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# Structure and Stability of $Be_5$, $Be_5^+$, and $Be_5^-$ Clusters

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The electronic structure and stability of $Be_5$, $Be_5^+$, and $Be_5^-$ clusters have been investigated at the B3LYP, B3PW91, and MP2 levels of theory, along with the 6-311G* basis set for neutral and cationic clusters and the 6-311+G* basis set for anion clusters. Six $Be_5$, six $Be_5^+$, and six $Be_5^-$ isomers are identified. Of these eighteen species, twelve have not been reported previously. The trigonal bipyramid structure is found to be the global minimum for the neutral $Be_5$ cluster, in agreement with the previous results. The most stable $Be_5^+$ and $Be_5^-$ clusters have trigonal bipyramid structures similar to the neutral global minimum. Natural bond orbital (NBO) analysis and molecular orbital (MOs) investigation suggest a delocalized $\pi$ bond in the three trigonal bipyramid structures, and the negative nucleus-independent chemical shift (NICS) values indicate aromatic character for them. For the planar pentagon structures, the NBO and MOs analyses show that there has no delocalized $\pi$ bond, and the NICS values show that both the cationic and the neutral clusters are antiaromatic, while the anionic cluster is nonaromatic.

## I. Introduction

As we all known, clusters behave as a link between the atom and the bulk material. They exhibit characteristics of both forms of matter, depending on their size and atomic and electronic structures.[1] For the rapidly growing spectroscopic data that has recently become available, structures and properties of small clusters are of interest.[2]

Beryllium clusters are the simplest alkaline-earth metal clusters. The drawback of beryllium is its toxicity; thus, experimental data for the clusters are rare, and, to our knowledge, there are only a few studies of the Be dimer via laser-induced fluorescence.[3,4]

The Be atom, with four electrons, has a closed-shell ground electronic state, and it is one of the lightest atoms to exhibit metallic character. Beryllium clusters, like those of lithium, display an inherent lack of bonding electrons, and their bonding properties are of special interest. Beryllium clusters have been theoretically studied using the different methods.[5−24] In 2000, Kolchin and Hall[23] determined the atomic and electronic structures for neutral and cationic beryllium clusters $Be_n/Be_n^+$ ($n = 2-6$) using density functional theory in the local spin density approximation. Later, Beyer and co-workers[24] optimized the geometry of neutral $Be_n$ ($n = 2-8$) at the B3LYP/6-311++G (3df) levels of theory. They also reported the vibrational frequencies and bonding energies. More recently, Wang et al.[18] studied the structure and electronic properties of beryllium clusters up to 21 atoms. However, the cationic and anionic clusters of beryllium are seldom investigated.

The clusters formed with the atoms for lack of bonding electrons, such as boron and aluminum clusters, have been predicted to have a multi-center bond: three-center bond or four-center peripheral bond.[25−27] The aromatic of pure all-metal clusters, such as $Li_3^{\pm}$,[28] $Al_3^-$, $Ga_3^-$,[29] and $Al_4^{2-}$,[30−33] have also been studied recently. In the present paper, we will try to answer the following two questions. Having one less electron than boron, can beryllium clusters form the multi-center bond? Do the $Be_5$ clusters and their ions perform with aromaticity? We studied the cationic, neutral, and anionic $Be_5$ clusters by performing geometry optimizations at the B3LYP, B3PW91, and MP2 levels of theory along with 6-311G* and 6-311+G* basis sets. The natural bond orbital (NBO) analysis is performed, and the nucleus-independent chemical shift (NICS) value is evaluated. The NICS value is a trustworthy criterion for the aromaticity of these species.

## II. Computational Methods

All calculations were performed using the Gaussian 98 program package.[34] Equilibrium geometric structures of the neutral $Be_5$ clusters and their corresponding ions were fully optimized by using the B3LYP, B3PW91, and MP2 methods. B3LYP is a density functional theory (DFT) method using Beck's three parameters functional[35] (B3) along with the Lee, Yang, and Parr correlation functional[36] (LYP). B3PW91 is B3 with Perdew-Wang 1991 correlation functional.[37] MP2 is the second-order Møller−Plesset perturbation theory.[38] The core is frozen in our MP2 study. Optimizations were performed with the 6-311G* basis set for the neutral and cationic clusters and the 6-311+G* basis set for the anionic clusters. The 6-311G* set is a split-valence basis set with polarization functions, and the 6-311+G* set is further augmented with the diffuse functions.[39]

Stationary points (minima or saddle points) were confirmed by evaluating their harmonic vibrational frequencies at each level of theory. Minima were characterized with no imaginary vibrational frequency, and transition states with one imaginary frequency. Zero-point vibrational energies (ZPVE) evaluated at each level of theory were used to correct the total energies.

The natural bond orbital (NBO)[40] analysis was performed for the most stable isomers identified at the B3LYP and MP2

