

Density Functional Theory Study of 11-Atom Germanium Clusters: Effect of Electron Count on Cluster Geometry

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Density functional theory (DFT) at the hybrid B3LYP level has been applied to the germanium clusters Ge_{11}^z ($z = -6, -4, -2, 0, +2, +4, +6$) starting from eight different initial configurations. The global minimum within the Ge_{11}^{2-} set is an elongated pentacapped trigonal prism distorted from D_{3h} to C_{2v} symmetry. However, the much more spherical edge-coalesced icosahedron, also of C_{2v} symmetry, expected by the Wade-Mingos rules for a $2n + 2$ skeletal electron system and found experimentally in $\text{B}_{11}\text{H}_{11}^{2-}$ and isoelectronic carboranes, is of only slightly higher energy (+5.2 kcal/mol). Even more elongated D_{3h} pentacapped trigonal prisms are the global minima for the electron-rich structures Ge_{11}^{4-} and Ge_{11}^{6-} . For Ge_{11}^{4-} the C_{5v} 5-capped pentagonal antiprism analogous to the dicarbollide ligand $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ is of significantly higher energy (~ 28 kcal/mol) than the D_{3h} global minimum. The C_{2v} edge-coalesced icosahedron is also the global minimum for the electron-poor Ge_{11} similar to its occurrence in experimentally known 11-vertex “isocloso” metallaboranes of the type $(\eta^6\text{-arene})\text{RuB}_{10}\text{H}_{10}$. The lowest energy polyhedral structures computed for the more hypoelectronic Ge_{11}^{4+} and Ge_{11}^{6+} clusters are very similar to those found experimentally for the isoelectronic ions E_{11}^{7-} ($\text{E} = \text{Ga}, \text{In}, \text{Tl}$) and $\text{Tl}_9\text{Au}_2^{9-}$ in intermetallics in the case of Ge_{11}^{4+} and Ge_{11}^{6+} , respectively. These DFT studies predict an interesting D_{5h} centered pentagonal prismatic structure for Ge_{11}^{2+} and isoelectronic metal clusters.

1. Introduction

Previous papers from our group discuss our results from density functional theory (DFT) computations on six-vertex atom clusters of the group 13 elements boron, indium, and thallium^{1,2} and on five-,³ six-,³ seven-,³ and nine-atom⁴ germanium clusters. We have now extended such calculations to eleven-atom germanium clusters. Eleven-atom clusters are of interest because of the variety of interesting polyhedra that are found in such clusters including the following (Figure 1):

(1) The C_{2v} edge-coalesced icosahedron is found in the 24 skeletal electron deltahedral boranes such as $\text{B}_{11}\text{H}_{11}^{2-}$ and

the isoelectronic carborane $\text{C}_2\text{B}_9\text{H}_{11}$. This 11-vertex deltahedron is unique among the so-called “most spherical” borane deltahedra⁵ in having a degree 6 vertex in addition to the usual degree 4 and 5 vertices.

(2) The C_{5v} capped pentagonal antiprism is found in the 26 skeletal electron *nido* ligand $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$. The open pentagonal face in this structure was originally shown by Hawthorne et al. in the 1960s to form stable transition metal complexes analogous to those formed by the cyclopentadienide anion.^{6,7}

(3) Unusual D_{3h} 11-vertex deltahedra derived from the pentacapped trigonal prism are found in intermetallics as bare anionic metal clusters including the 18 skeletal electron E_{11}^{7-} ($\text{E} = \text{Ga}, \text{In}, \text{Tl}$)⁸ found in K_8E_{11} and the 16 skeletal electron $\text{Tl}_9\text{Au}_2^{9-}$ found in the intermetallic $\text{K}_{18}\text{Tl}_{20}\text{Au}_3$.¹⁰

