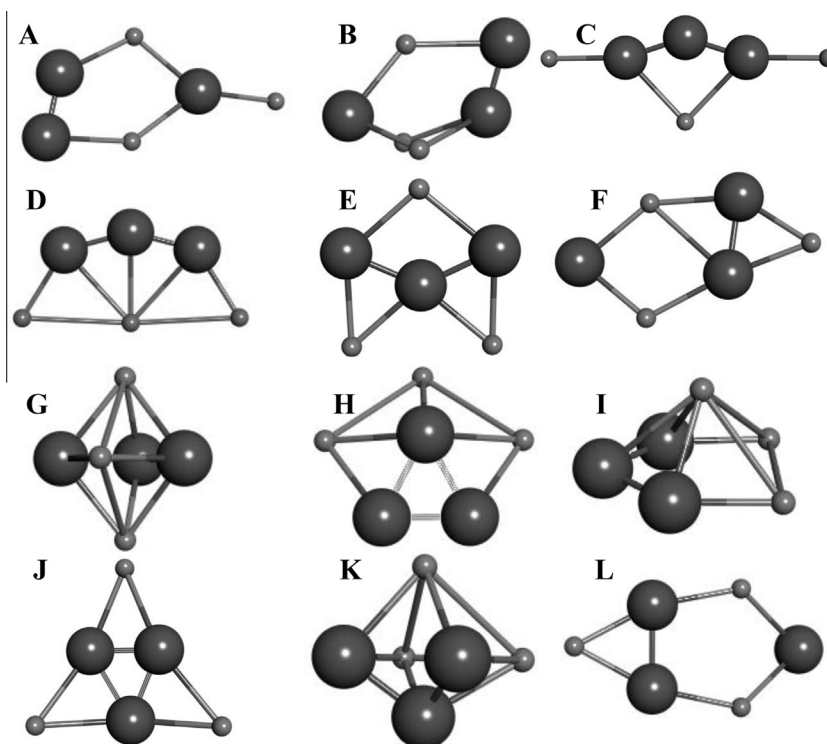


Fig. 3. Optimized structures of low-energy Be_3C_3 clusters labeled from A to L in order of decreasing stability.