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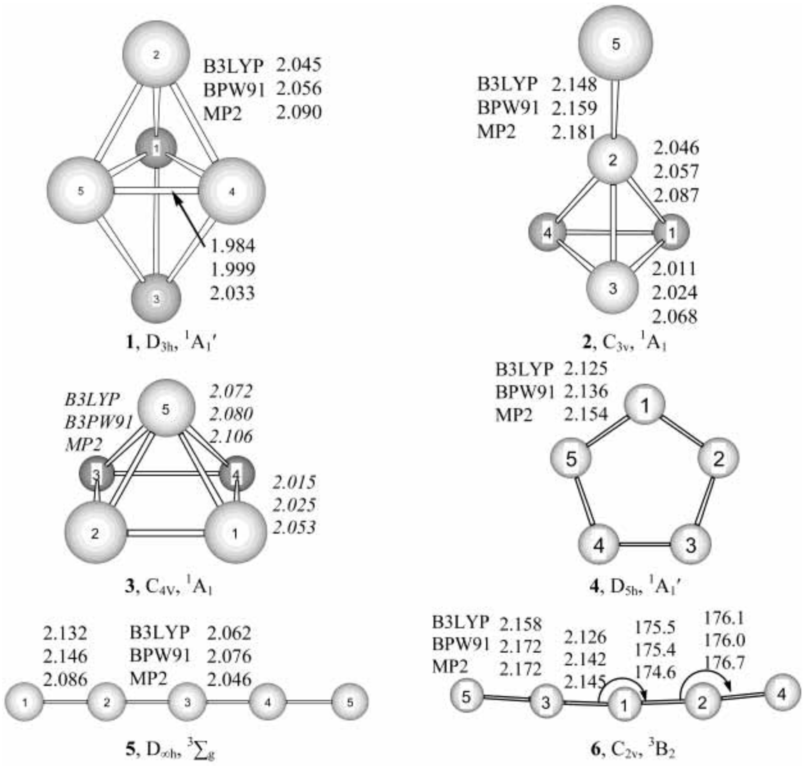


**1**, $D_{3h}$, $^1A_1'$

**2**, $C_{3v}$, $^1A_1$

**3**, $C_{4V}$, $^1A_1$

**4**, $D_{5h}$, $^1A_1'$

**5**, $D_{\infty h}$, $^3\Sigma_g$

**6**, $C_{2v}$, $^3B_2$

**Figure 1.** B3LYP, B3PW91, and MP2 methods with 6-311G* set optimized geometries (bond lengths in Å, bond angles in degrees) of various minima characterized on the Be$_5$ potential energy surface. Structure **3** is a transition state with an imaginary frequency at three levels.

methods using the optimized geometries at the same level. The B3LYP molecular orbitals (MOs) for neutral, cationic, and anionic species were drawn by using the MOLDEN 3.4 program.[41]

The integrals are accurate to $1 \times 10^{-5}$ $E_h$, the density was converged to $1 \times 10^{-8}$ $E_h$, and the Cartesian gradients were converged to at least $10^{-6}$ a.u. The default integration grid (75 302) of Gaussian 98 was initially applied, but we also used the finer grid (99 590) to check suspicious results, and sometimes this finer integration grid was important for beryllium clusters.

## III. Results and Discussion

The structures and geometrical parameters of Be$_5$ (**1**−**6**), Be$_5^+$ (**1**$^+$−**6**$^+$), and Be$_5^-$ (**1**$^-$−**6**$^-$) isomers optimized are shown in Figures 1−3, respectively. The total and zero-point vibrational energies (ZPVE, in hartree) of these isomers are listed in Table 1. The relative energies with ZPVE corrections (in cackle/moll) and the number of imaginary frequencies are also listed in Table 1.

**A. Neutral Be$_5$ Clusters.** For the neutral Be$_5$ clusters, we have identified five stationary structures: two linear (or quasi-linear), one planar, and two three-dimensional geometries. (See Figure 1 and Table 1).

Among them, the trigonal bipyramid structure **1**, with $D_{3h}$ symmetry in its $^1A_1'$ state, is the global minimum, in agreement with the results obtained by Wang et al.,[18] Pacchioni et al.,[6] and Kato et al.[22] Sudhakar et al.[19] reported that the bond distances in plane are 2.031 Å, and the other bonds are 2.085 Å at the MP2(full)/6-311+G* levels of theory. Marino and Ermler[20] reported the MP4/6-31G bond distances to be 2.040 and 2.116 Å, respectively. Whiteside et al.[21] reported the SCF bond distances are 2.028 and 2.099 Å. Lee et al.[15] determined that the CCSD/*7s3p2d* optimized bond distances are both 2.079 Å. We obtained the bond lengths to be (1.984, 2.045 Å), (1.999, 2.056 Å), and (2.033, 2.090 Å) at the B3LYP, B3PW91, and MP2 methods, respectively. Bond lengths optimized at the MP2/6-311G* level are longer than those with the DFT methods, and our results are somewhat shorter than those reported previously.

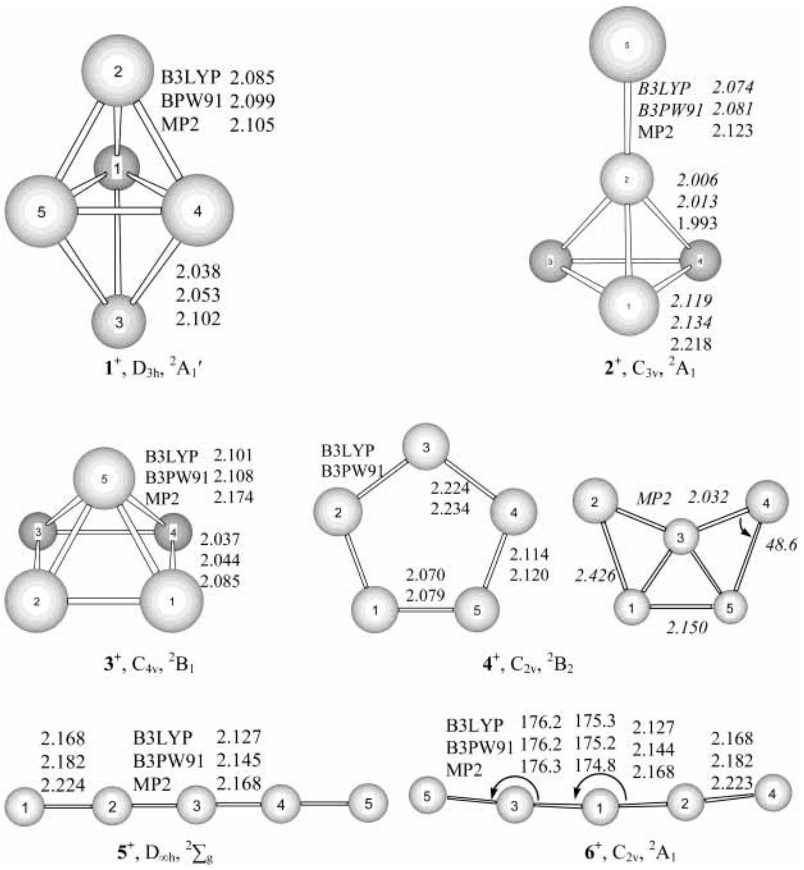
In terms of NBO analysis, the Be1 atom has the *sp3* hybridization. The Wiberg bond index (WBI) for the bonds in plane (i.e., Be1−Be5, etc.) are all 0.48, and those for the other bonds (i.e., Be1−Be2, etc.) are all 0.38. The small WBI values indicate the existence of a multi-center bond.

