

Aromatic Cages $B_{42}^{0/+}$: Unprecedented Existence of Octagonal Holes in Boron Clusters

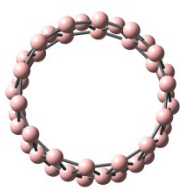
Truong Ba Tai,* Sang Uck Lee and Minh Tho Nguyen*

Supplementary Information. The file contains

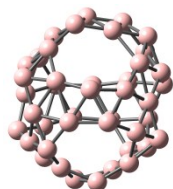
- Computational methods
- Shapes and relative energies of the low-lying isomers of $B_{42}^{0/+}$ obtained at the PBE0/6-311+G(d) level (Figure S1 and S2)
- Born-Oppenheimer molecular simulations of the lowest isomers $B_{42}^{0/+}$ at 500K. The root-mean square deviation (RMSD) values are analyzed using VMD code (Figure S3)
- Cartesian coordinates of the low-lying isomers (Table S1)

Computational methods

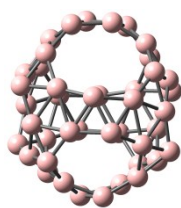
All electronic structure calculations were carried out using the Gaussian 09, Molpro 09 and Turbomole 7.0 packages. Initial searches for possible lower-lying isomers of $B_{42}^{0/+}$ clusters were performed using a stochastic search algorithm that was implemented by us. Firstly, the possible structures of the clusters were generated by a random kick method, and then rapidly optimized using density functional theory with the PBE0 functional and the small 3-21G basis set. In this search procedure, the minimum and maximum distances between atoms were limited to 1.5 and 20 Å, respectively. With 5000 initial structures generated, there are over 1000 isomers located at the PBE0/3-21G level of theory in which many structures have energy and geometries overlapped. Geometries of over 200 local minima with relative energies lying in the range of 0.0 - 5.0 eV (at the PBE0/3-21G) and their harmonic vibrational frequencies were further refined using the PBE0 functional but in conjunction with the larger 6-311+G(d) basis set. Single-point electronic energies of few low-lying isomers obtained from PBE0/6-311+G(d) computations were subsequently calculated using the coupled-cluster theory CCSD(T)/6-31G(d) for the neutral B_{42} and MP4(SDQ)/6-31G(d), CCSD(T)/def-SV(P) for the cation B_{42}^+ . The def-SV(P) basis set was widely used in Turbomole and has quality similar to the 6-31G(d) basis set.



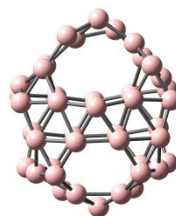
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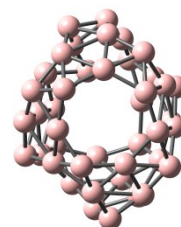
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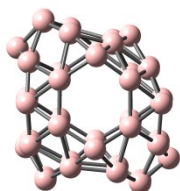
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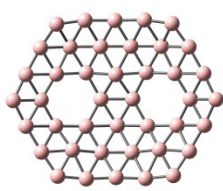
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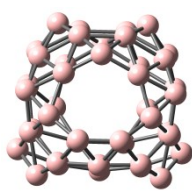
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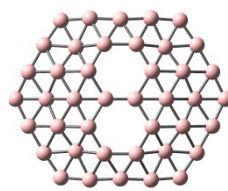
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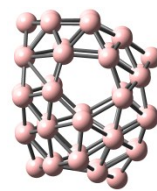
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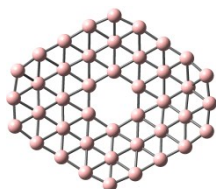
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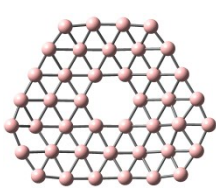
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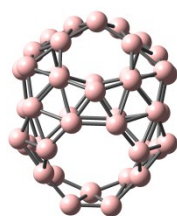
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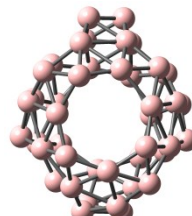
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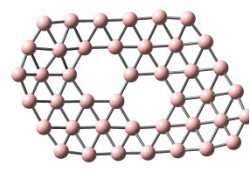
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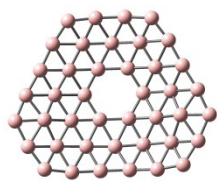
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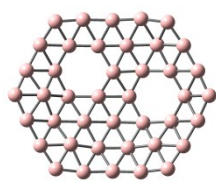
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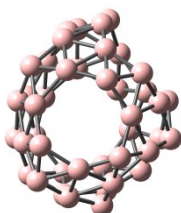
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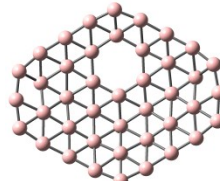
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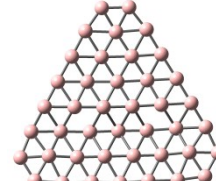
B42.n.17
1.74