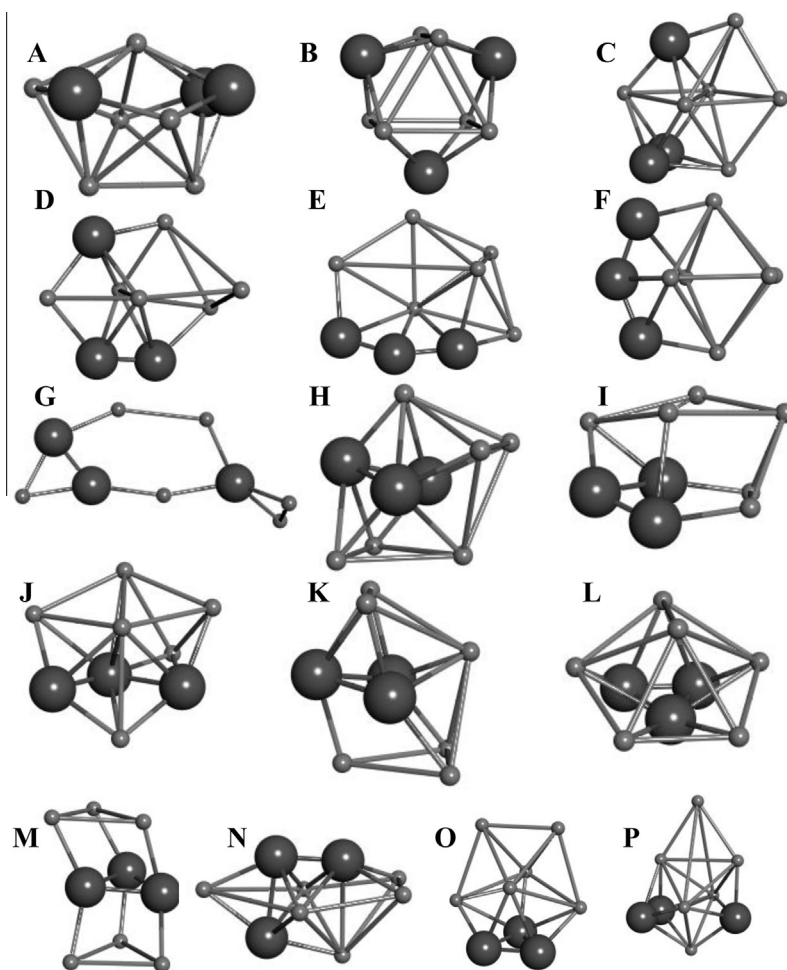


Fig. 4. Optimized structures of low-energy Be_6C_3 clusters labeled from A to P in order of decreasing stability.

methods that correct at a high level for dynamic correlation indicates that effective accounting for dynamic correlation is needed to accurately order the isomer energies.

The comparison of Be_2C and Be_2Si offers no surprises. The minimum energy isomer of both is the bent $^1\text{A}_1$ state. The linear isomers found in Be_2C were not found in Be_2Si , where the linear Be-Si-Be structure is a saddle point on the potential surface. The bent structures differ somewhat because Be-C bonds are shorter (1.6–1.7 Å) than Be-Be (about 2.1–2.2 Å), whereas Be-Si bonds are similar in length to Be-Be . Thus bent Be_2C is distinctly isosceles where Be_2Si is nearly equilateral.

Be_2C_2 and Be_4C_2 . The ground-state structure is a singlet planar quadrilateral, Fig. 1 Be_2C_2 structure A, in which there is a C–C triple bond, strong interaction between the two Be atoms and a bond between the nearest C–Be pair. The higher-energy isomers include B, a rhombic quadrilateral structure slightly distorted from D_{2h} symmetry, and three linear structures C, D and E. These results disagree with those of the other extant studies of Be_2C_2 , each of which finds the $\text{D}_{\infty h}$ isomer D in the triplet state to be lowest in energy. Ghouri et al. [14] report structure A but find it 0.61 eV (14.03 kcal/mol) higher in energy than structure D. Koch et al. [9] and Patrick et al. [10] find the triplet state of the linear isomer to be the global minimum, followed in energy by singlet isomers A and B. Neither reported structures C nor E, so the discrepancy is really in the relative position of structure D in its singlet, triplet and quintet states; the quintet must be considered because (Table 1) it lies lower in energy than the singlet and triplet.

Reoptimization of the Be_2C_2 isomers A, B and D in QCISD/cc-pVTZ calculations, followed by QCISD(T) energy evaluation at the minimum energy geometry revealed almost no changes in geometry nor any alteration in the energy ordering shown in Table 1. The singlet states of isomers A and B, respectively, remained the low-energy forms followed by the triplet states in the same order. The quintet state of isomer D was found to be lower in energy than the triplet, which in turn was slightly more stable than the singlet. A clue to the relative stability of the quintet in structure D may lie in the spin density analysis, which places one unpaired electron on each of the four atoms. Whereas in the singlet and triplet the carbons are triply bonded, in the quintet the bond is double. The relative energy lowering may therefore be attributed to a lowering of electron kinetic energy rather than of potential energy. The fact that the study by Koch et al. [9] found a different ground state, even though they employed MP2 to recover correlation energy, focuses attention on the absence of f-type polarization functions in that study, and indeed Koch et al. [9], Patrick et al. [10] and Ghouri et al. [14] all rely on d-type functions for polarization, whereas the carbide clusters feature some quite acute angles, accurate description of which may well be expected to require higher- l polarization.

There are interesting parallels to be seen between the Be_2C_2 and Be_2Si_2 isomers. In Be_2Si_2 [16] the ground state resembles Be_2C_2 structure B (except that the Si–Si bond is single) followed in energy by A and then by a distorted tetrahedral structure that was not found in Be_2C_2 . No linear structures were found for Be_2Si_2 .