Besides structure **1**, another 3-dimensional structure **2** with $C_{3v}$ symmetry at the $^1A_1$ state is found to be the second stable structure, which has not been reported before. It is predicted to be 18.5, 19.8, and 28.8 kcal/mol higher in energy than structure **1** at the B3LYP/6-311G*, B3PW91/6-311G*, and MP2/6-311G* levels of theory, respectively.

The rectangular pyramid structure **3** is also a 3-dimensional shape, with $C_{4v}$ symmetry in its $^1A_1$ state. Pacchioni and Koutecký[6] have reported this structure with the ab initio pseudopotential method followed by multireference double-excitation configuration interaction. It is a transitional state at all of three levels with a large imaginary frequency (1020i cm$^{-1}$ with B3LYP, 1001i cm$^{-1}$ with B3PW91, and 855i cm$^{-1}$ with the LSDA method). Following this mode, it collapses to structure **1**.

The planar five-membered ring structure **4** ($D_{5h}$ symmetry), is the local minimum with all real vibrational frequencies at the B3LYP/6-311G*, B3PW91/6-311G*, and MP2/6-311G* levels of theory. The WBI of bonds between two adjacent beryllium atoms is 0.45, indicating the existence of multicentered bonds.

For a linear structure **5**, the triplet $^3\Sigma_g$ state is more stable than the singlet $^1\Sigma_g$ state by 11.3, 14.6, and 1.0 kcal/mol at the B3LYP, B3PW91, and MP2 levels, respectively. The MP2 bond



$1^+$, $D_{3h}$, $^2A_1'$ $2^+$, $C_{3v}$, $^2A_1$ $3^+$, $C_{4v}$, $^2B_1$ $4^+$, $C_{2v}$, $^2B_2$ $5^+$, $D_{\infty h}$, $^2\Sigma_g$ $6^+$, $C_{2v}$, $^2A_1$

**Figure 2.** B3LYP/6-311G*, B3PW91/6-311G*, and MP2/6-311G* optimized geometries (bond lengths in Å, bond angles in degrees) of various minima characterized on the $Be_5^+$ potential energy surface. Italics fonts for structures $\mathbf{4}^+$ indicate transition state, and for $\mathbf{2}^+$ indicate it has two imaginary frequencies.

lengths are shorter than the DFT ones. It is different from the usual cases that the MP2 lengths are longer than the DFT lengths.

The $C_{2v}$ arcuate structure **6** is characterized as local minima which have all real vibrational frequencies at all of the B3LYP/6-311G*, B3PW91/6-311G*, and MP2/6-311G* levels of theory. Structure **5** is less stable than structure **6** by 13.1 kcal/mol (B3LYP), 11.7 kcal/mol (B3PW91), and 43.1 kcal/mol (MP2), respectively.

**B. Cationic $Be_5^+$ Clusters.** The five minimum optimized structures for the $Be_5^+$ cluster are shown in Figure 2. Similar to the neutral $Be_5$ cluster**,** the global minimum is a trigonal bipyramid structure $\mathbf{1}^+$, with $D_{3h}$ symmetry in its $^2A_1'$ state, predicted by the B3LYP and B3PW91 methods, but the MP2 method predicts it as a third stationary point. Its equatorial bond lengths are 2.085 Å (B3LYP), 2.099 Å (B3PW91), and 2.105 Å (MP2), and the corresponding WBI is 0.37. The other bond distances are 2.038 Å (B3LYP), 2.053 Å (B3PW91), 2.102 Å (MP2), and the corresponding WBI is 0.28. These small WBI values indicate the existence of multi-center bonds.

Kolchin and Hall[23] reported the trigonal bipyramid as the equilibrium structure of $Be_5^+$ from the LSD method. Their bond lengths were 2.111 Å for an equatorial bond, and 2.158 Å for a base bond, which are longer than our theoretical bond lengths.

The $C_{3v}$ structure $\mathbf{2}^+$ has two imaginary frequencies at the B3LYP/6-311G* and B3PW91/6-311G* levels of theory, and finally it collapses to structure $\mathbf{1}^+$. The MP2/6-311G* predicts that structure $\mathbf{2}^+$ is a local minimum with all real vibrational frequencies.

The rectangular pyramid structure $\mathbf{3}^+$ has $C_{4v}$ symmetry at the $^2B_1$ state. It is a local minimum slightly higher (~4 kcal/mol) than structure $\mathbf{1}^+$ with the DFT methods, but the MP2/6-311G* method predicts structure $\mathbf{3}^+$ to be the global minimum, lying 21 kcal/mol below structure $\mathbf{1}^+$.