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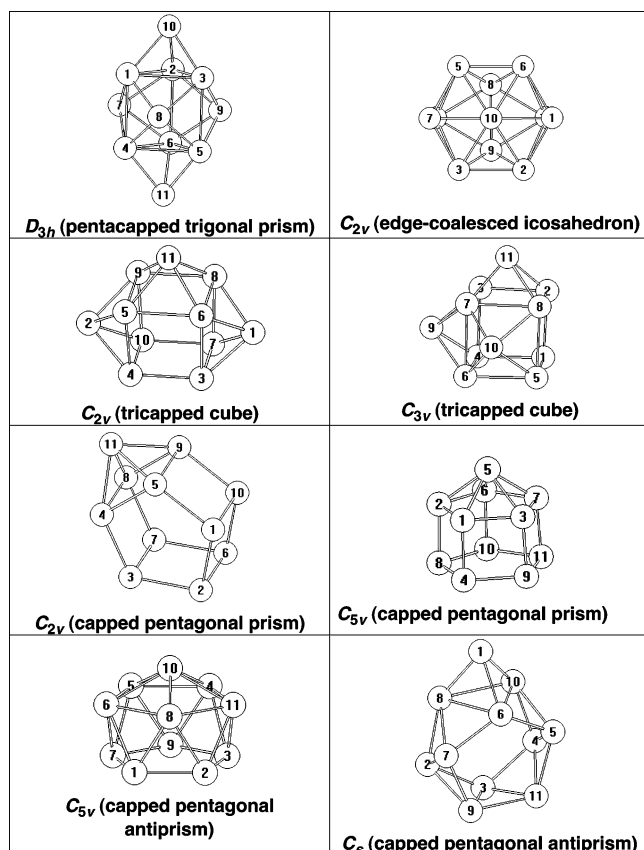


Figure 1. The eight initial 11-vertex polyhedra geometries used in these calculations.

These experimental observations indicate a considerable variety in the 11-vertex deltahedra found in cluster structures depending on the skeletal electron count.

The objective of the research discussed in this paper is to extend our DFT studies to 11-vertex cluster structures in order to study effects of electron count on cluster geometry. The germanium clusters Ge_{11}^z ($z = -6, -4, -2, 0, +2, +4, +6$) were chosen as tractable systems having vertices isolobal to either the BH vertices in borane structures or the bare post-transition metal vertices in bare anionic Zintl ion type clusters. The range of charges on Ge_{11}^z chosen for this work spans the 28 skeletal electrons required for an *arachno* 11-vertex cluster ($28 = 2n + 6$ for $n = 11$), i.e., Ge_{11}^{6-} , to the 16 skeletal electrons found in $\text{Tl}_9\text{Au}_2^{9-}$ (ref 10), i.e., Ge_{11}^{6+} . Furthermore, the choice of germanium as the vertex atom for this study of 11-vertex clusters minimizes the maximum charge required for the range of 28 to 16 skeletal electrons in 11 vertex clusters with bare vertex atoms. Isoelectronic and isolobal relationships provide analogies of our computational results on Ge_{11}^z clusters to experimentally known borane and Zintl ion structures.

2. Computational Methods

Geometry optimizations were carried out at the hybrid DFT B3LYP/6-31G(d) level¹¹ within the Gaussian 98 package of programs.¹² Computations were carried out using eight initial geometries (Figure 1) including examples of 11-vertex polyhedra with 3-fold and 5-fold symmetry. The symmetries were maintained during the geometry optimization processes. For this reason less

symmetrical polyhedra with only C_{2v} or C_s symmetry were also chosen as starting points.

Vibrational analyses show that all of the optimized structures discussed in this paper are genuine minima at the B3LYP/6-31G* level without any significant imaginary frequencies ($N_{\text{imag}} = 0$). However, for several structures relatively small imaginary frequencies were computed. Such low-magnitude imaginary frequencies are suspect with all currently available DFT methods.¹³ Thus, if imaginary frequencies smaller than $100i \text{ cm}^{-1}$ are calculated, one can conclude that “there is a genuine minimum of energy identical or very close to the corresponding stationary point.” In two particular instances, namely, the D_{3h} pentacapped trigonal prism Ge_{11}^{2-} and the C_{2v} capped pentagonal prism Ge_{11}^{2+} where the imaginary frequencies are $102i \text{ cm}^{-1}$ and $198i \text{ cm}^{-1}$, we followed the corresponding normal modes and located genuine minima with C_{2v} and C_s symmetry, respectively.

The optimized structures found for the Ge_{11}^z clusters are depicted in Figures 2, 3, 4, 5, 7, 8, and 10. To distinguish between the large number of structures, they are labeled by the number of skeletal electrons and relative energies. Thus, the lowest energy structure with 24 skeletal electrons (i.e., Ge_{11}^{2-}) is designated as **24–1**. The letter “T” is used to designate triplet structures. More details of all of the optimized structures, including all interatomic distances and the initial geometries (Figure 1) leading to a given optimized structure, are provided in the Supporting Information. In assigning polyhedra to the optimized structures, the Ge–Ge distances less than $\sim 3.0 \text{ \AA}$ were normally considered as polyhedral edges; significant exceptions are noted in the text.