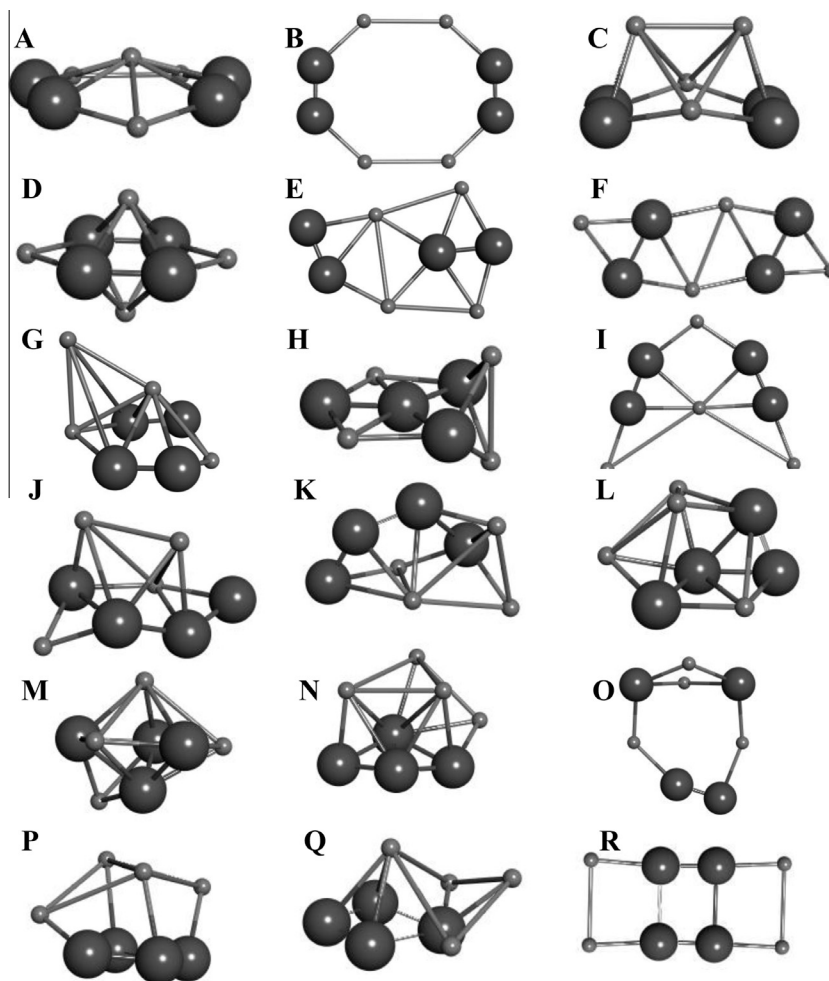


Fig. 5. Optimized structures of low-energy Be_4C_4 clusters labeled from A to R in order of decreasing stability.

The presence of the three-dimensional isomer in Be_2Si_2 , its absence in Be_2C_2 and the absence of linear isomers among those of Be_2Si_2 are illustrative of the differences in general structural properties of carbon and silicon clusters. Be_2C_2 isomer B exhibits more charge transfer than any other carbide cluster in this study. Each C transfers 0.4 electron to the Be atoms. While much greater charge transfer is common in the silicides, in the carbides transfer of more than 0.1 electron is uncommon.

A dozen Be_4C_2 structures were identified (Fig. 2), eight of which lie within 1 eV of each other. For Be_4C_2 Ghouri et al. [14] found two planar, singlet isomers, both similar to structure E, in which a C–C pair is bonded to a quadrilateral of beryllium atoms. The structures of Patrick et al. [10] are represented in Fig. 2 though they are ordered differently in energy. Structure F is found to be lowest in energy in that study, followed by G, B and D.