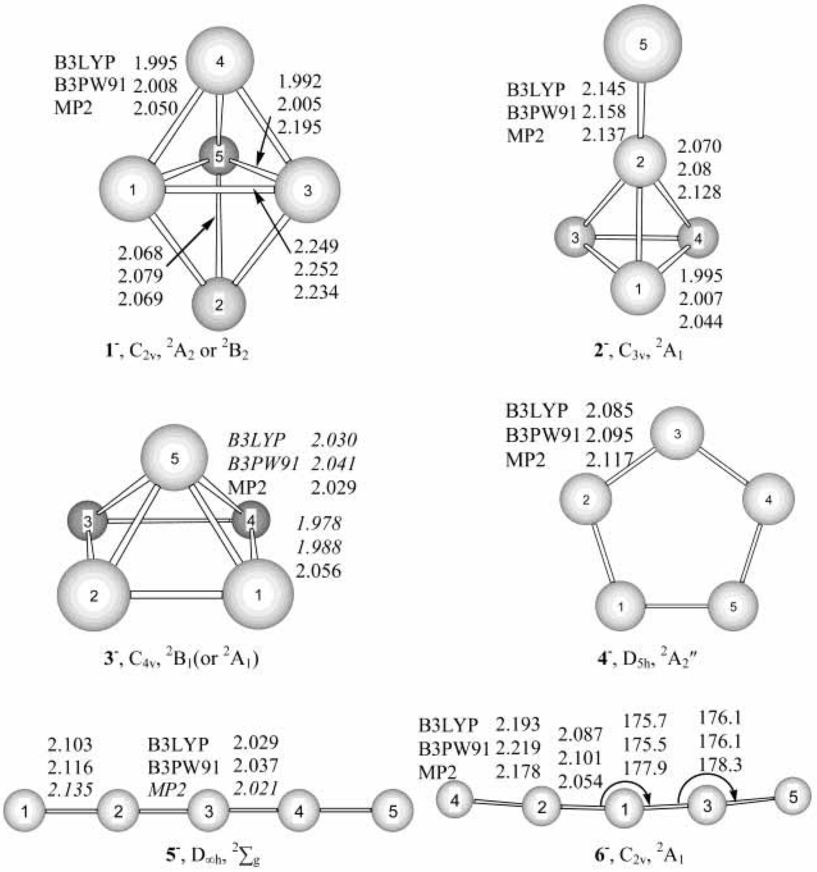
The $C_{2v}$ ($^2B_2$ state) distorted pentagon structure $\mathbf{4}^+$ has the highest energy of all the five $Be_5^+$ structure. It lies 30.1 and 37.4 kcal/mol in energy above structure $\mathbf{1}^+$ at the B3LYP/6-311G* and B3PW91/6-311G* levels, respectively. The average WBI of bonds between adjacent beryllium atoms is 0.57. The MP2 method gives another planar form with one imaginary frequency (94i $cm^{-1}$), and it is less stable than structure $\mathbf{3}^+$ by 58.8 kcal/mol.

Structure $\mathbf{5}^+$ with $D_{\infty h}$ symmetry is similar to its neutral counterpart. The bond lengths of the cationic form are little longer than those for the neutral form. Unlike the linear neutral structure **5**, the MP2 lengths of the cationic structure $\mathbf{5}^+$ are longer than the DFT lengths.

The bond lengths of bend structure $\mathbf{6}^+$ are more similar to structure $\mathbf{5}^+$. The total energy of $\mathbf{6}^+$ is almost equal to $\mathbf{5}^+$ at the DFT levels, while at MP2 levels $\mathbf{6}^+$ is more stable than $\mathbf{5}^+$ by about 10 kcal/mol.

**C. Anionic $Be_5^-$ Clusters.** Figure 3 depicts the structures of six minima located on the $Be_5^-$ potential energy hypersurface, optimized at the B3LYP/6-311+G*, B3PW91/6-311+G*, and MP2/6-311+G* levels of theory. Note that we have used the 6-311+G* basis set including diffuse functions to describe the electron distribution for the anions.

Energetically, the global minimum is structure $\mathbf{1}^-$ with $C_{2v}$ symmetry in its $^2A_2$ state at the B3LYP/6-311+G* and B3PW91/6-311+G* levels, just like the cationic and neutral structures. However, at the MP2/6-311+G* level, the structure $\mathbf{1}^-$ is in its $^2B_2$ state, not $^2A_2$ state. And its energy is higher



$1^-$, $C_{2v}$, $^2A_2$ or $^2B_2$

$2^-$, $C_{3v}$, $^2A_1$

$3^-$, $C_{4v}$, $^2B_1$(or $^2A_1$)

$4^-$, $D_{5h}$, $^2A_2''$

$5^-$, $D_{\infty h}$, $^2\Sigma_g$

$6^-$, $C_{2v}$, $^2A_1$

**Figure 3.** B3LYP, B3PW91, and MP2 methods along with 6-311+G* set optimized geometries (bond lengths in Å, bond angles in degrees) of various minima characterized on the $Be_5^-$ potential energy surface. Italics fonts for structures **5**⁻ indicate it has two imaginary frequencies.