B42.n.18
1.97



B42.n.19
2.20



B42.n.20
2.26

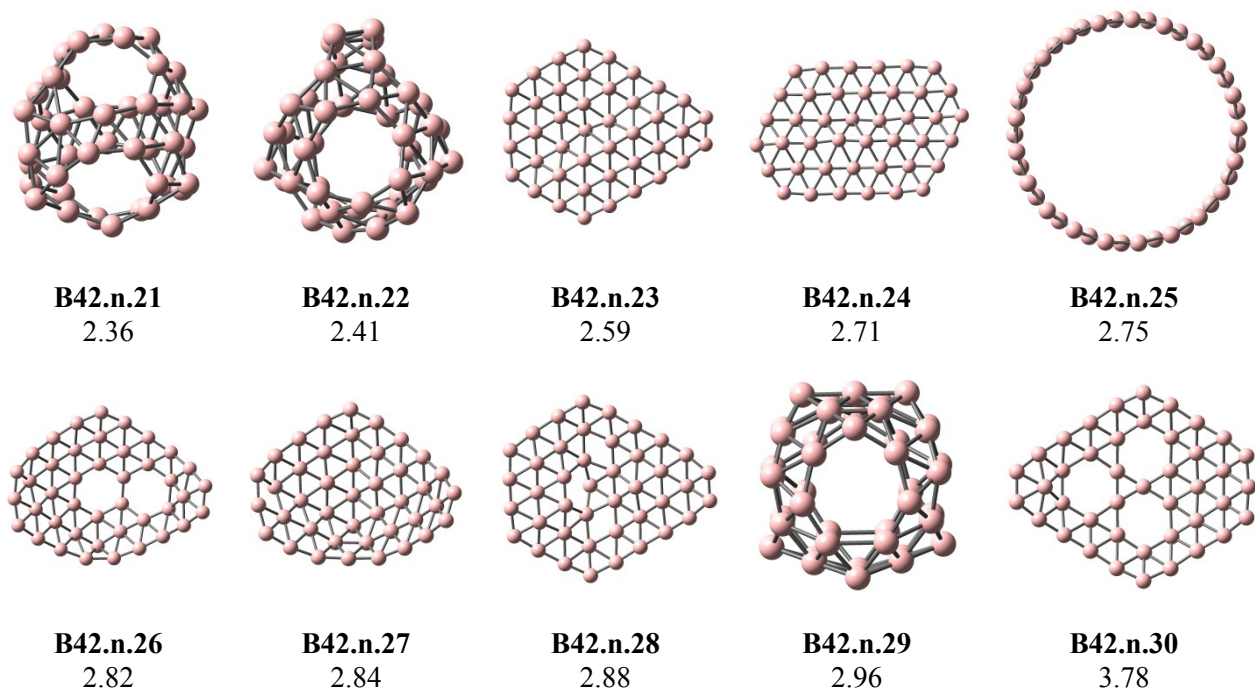


Figure S1 Shapes and relative energies (eV) of the low-lying isomers B_{42} obtained at the PBE0/6-311+G(d) level