As with Be_2C_2 and its silicon analogs Be_4C_2 and Be_4Si_2 present similarities. Four Be_4Si_2 clusters were found [16], and their structures appear among the isomers shown in Fig. 2. The global minimum Be_4Si_2 structure is similar to isomer G, a nearly planar, nearly regular Be_3Si_2 pentagon with a Be cap. The silicide cluster differs from the carbide in that the distances from cap to planar atoms in the former are almost equal, whereas in Be_4C_2 the cap is much nearer two of the plane berylliums than to the third, and the pentagon itself is not approximately regular. Be_4Si_2 analogs to isomers C and F were optimized, as was a distorted octahedral cluster, analogous to either I or L in Fig. 2. The low-energy form of Be_6 is octahedral [21]. There are five planar Be_4C_2 clusters, B, D, E, K and M, but no planar isomers of Be_4Si_2 were found.

Be_3C_3 and Be_6C_3 . Again some similarity between the clusters of Be_3C_3 (Fig. 3) and Be_3Si_3 present themselves. The three low-energy Be_3Si_3 isomers all have analogs among the Be_3C_3 isomers, though the energy ordering differs. The three Be_3Si_3 structures among the isomers of Fig. 3 are, respectively in energy from low to high, G, I and F. Be_3C_3 structure F is planar whereas the Be_3Si_3 analog is slightly buckled. In fact Be_3C_3 clusters C, D, E, F, J and K are all planar, while again no planar Be_3Si_3 structures were optimized. Be_3C_3 structures A and C contain dangling beryllium atoms, another feature absent in the isomers of Be_3Si_3 . In addition the ground electronic states of all Be_3Si_3 [16] clusters were singlet, while the three low-energy isomers of Be_3C_3 are, respectively, triplet, singlet and quintet.

Patrick et al. [10] optimized structures of five Be_3C_3 clusters, three planar and one three-dimensional, and four of the structures appear in Fig. 3. The non-planar structure was found to be the lowest in energy; it is structure B, the second-lowest energy cluster in Fig. 3. The planar clusters have structures D, C and E in order of energy. The one structure not present in the figure is a slightly distorted version of C. Attempts to optimize this structure failed, leading either to C or E. Ghouri et al. [14] found two planar structures, the lowest in energy being D and the other the distorted version of C found by Patrick et al.

Isomers H and I display capped pentagonal structures, interesting because the capped pentagon is a stable geometry for Be_6 [21], and is the most stable structure for Be_4Si_2 [16]. H is a Be_3C_2 pentagon capped by a C, while I features a Be_2C_3 pentagon capped by Be.