**TABLE 1: Total Energies (*E*) in hartree, Zero-Point Vibrational Energies (ZPVE)$^a$ in hartree, and Relative Energies in kcal/mol for $Be_5$, $Be_5^+$, and $Be_5^-$ Isomers**

| | B3LYP/6−311(+)$^b$G* | | | B3PW91/6−311(+)$^b$ G* | | | MP2/6−311(+)$^b$ G* | | |
|---|---|---|---|---|---|---|---|---|---|
| isomer | *E*$^a$ | ZPVE$^b$ | relative energy$^c$ | *E*$^a$ | ZPVE$^b$ | relative energy$^c$ | *E*$^a$ | ZPVE$^b$ | relative energy$^c$ |
| $Be_5$ **1** | −73.56805 | 0.01060 | 0.0(0) | −73.51778 | 0.01053 | 0.0(0) | −73.21714 | 0.01206 | 0.0(0) |
| **2** | −73.53694 | 0.00893 | 18.5(0) | −73.48450 | 0.00876 | 19.8(0) | −73.16786 | 0.00866 | 28.8(0) |
| **3** | −73.53448 | 0.00870 | 19.9(1) | −73.48480 | 0.00876 | 19.6(1) | −73.15318 | 0.00839 | 37.8(1) |
| **4** | −73.51053 | 0.00858 | 34.8(0) | −73.45024 | 0.00842 | 41.1(0) | −73.11816 | 0.00866 | 60.0(0) |
| **5** | −73.47082 | 0.00731 | 58.9(0) | −73.41001 | 0.00716 | 65.5(0) | −73.04038 | 0.00738 | 108.0(0) |
| **6** | −73.49173 | 0.00731 | 45.8(0) | −73.42868 | 0.00712 | 53.8(0) | −73.11055 | 0.00889 | 64.9(0) |
| $Be_5^+$ **1**$^+$ | −73.32558 | 0.00972 | 0.0(0) | −73.27684 | 0.00961 | 0.0(0) | −72.96355 | 0.07329 | 20.8(0) |
| **2**$^+$ | −73.29063 | 0.00800 | 20.9(2) | −73.23825 | 0.00807 | 23.2(2) | −72.90944 | 0.01015 | 15.1(0) |
| **3**$^+$ | −73.31932 | 0.00944 | 3.8(0) | −73.27043 | 0.00945 | 3.9(0) | −72.93248 | 0.00906 | 0.0(0) |
| **4**$^+$ | −73.27-504 | 0.00712 | 30.1(0) | −73.21487 | 0.00720 | 37.4(0) | −72.84278 | 0.01313 | 58.8(1) |
| **5**$^+$ | −73.28063 | 0.00735 | 26.7(0) | −73.21582 | 0.00718 | 36.8(0) | −72.86297 | 0.01046 | 44.5(0) |
| **6**$^+$ | −73.28049 | 0.00729 | 26.8(0) | −73.21567 | 0.00710 | 36.8(0) | −72.87547 | 0.00719 | 34.6(0) |
| $Be_5^-$ **1**$^-$ | −73.62529 | 0.01014 | 0.0(0) | −73.57846 | 0.01013 | 0.0(0) | −73.20299 | 0.010553 | 18.0(0) |
| **2**$^-$ | −73.60473 | 0.00902 | 12.2(0) | −73.55423 | 0.00896 | 14.5(0) | −73.23100 | 0.00980 | 0.0(0) |
| **3**$^-$ | −73.62156 | 0.01003 | 2.3(1) | −73.57432 | 0.01004 | 2.5(1) | −73.21256 | 0.01019 | 11.8(0) |
| **4**$^-$ | −73.56510 | 0.00813 | 36.5(0) | −73.50979 | 0.00781 | 41.6(0) | −73.16597 | 0.00801 | 39.7(0) |
| **5**$^-$ | −73.52149 | 0.00732 | 63.4(0) | −73.46417 | 0.01188 | 72.8(0) | −73.11515 | 0.00635 | 70.5(2) |
| **6**$^-$ | −73.51423 | 0.00625 | 67.2(0) | −73.45102 | 0.00587 | 77.3(0) | −73.10879 | 0.00841 | 75.8(0) |

[a] The relative energies with ZPVE corrections in kcal/mol. The integers in parentheses are the number of imaginary frequencies (NIMAG). [b] 6-311+G* basis sets are used for the anion $Be_5^-$ clusters. [c] With ZPVE corrections.

than the structure **2**⁻ (with $C_{3v}$ symmetry in its $^2A_1$ state) by 18.0 kcal/mol, and structure **2**⁻ is the global minimum at the MP2/6-311+G* level. Structure **2**⁻ ($C_{3v}$) predicted by the B3LYP and B3PW91 methods lies above structure **1**⁻ by 12.2 and 14.5 kcal/mol in energy, respectively.

The rectangular pyramid structure **3**⁻ has $C_{4v}$ symmetry. It has one imaginary vibrational frequency at both the B3LYP/6-311+G* (180i cm$^{-1}$) and the B3PW91/6-311+G* (186i cm$^{-1}$) levels of theory at the $^2B_1$ state. Following the corresponding normal mode, it goes to structure **1**⁻. But at the MP2/6-311+G* level, structure **3**⁻ in its $^2A_1$ state is a local minimum with all real vibrational frequencies. It is higher in energy than structure **2**⁻ by 11.8 kcal/mol but lower than structure **1**⁻ by 6.2 kcal/mol (Table 1).