B42.c.1
0.00



B42.c.2
0.00



B42.c.3
0.15



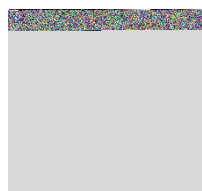
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B42.c.5
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B42.c.6
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B42.c.7
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B42.c.8
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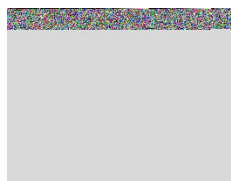
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B42.c.10
0.89



B42.c.11
1.20



B42.c.12
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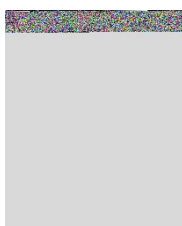
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B42.c.14
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B42.c.15
1.41



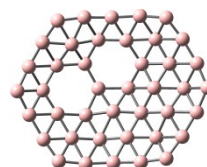
B42.c.16
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B42.c.17
1.42



B42.c.18
1.61



B42.c.19
1.76



B42.c.20
1.85

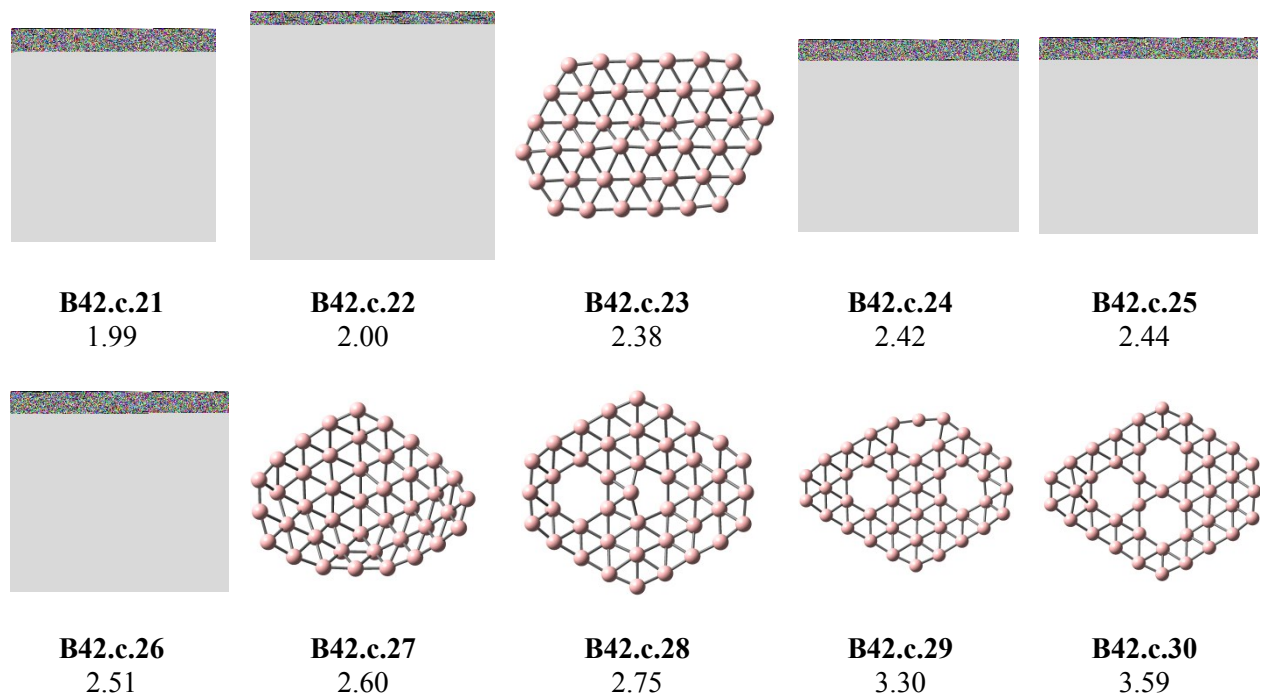


Figure S2 Shapes and relative energies (eV) of the low-lying isomers for cation B_{42}^+ obtained at the PBE0/6-311+G(d) level