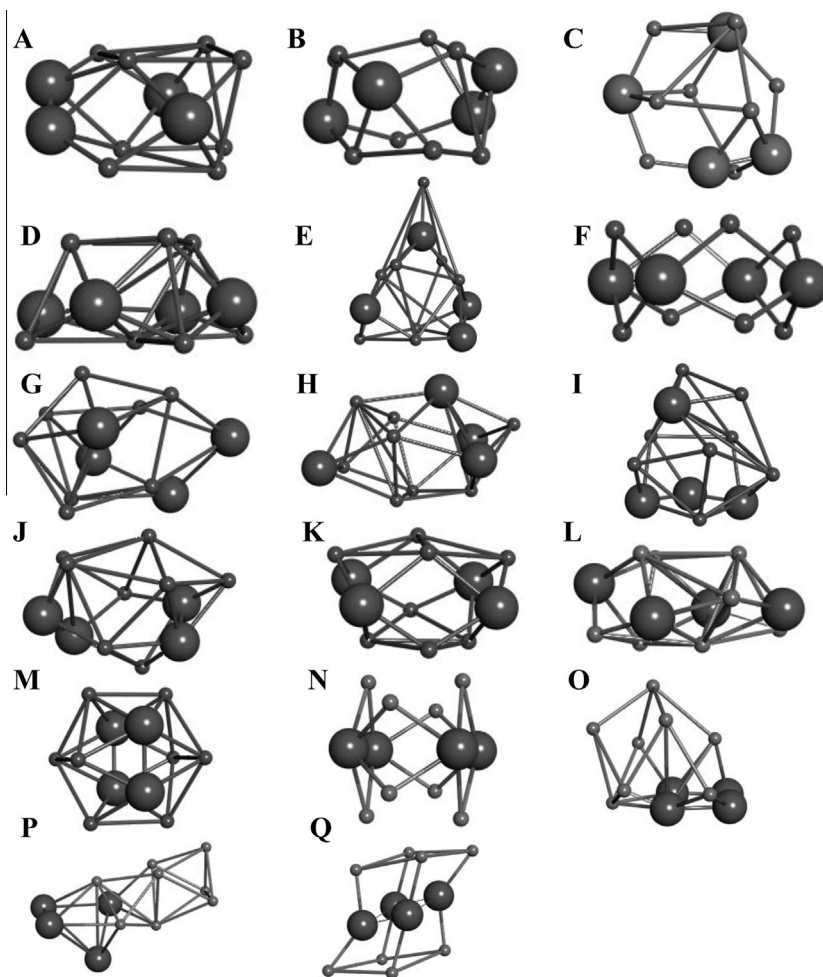


Fig. 6. Optimized structures of low-energy Be_8C_4 clusters labeled from A to Q in order of decreasing stability.

The Be_6C_3 clusters (Fig. 4) share several features with their Be_6Si_3 counterparts. The global minimum energy cluster of Be_6Si_3 is a trigonal prism of beryllium atoms with silicon face caps, similar to structure B, the second-low energy isomer of Be_6C_3 . The lowest energy Be_6C_3 cluster gives the appearance of being constructed from two bent rhombic Be_2C_2 units joined on an edge and connected by Be–Be bonds to a Be_3 triangle. This structure is second-lowest among the optimized Be_6Si_3 clusters. As the two low-energy isomers of Be_6Si_3 and Be_6C_3 correspond but interchange places in the order, so also do the third and fourth clusters. From here a step in energy separates the four low-energy Be_6C_3 isomers from the rest. Several may be seen to incorporate a distinctive C_3 moiety, but all such structures are higher in energy than the four low-energy isomers that feature bridging Be atoms.

Overall the Be_6C_3 clusters are quite compact; linear and planar structures are absent from Fig. 4. Ghouri et al. [14] did optimize a planar structure similar to structure G. Structure G consists of a C_2 unit (bond length 1.44 Å), bonded to three Be atoms, two of which are bridged by another Be. The third C bridges two beryllium atoms, and the entire Be_4C_3 moiety is nearly planar. However, two terminal Be atoms coordinate to the third C and are out-of-plane by about 90° , providing tetrahedral coordination to the single carbon. The completely planar structure reported by Ghouri et al. is a saddle point on the B3LYP/6-31G(2df) surface. Ghouri et al. report a triplet ground state, in which the B3LYP calculation concurs. At the QCISD(T) level, however, the singlet is lower in energy than the triplet by 0.12 eV (2.76 kcal/mol).

Be_4C_4 and Be_5C_4 . Eighteen low-lying structures of Be_4C_4 are presented in Fig. 5. L and M, clusters similar to the two lowest-energy isomers of Be_4Si_4 appear among them, and in fact only two of the seven optimized Be_4Si_4 structures have no analogs among those of Be_4C_4 . The four planar Be_4C_4 structures in the figure have no counterparts among the Be_4Si_4 clusters.

Ghouri et al. [14] found six structures, planar or partly so with one or two atoms out of the plane. The lowest in energy among these is a slightly distorted form of structure B, and F was also found. The low-energy structure in Fig. 5 appears as well, but with a Be and C interchanged, and there is a structure similar to I, but with a single Be displaced somewhat.

In the Be_8C_4 clusters both the structural similarities and differences with the Be_8Si_4 manifest themselves. The two lowest-energy isomers of Be_8Si_4 are symmetric, D_{2h} and D_{2d} [16]. In the global minimum energy isomer the atoms are arranged at the vertices of an almost-regular icosahedron. The analogous structure (M in Fig. 6) appears among the isomers of Be_8C_4 , but it is neither low in energy nor as symmetrical as the corresponding Be_8Si_4 isomer. The symmetry of the silicide clusters owe to the similarity in length of the Be–Be and Be–Si bonds. The D_{2d} isomer of Be_8Si_4 is also reflected among the Be_8C_4 structures; both structures F and N are similar, yet again lower in symmetry than the Be_8Si_4 cluster. Among the low-energy clusters of Be_8C_4 only structure B reflects a low-energy Be_8Si_4 structure. It is similar to the fourth-lowest-energy cluster. Thus, although all the low-energy cluster structures of Be_8Si_4 appear in Fig. 6, the overall cluster structures of Be_8Si_4 and Be_8C_4 are more different than alike.