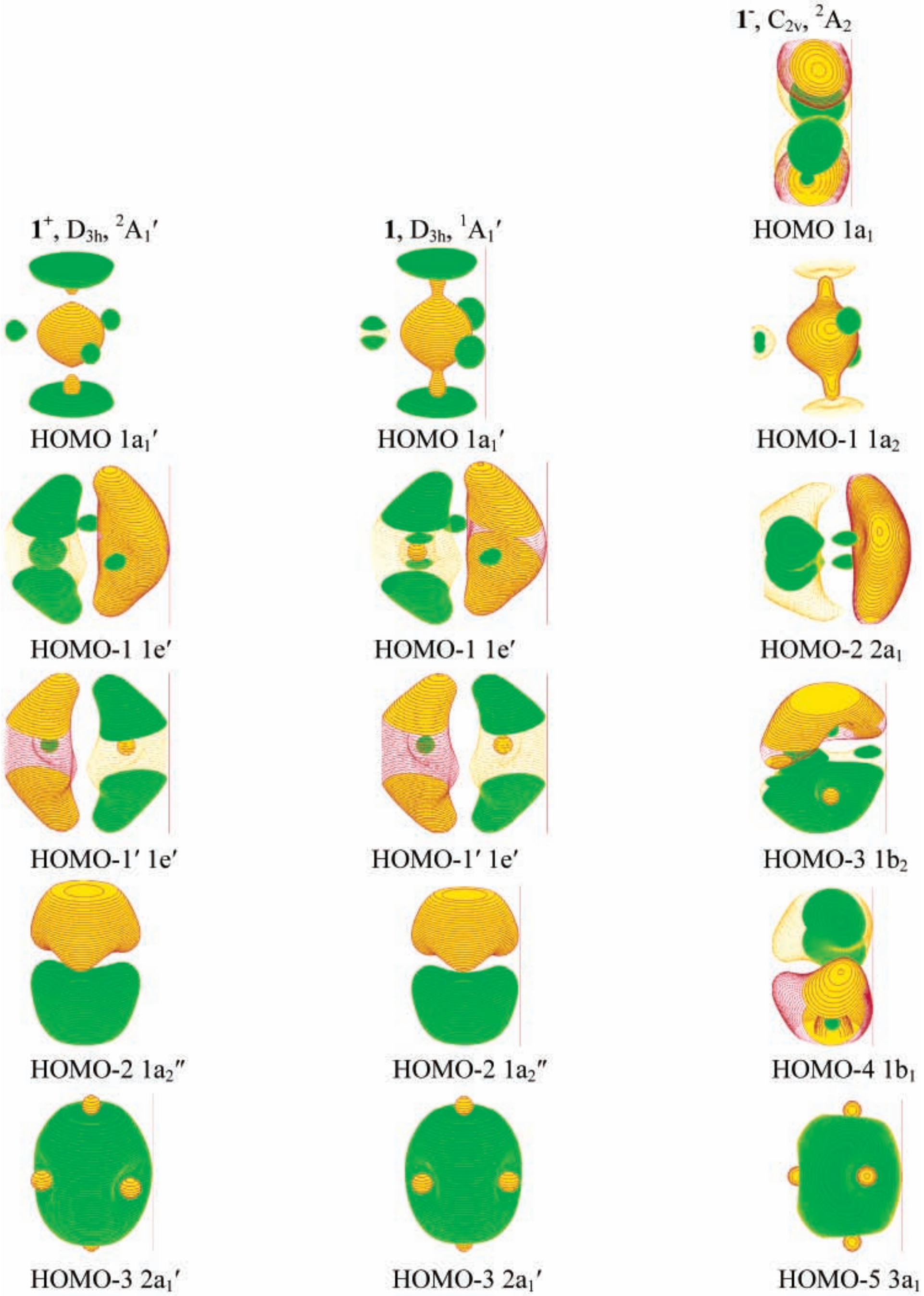


**Figure 4.** Molecular orbital pictures of the **1**$^+$, **1**, and **1**$^-$ species, showing the HOMO down to the last valence molecular orbital.

The regular pentagon structure **4**$^-$, with $D_{5h}$ symmetry at the $^2$A$_2''$ state, is a local minimum at all three levels of theory. It is higher in energy than structure **1**$^-$ by 36.5 and 41.6 kcal/mol at the B3LYP/6-311+G* and the B3PW91/6-311+G* levels, respectively, and by 39.7 kcal/mol than structure **2**$^-$ at the MP2/6-311+G* level.

The linear structure **5**$^-$($D_{\infty h}$) at the $^2\Sigma_g$ state, does not differ much from the neutral and anionic isomers. The MP2/6-311+G* method gives two imaginary vibrational frequencies at the $^2\Sigma_g$ state, and then collapses to structure **6**$^-$. Structure **6**$^-$ ($C_{2v}$) is similar to the neutral structure **6** ($C_{2v}$), with only little changes in bond lengths and bond angles. Structure **5**$^-$ is more stable than structure **6**$^-$, and the energy is less 3.8, 4.5, and 5.3 kcal/mol than structure **6**$^-$ with B3LYP, B3PW91, and MP2 methods, respectively.

## IV. Bonding and Aromaticity of Some Neutral, Cationic, and Anionic Be$_5$ Isomers

As has been mentioned, the trigonal bipyramid structures are the most stable isomers for all the neutral and charged Be$_5$ clusters on the potential hypersurfaces at the B3LYP/6-311(+)G* levels. Its selected MOs for α electrons are shown in Figure 4. MOs analysis shows that the neutral and cationic forms have very similar bonding characters. The highest occupied MO (HOMO, 1A$_1'$) of structures **1** and **1**$^+$ is a multi-centered $\sigma$ bonding MO and has most of its electron density in the center of the Be$_5$ trigonal bipyramid. It corresponds to the combination of the radial *p* orbitals from atoms Be1, Be4, and Be5, and the *s* orbital from Be2 and Be3. The doubly degenerated orbital HOMO-1 (1e′) consists of bonding−antibonding orbitals formed primarily from the filled valence 2*p* orbitals of Be. The