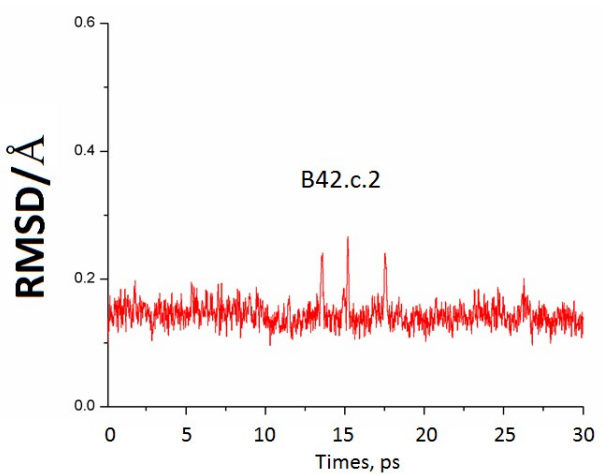
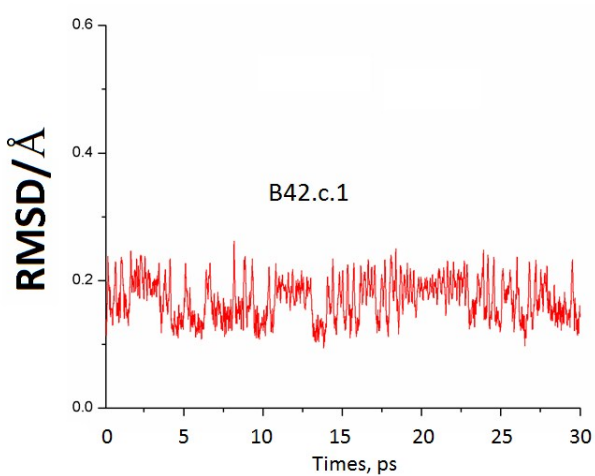
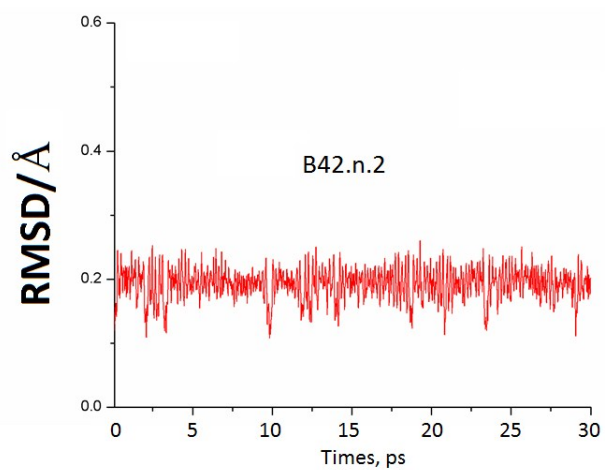
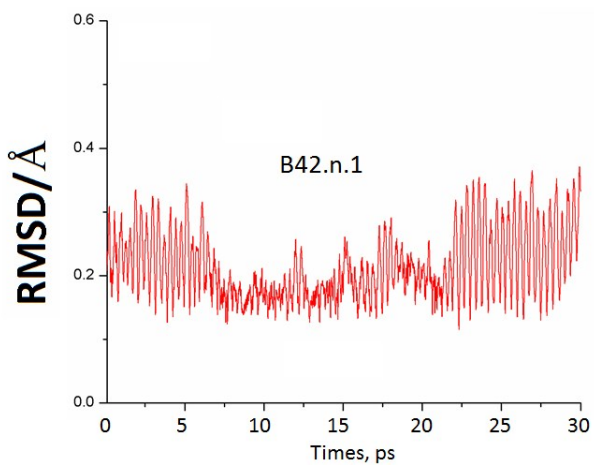


Figure S3 Born-Oppenheimer molecular simulations of the lowest isomers B_{42} at 500K. The root-mean square deviation (RMSD) values are analyzed using VMD code