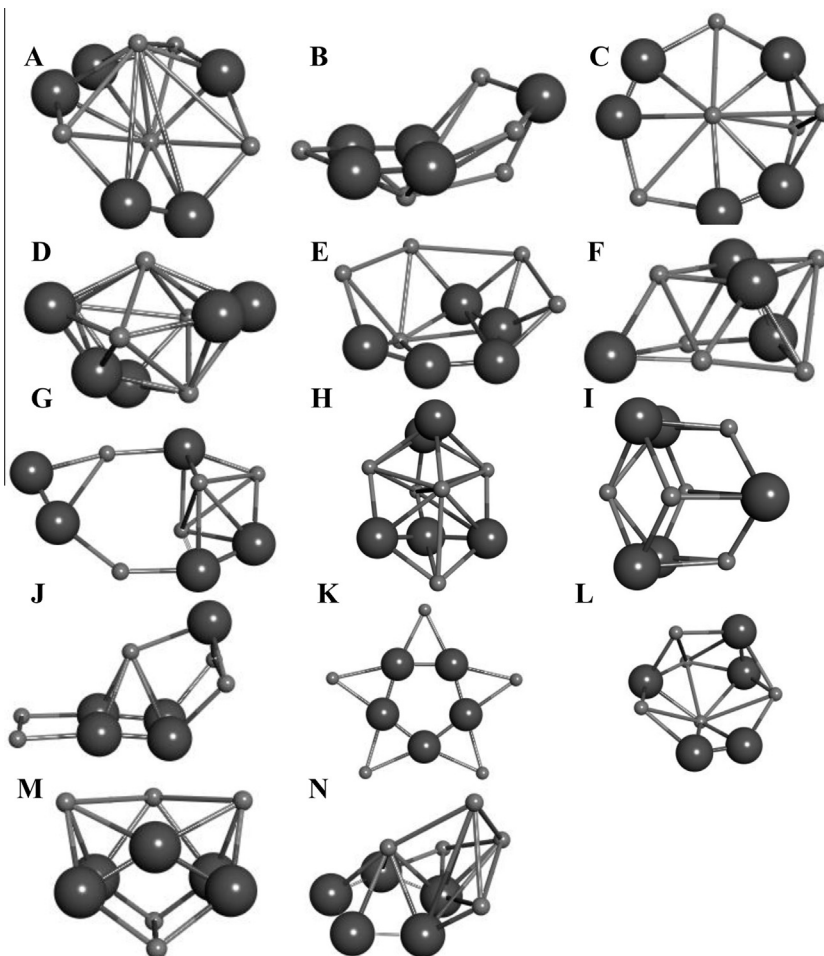


Fig. 7. Optimized structures of low-energy Be_5C_5 clusters labeled from A to N in order of decreasing stability.

Be_5C_5 . Ghouri et al. [14] identified twelve Be_5C_5 geometries. However, because of the emphasis of their study on planar and partial-planar structures most are higher in energy than the structures shown in Fig. 7. The low-energy cluster found by Ghouri et al. is a planar Be-centric structure, somewhat similar to structure C of Fig. 7. The latter structure, though, displays a pair of out-of-plane Be atoms. Their next lowest energy cluster is non-planar and similar to J. The one planar structure displayed in Fig. 7, K, does not appear among those determined by Ghouri et al. K features a regular pentagonal arrangement of carbons, with C–C length of 1.41 Å, and one Be bridge per side that appears to be a candidate upon which to base a stable cage cluster. The global minimum energy structure, Fig. 7A, is distinctly three-dimensional, with two C–C pairs and a single C surrounding a central Be, the rest of the Be atoms acting as bridges.