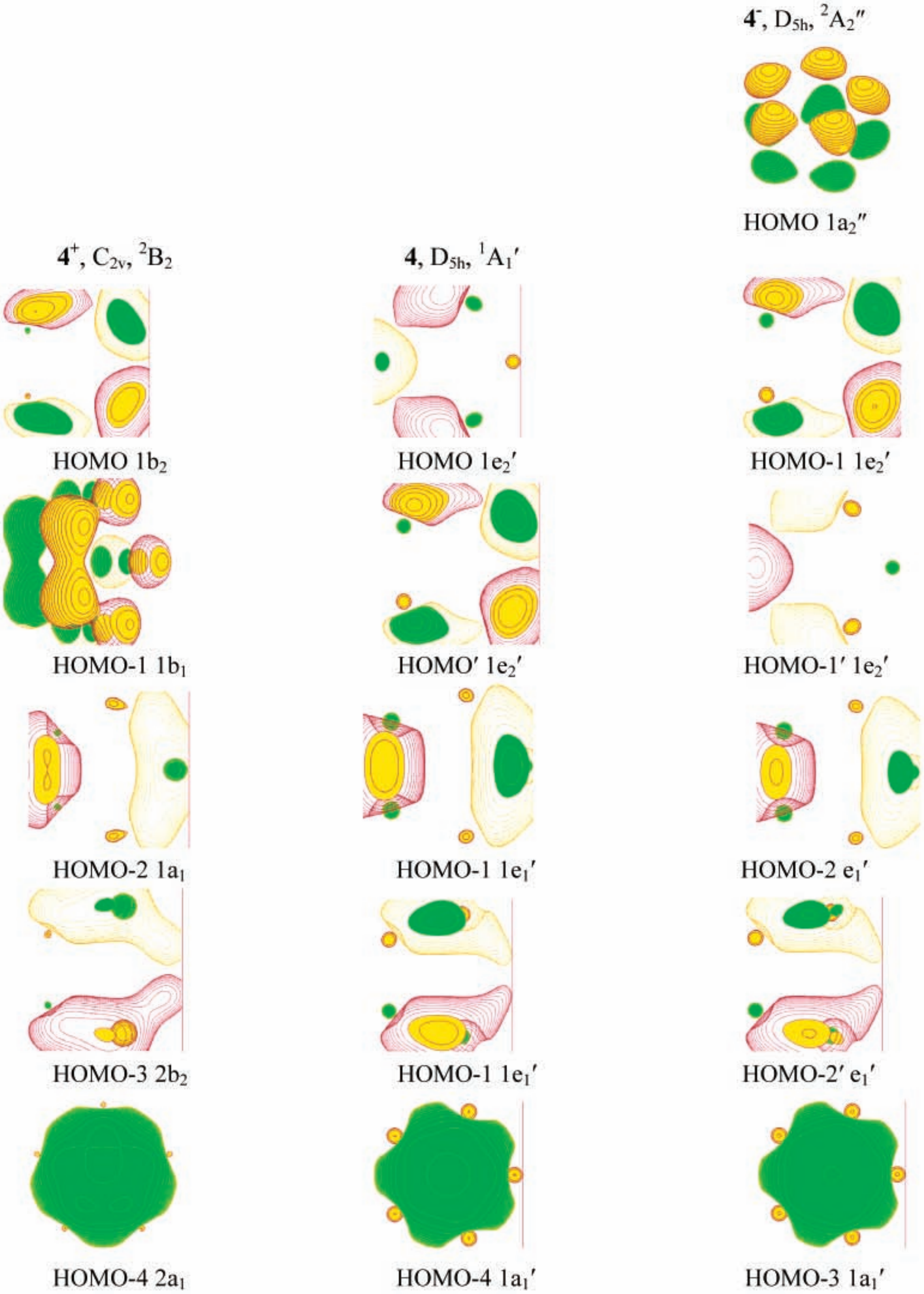


**Figure 5.** Molecular orbital pictures of the **$4^+$**, **4**, and **$4^-$** species, showing the HOMO down to the last valence molecular orbital.

HOMO-2 ($1a_2''$) is also a bonding orbital formed from the $2p_z$ orbitals from Be1, Be4, and Be5, and the 2*s* orbital from Be2 and Be3, and it is a delocalized $\pi$ bonding MO which renders $\pi$-aromaticity. There are two $\pi$ electrons all together, consistent with the $4n + 2$ rules. Then we can determine that the neutral **1** and the cationic **$1^+$** are aromatic molecules. For the anionic **$1^-$**, HOMO-4 is a delocalized $\pi$ bonding MO. However, due to one more electron, the symmetry of the anion collapses to $C_{2v}$, the delocalization is infected, and its aromaticity is lower than the neutral and cationic forms.

Compared with the delocalized $\pi$ bonding orbitals in the planar pentagon boron clusters $B_5$ and its ions,[25] we would discuss the MOs in the analogous beryllium clusters. MOs of structure **4**, **$4^+$**, and **$4^-$** are shown in Figure 5. HOMO-1 ($1b_1$) of structure **$4^+$** and HOMO ($1a_2''$) of structure **$4^-$** are all $\pi$ bonding MOs. And it seems that these two structures should have some aromatic characters. There is no delocalized $\pi$ bonding MO in neutral structure **4**, and it should has no aromatic character.