Table S1 Cartesian coordinates (in unit of Angstrom) of the low-lying isomers

B42.n.1			
5	-0.796707000	3.490235000	-1.503719000
5	0.798348000	3.497879000	-1.502981000
5	2.232037000	2.799017000	-1.503719000
5	3.580012000	0.000082000	-1.503719000
5	3.232531000	-1.556683000	-1.502981000
5	2.232165000	-2.798915000	-1.503719000
5	0.798386000	-3.497871000	-1.502981000
5	-0.796548000	-3.490272000	-1.503719000
5	-2.236960000	-2.805090000	-1.502981000
5	-3.225444000	-1.553383000	-1.503719000
5	-3.587829000	-0.000020000	-1.502981000
5	-3.225515000	1.553235000	-1.503719000
5	-2.236990000	2.805066000	-1.502981000
5	3.232514000	1.556718000	-1.502981000
5	-0.000114000	3.763087000	-0.000030000
5	1.632276000	3.389810000	0.000013000
5	2.942028000	2.346335000	-0.000030000
5	3.668764000	-0.837254000	-0.000030000
5	2.941604000	-2.345655000	0.000013000
5	1.632845000	-3.390374000	-0.000030000
5	0.000153000	-3.762331000	0.000013000
5	-1.632639000	-3.390473000	-0.000030000
5	-2.941413000	-2.345895000	0.000013000
5	-3.668713000	-0.837477000	-0.000030000
5	-3.668036000	0.837048000	0.000013000
5	-2.942171000	2.346157000	-0.000030000
5	-1.632552000	3.389676000	0.000013000
5	-0.798449000	3.498063000	1.502827000
5	0.796576000	3.490029000	1.503889000
5	2.237071000	2.805259000	1.502827000
5	3.588031000	0.000038000	1.502827000
5	3.225271000	-1.553209000	1.503889000
5	2.237130000	-2.805212000	1.502827000
5	0.796576000	-3.490029000	1.503889000
5	-0.798375000	-3.498080000	1.502827000
5	-2.231957000	-2.798785000	1.503889000
5	-3.232688000	-1.556822000	1.502827000
5	-3.579781000	0.000000000	1.503889000
5	-3.232720000	1.556754000	1.502827000
5	-2.231957000	2.798786000	1.503889000
5	3.225272000	1.553209000	1.503889000
5	3.667967000	0.837347000	0.000013000

B42.n.2

5	1.703396000	-2.653534000	0.344459000
5	2.985434000	-1.642623000	0.667360000
5	1.740889000	0.306696000	2.509126000
5	0.618224000	-0.700735000	3.039089000
5	-1.031967000	-2.791074000	1.034786000
5	-1.878052000	-1.415843000	1.823544000
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5	3.122059000	-0.431989000	-0.505864000
5	1.303058000	-2.495029000	-1.445435000
5	-0.152547000	-1.937840000	2.245978000
5	-0.954008000	-0.564465000	2.827353000
5	2.940581000	-0.181370000	1.315963000
5	2.698100000	-2.001356000	-0.854026000
5	0.525453000	-3.103656000	1.349588000
5	-2.534350000	-2.346039000	0.628490000
5	0.148765000	-3.136913000	-0.241748000
5	1.167988000	1.908975000	2.023924000
5	2.689334000	1.362846000	1.730451000
5	2.999530000	1.159926000	0.136398000
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5	1.651331000	1.029581000	-2.303811000
5	0.302082000	-1.568313000	-2.585204000
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5	0.757887000	-0.139078000	-3.118447000
5	-2.637365000	-1.522481000	-0.802451000
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5	0.348501000	2.960402000	0.901583000
5	1.053890000	3.260639000	-0.545060000
5	-0.548531000	3.091542000	-0.655142000
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B42.n.3

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5	2.592899000	0.153525000	-1.880364000
5	-2.484241000	1.701153000	0.111725000
5	-2.808418000	1.415464000	-1.477550000
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5	0.163336000	-3.076136000	-0.821664000
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B42.n.4