Though the Be_5Si_5 clusters were not included in the previous small-cluster study [16], six clusters were optimized for this study. The low-energy Be_5C_5 geometry is quite similar to structure D of Fig. 7, one cluster is similar to I, but the remainder are unlike the carbides. Again it should be noted that the low-energy clusters feature extensive C–Be–C bridging. A number feature C–C pairs, but separation into Be and C clusters is not seen except in the very high-energy cluster N. Planar clusters and clusters such as K and N that feature regular pentagons of carbon atoms do not have analogous structures among the silicides.

4. Conclusions

The small beryllium carbide clusters examined in this study display many more stable structures than the corresponding beryllium silicides [16]. Besides the fact that the small and similar size of C and Be abets compactness, the capacity of C atoms to form multiple bonds to each other facilitates the sort of subtle variations in structure that characterizes carbon compounds in general. The 3-, 4- and 5-carbon clusters each have isomers with single, double and triple C–C bonds. Thus, though the most stable clusters larger than Be_2C_2 are three-dimensional, linear and planar clusters, or clusters with linear or planar portions, features almost lacking among the beryllium silicides, are found among the carbides. Planarity is seen among the most stable Be_3C_3 and Be_4C_4 clusters, though not in Be_6C_3 or Be_8C_4 . Even Be_5C_5 has two low-energy isomers in which the carbons lie in a plane, with only bridging Be atoms out of the plane. Planar structures are more fully explored in the work of Ghouri et al. [14], who have found several that, though too high in energy to be included among the isomers presented in this study, are nonetheless potentially important on the surfaces of interstellar dust particles.

Pairing of carbon atoms is seen in most of the clusters, but no tendency toward division into C and Be domains is to be found. Though in 7 of the 9 lowest-energy isomers of Be_4C_2 the two carbons are bonded, in the global minimum energy structure they

are not. Similarly in the 3-, 4- and 5-C clusters there are isomers in which the carbon atoms are all bonded to each other, but they are not the lowest structures in energy. In this the carbide clusters resemble the silicides; Be seems to be an effective bridging component. On the other hand face-capping by C is not as common as is Si face-capping in the silicides, primarily because C–Be bonds are not long enough to accommodate face-capped structures without considerable strain. Perhaps corollary is the observation that, though carbide structures similar in form to the corresponding silicides appear in each set of clusters, these are not among the most stable except in Be_2C and Be_2C_2 .

Charge transfer on the scale seen in the silicides, where transfer of as much as three-quarters of an electron charge from Si to Be is seen, is rare in the carbides. Carbon does act as an electron donor in some clusters, but the magnitude of charge transferred is typically less than 0.1 electron. The bonding in these complexes is therefore much more purely covalent.

The atomization energies divided by $N_{\text{atoms}} - 1$ provide a measure of the stability of each cluster per added atom. Cluster stability per atom increases with cluster size, but incremental increases decrease with size. This is expected; the incremental increase should approach zero as clusters approach the bulk solid. Stability per atom appears to alternate between the Be_nC_n and the Be_{2n}C_n clusters; $E_{\text{atomization}}/N_{\text{atoms}} - 1$ is greater for the 1:1 clusters than for their 2:1 counterparts. The alternation seems to arise from the fact that each C contributes twice the number of valence electrons to each cluster as does each Be; thus the clusters with the lower Be:C ratio can potentially form more bonds per atom. If we compare Be_6C_3 with Be_4C_4 , clusters with equal numbers of valence electrons and nearly equal size, we see that the average atomization energies are quite close.

The search for structural elements among the small carbides from which to fabricate larger clusters finds comparatively few, though the sheer number of clusters of each stoichiometry does produce some interesting possibilities, especially among the 4- and 5-C clusters. Among the interesting examples are structures B and C of Fig. 5, F and M of Fig. 6 and I and K of Fig. 7.

Conflict of interest

There is no conflict of interest.

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