Conventionally, aromaticity is often discussed in term of various criteria, such as energetic criterion[41] (resonance and aromatic stabilization energies ASE), magnetic criterion[42] (NMR chemical shifts, magnetic stability anisotropies and their exaltations), and geometric criterion[43] (bond length equalization). Especially, NICS (nucleus-independent chemical shift), proposed by Schleyer and co-workers,[44,45] is based on magnetic shieldings, and now it can be computed with modern ab initio technique. NICS is the negative value of the shielding at or above the geometrical centers of rings or clusters. Aromaticity is characterized by negative NICS, antiaromaticity by positive NICS,

**TABLE 2: Nucleus-Independent Chemical Shifts (NICS) for Some $Be_5$, $Be_5^+$, and $Be_5^-$ Isomers (in ppm) with the B3LYP Method**

| | isomer | | | | | |
|---|---|---|---|---|---|---|
| | **$1^-$** | **1** | **$1^+$** | **$4^-$** | **4** | **$4^+$** |
| symmetry | $C_{2v}$ | $D_{3h}$ | $D_{3h}$ | $D_{5h}$ | $D_{5h}$ | $C_{2v}$ |
| state | $^2A_2$ | $^1A_1'$ | $^2A_1'$ | $^2A_2''$ | $^1A_1'$ | $^2B_2$ |
| NICS[a] | −22.3 | −46.5 | −54.6 | −4.8(−4.6) | 13.2(5.9) | 41.7 (30.6) |

[a] NICS at the ring centers. The figures in parentheses are NICS at 1 Å above the ring centers.

and nonaromatic compounds by NICS close to zero. The effectiveness of NICS as a simple and efficient criterion to probe aromaticity has been demonstrated by the previous studies.[42−44] Our computed NICS values with the B3LYP method are shown in Table 2, for the planar five-membered ring structures **4**, **$4^+$**, and **$4^-$**, as well as the trigonal bipyramid neutral **1**, cationic **$1^+$**, and anionic **$1^-$** isomers.

According to the NICS criterion, Table 2 shows that the trigonal bipyramid structures **1**, **$1^+$**, and **$1^-$** are all aromatic. The NICS value of −46.5 ppm of structure **1** suggests that this neutral $Be_5$ isomer is aromatic, but it is less aromatic than the corresponding cationic isomer **$1^+$**, which has a NICS value of −54.6 ppm. The anionic structure **$1^-$** is also aromatic with a relative lower NICS value of −22.3 ppm. For the planar pentagon structures, the NICS value for neutral **4** is 13.2 ppm and for cationic structure **$4^+$** is 41.7 ppm, which indicate they are both antiaromatic. Adding an electron to neutral structure **4** leads to the anionic five-membered ring structure **$4^-$** and makes it nonaromatic with a small NICS value of −4.8 ppm. It is said[44] that NICS(0) is influenced by the local effects arising mainly from the $\sigma$ bonds. The number "0" in parentheses represents the position exactly at the geometrical center of the ring. Their experience has shown that NICS (1) (out of plane by 1 Å above the center of the ring) mainly reflects the $\pi$ effects and often is a better indicator of the ring current than the value in the plane. The NICS value computed at 1 Å above the ring center for structure **4** is 5.9 ppm, and that for structures **$4^+$** and **$4^-$** are 30.6 ppm and −4.6 ppm, respectively. Though the NICS (1) values are somewhat different from NICS (0), the conclusion is the same: the neutral and cationic pentagon structures **4** and **$4^+$** are antiaromatic, and the anionic structure **$4^-$** is nonaromatic. For charged structures **$4^+$** and **$4^-$**, the aromatic characters inferred from NICS are somewhat difficult from MOs. It needs more detailed theoretical and experimental studies to judge which one is right.

As reported previously, a trigonal bipyramid structure for the neutral form is more stable than the planar one. This is also true for the anionic cluster, due to, at least in part, the fact that the trigonal bipyramid structures are stabilized by $\pi$ electron delocalization.

## V. Conclusion

We have studied 18 isomers of the $Be_5$, $Be_5^+$, and $Be_5^-$ clusters. Six neutral $Be_5$ and six cationic $Be_5^+$ structures are identified at the B3LYP/6-311G*, B3PW91/6-311G*, and MP2/6-311G* levels of theory. And six anionic $Be_5^-$ are studied at the B3LYP/6-311+G*, B3PW91/6-311+G*, and MP2/6-311+G* levels of theory. Among them, twelve isomers are introduced for the first time.

The global minimum for the neutrals is the trigonal bipyramid structure (**1**) with $D_{3h}$ symmetry in its $^1A_1'$ state. According to the NBO analysis, there is a strong electron delocalization that enhances the stability of this neutral form. The global minimum for the cationic structure **$1^+$** has an arrangement of atoms similar to that of the neutral **1**. The bond lengths increase in this cation due to one less electron. For anions, the global minimum given by B3LYP and B3PW91 methods is the trigonal bipyramid structure **$1^-$**. It has an arrangement of atoms similar to that of the neutral **1**, and the NBO analysis is also similar to the neutral **1**. The MP2 method predicts the global minimum for the anion is structure **$2^-$** with $C_{3v}$ symmetry. The MP2 method gives longer bond lengths than those given by DFT methods. Considering that the MP2 method is usually liable in overestimating the electron correlation effect, our view at present is that the results obtained with the DFT methods are preferable to those obtained with the MP2 method.

The NICS values have been computed for the trigonal bipyramid structures **1**, **$1^+$**, and **$1^-$** as well as the planar pentagon structures **4**, **$4^+$**, and **$4^-$** with the B3LYP method along with 6-311G* basis set for neutrals and cations, and 6-311+G* basis set for anions. The results show that the trigonal bipyramid structures **1**, **$1^+$**, and **$1^-$** are all aromatic, while structures **4** and **$4^+$** are both antiaromatic and structure **$4^-$** is nonaromatic. Among them, structure **$1^+$** has the stronger aromaticity with a larger NICS value than **1** and **$1^-$**.

According to our study, the three-dimensional structures for the neutral, cationic, and anionic $Be_5$ clusters are more stable than the planar structures.

## References and Notes

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