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B42.c.1

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5	-3.378438000	0.328425000	0.722195000
5	-2.088447000	2.128896000	-1.696166000
5	0.884494000	3.192239000	-0.989941000
5	-1.874388000	2.590634000	-0.154362000
5	0.106940000	-2.481567000	-1.723729000
5	-1.469893000	-2.801895000	-1.412186000
5	-1.872597000	-2.591868000	0.154381000
5	0.531835000	1.037086000	2.610248000
5	0.569983000	-0.609108000	2.914115000
5	3.383527000	-1.226210000	0.699838000
5	3.521936000	0.403295000	0.720487000
5	1.652970000	1.971051000	1.924615000
5	3.382646000	1.228442000	-0.699884000
5	2.734822000	-1.789032000	-0.722617000
5	-0.849918000	-1.401660000	2.452889000
5	-1.241488000	1.523098000	2.371588000
5	2.733444000	1.790594000	0.722651000
5	3.521935000	-0.400990000	-0.720624000
5	0.846077000	-1.930179000	2.044703000
5	-0.820781000	0.144003000	3.066170000
5	1.332698000	2.772769000	0.549392000
5	0.105253000	2.481711000	1.723783000
5	1.334603000	-2.771935000	-0.549408000
5	0.886662000	-3.191664000	0.989955000
5	2.189728000	-2.260810000	0.989578000
5	-0.624758000	-2.755200000	1.400332000
5	1.654323000	-1.969780000	-1.924528000
5	2.188156000	2.262231000	-0.989597000
5	-1.471795000	2.800931000	1.412203000
5	-2.086963000	-2.130265000	1.696180000

B42.c.2

5	-0.958780000	2.865877000	1.565568000
5	0.324878000	3.611362000	-0.837700000
5	-2.476091000	0.232806000	-1.464633000
5	-0.415244000	1.573056000	-2.687141000
5	2.704924000	1.218016000	0.000000000
5	2.419306000	-1.457093000	1.751434000
5	0.858722000	2.597102000	1.955579000
5	1.794875000	-0.071227000	2.469440000
5	1.021247000	-3.351396000	0.000000000
5	-1.630442000	-2.550652000	-1.694679000
5	-0.319080000	-3.092436000	0.881638000
5	2.731541000	-0.146715000	-0.876167000
5	1.231559000	-1.615790000	-2.783160000
5	-2.466015000	-1.396286000	-0.878246000
5	-2.476091000	0.232806000	1.464633000
5	-1.638632000	-1.126587000	2.438971000
5	-0.319080000	-3.092436000	-0.881638000
5	-3.034460000	-0.142538000	0.000000000
5	-1.638632000	-1.126587000	-2.438971000
5	-1.583016000	0.398290000	-2.899274000
5	1.251019000	-2.575989000	1.398338000
5	-2.466015000	-1.396286000	0.878246000
5	-0.227750000	-2.150897000	2.411751000
5	-1.017422000	3.285586000	0.000000000
5	1.251019000	-2.575989000	-1.398338000
5	2.731541000	-0.146715000	0.876167000
5	2.014025000	1.353287000	-1.476806000
5	1.794875000	-0.071227000	-2.469440000
5	-1.949141000	1.688799000	2.050491000
5	2.014025000	1.353287000	1.476806000
5	-0.415244000	1.573056000	2.687141000
5	0.324878000	3.611362000	0.837700000
5	-1.583016000	0.398290000	2.899274000
5	-1.949141000	1.688799000	-2.050491000
5	1.231559000	-1.615790000	2.783160000
5	2.419306000	-1.457093000	-1.751434000
5	0.858722000	2.597102000	-1.955579000
5	1.201122000	1.358260000	2.910731000
5	-0.227750000	-2.150897000	-2.411751000
5	-1.630442000	-2.550652000	1.694679000
5	1.201122000	1.358260000	-2.910731000
5	-0.958780000	2.865877000	-1.565568000

B42.c.3

5	3.090260000	1.269724000	-0.661075000
5	3.090299000	-1.269702000	0.661066000
5	1.110638000	-1.519548000	-2.156790000
5	1.868568000	-2.546818000	0.315006000
5	0.697852000	0.186642000	3.008865000
5	-1.691162000	2.085692000	2.086081000
5	2.493124000	1.656132000	1.072247000
5	-0.163310000	2.587327000	1.608852000
5	-3.634667000	0.505202000	0.610264000
5	-1.691131000	-2.085711000	-2.086081000
5	-2.889985000	1.005210000	-0.813590000
5	-0.662778000	-0.632387000	2.629185000
5	-1.836781000	-2.400606000	0.716933000
5	-0.578603000	-1.120619000	-2.695007000
5	0.931521000	1.319903000	-2.486487000
5	-0.534737000	2.276110000	-1.877605000
5	-2.742421000	-1.799806000	-0.799370000
5	0.697858000	-0.186630000	-3.008866000
5	-0.163274000	-2.587332000	-1.608861000
5	1.381389000	-2.823783000	-1.213785000
5	-2.742441000	1.799765000	0.799367000
5	-0.662784000	0.632381000	-2.629182000
5	-1.836812000	2.400580000	-0.716928000
5	3.390317000	-0.380185000	-0.692409000
5	-2.889967000	-1.005249000	0.813587000
5	-0.578621000	1.120613000	2.695004000
5	0.931539000	-1.319891000	2.486496000
5	-0.534699000	-2.276111000	1.877602000
5	2.299588000	2.006770000	-1.834463000
5	1.110612000	1.519569000	2.156794000
5	1.868535000	2.546849000	-0.315003000
5	3.390300000	0.380227000	0.692407000
5	0.956247000	2.819995000	-1.706307000
5	2.493154000	-1.656107000	-1.072248000
5	-1.548396000	2.955923000	0.780078000
5	-1.936729000	-1.470854000	2.039755000
5	2.299619000	-2.006729000	1.834462000
5	1.381352000	2.823805000	1.213791000
5	-1.548352000	-2.955939000	-0.780076000
5	-1.936749000	1.470828000	-2.039754000
5	0.956289000	-2.819979000	1.706313000
5	-3.634664000	-0.505256000	-0.610269000

B42.c.4

5	-1.679820000	-2.678867000	-0.394017000
5	-2.951474000	-1.668756000	-0.748400000
5	-1.663752000	0.272018000	-2.534159000
5	-0.506490000	-0.721828000	-3.014147000
5	1.110560000	-2.845451000	-0.996446000
5	1.964109000	-1.402919000	-1.739338000
5	0.094068000	0.821121000	-2.702854000
5	-3.137669000	-0.473178000	0.431411000
5	-1.344743000	-2.503070000	1.425740000
5	0.273325000	-1.933289000	-2.205877000
5	1.055065000	-0.547449000	-2.763740000
5	-2.895104000	-0.209380000	-1.403652000
5	-2.720711000	-2.042767000	0.776925000
5	-0.443497000	-3.106432000	-1.339175000
5	2.584486000	-2.353545000	-0.531729000
5	-0.129607000	-3.136393000	0.252943000
5	-1.123766000	1.906642000	-2.083696000
5	-2.632882000	1.334265000	-1.794748000
5	-2.990532000	1.131309000	-0.208284000
5	0.793624000	-0.065378000	2.623951000
5	-0.155567000	1.282620000	2.862365000
5	2.057965000	2.777872000	0.603456000
5	2.819705000	1.332417000	0.853642000
5	2.231342000	-0.163740000	1.876591000
5	3.601193000	0.716152000	-0.564976000
5	1.344951000	2.732242000	-0.916053000
5	-1.723159000	1.015453000	2.274322000
5	-0.330076000	-1.568990000	2.621845000
5	3.533597000	-0.085948000	0.860726000
5	2.838435000	2.116922000	-0.671596000
5	-0.593397000	2.396589000	1.806167000
5	-0.833309000	-0.127001000	3.111896000
5	2.657909000	-1.495617000	0.910027000
5	1.187779000	-1.532279000	1.752195000
5	-0.352760000	2.946639000	-0.917498000
5	-1.101167000	3.243829000	0.514657000
5	0.499054000	3.125551000	0.666360000
5	-2.167092000	2.111887000	1.001393000
5	0.455563000	2.312175000	-2.188769000
5	3.249185000	-0.895666000	-0.701750000
5	0.191249000	-2.838140000	1.807182000
5	-3.066591000	0.820381000	1.387110000