For the more highly charged structures ($\text{Ge}_{11}^{\pm 6}$) the lowest energy optimized “structures” involved fragmentation of the 11-vertex cluster into smaller units, e.g., a distorted cube and three isolated germanium atoms for the optimization of Ge_{11}^{+6} starting with the C_{2v} tricapped cube. In the energy ordering for $\text{Ge}_{11}^{\pm 6}$ only structures in which the 11 germanium vertices remain intact are considered.

3. Results

3.1. The 24 Skeletal Electron Ge_{11}^{2-} (Figure 2). The Ge_{11}^{2-} cluster has the 24 skeletal electrons ($= 2n + 2$ for $n = 11$) required by the Wade-Mingos rules^{14–17} for a *closo* deltahedron and is thus isoelectronic with the known¹⁸ deltahedral borane $\text{B}_{11}\text{H}_{11}^{2-}$. However, the lowest energy structure computed for Ge_{11}^{2-} (**24–1**) is not the “most

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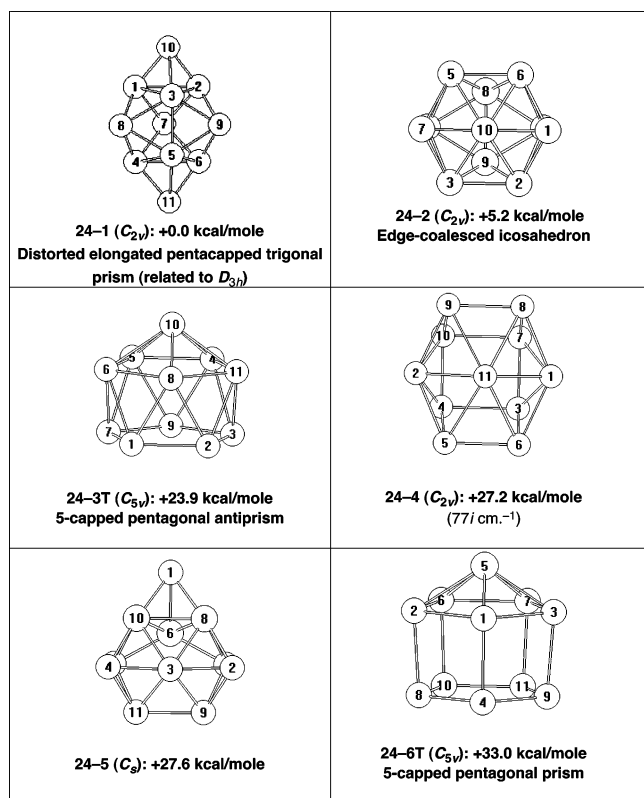


Figure 2. The six optimized structures computed for Ge_{11}^{2-} .

spherical” C_{2v} edge-coalesced icosahedron found experimentally in $\text{B}_{11}\text{H}_{11}^{2-}$ but instead a more prolate (elongated) polyhedron closely related to the D_{3h} pentacapped trigonal prism. This Ge_{11}^{2-} global minimum **24-1** has C_{2v} symmetry like the edge-coalesced icosahedron but has two quadrilateral faces and thus is not a deltahedron. However, the next higher energy structure found for Ge_{11}^{2-} and also of C_{2v} symmetry, namely, **24-2** at +5.2 kcal/mol, is indeed the $\text{B}_{11}\text{H}_{11}^{2-}$ edge-coalesced icosahedron. The reason the lowest energy structure **24-1** rather than **24-2** is not found for $\text{B}_{11}\text{H}_{11}^{2-}$ and its derivatives, including 11-vertex *closo*-carboranes, may relate to the extreme prolate (elongated) shape of **24-1**, its two quadrilateral faces, and its two degree 3 vertices.

The edge-coalesced icosahedral structure **24-2** for Ge_{11}^{2-} can be viewed from the unique degree 6 vertex (Ge10 in Figure 2). The triangulated network emanating from this vertex can be opened up by breaking edges to make quadrilateral faces. In this connection the next highest energy singlet structure at +27.2 kcal/mol found in this work was **24-4** of C_{2v} symmetry containing 12 triangular faces and three quadrilateral faces. This structure can be derived from the original edge-coalesced icosahedron by breaking three edges followed by some distortion.

The other singlet structure of comparable energy for Ge_{11}^{2-} (**24-5**) at +27.6 kcal/mol can be derived from a rather unsymmetrical *nido* 10-vertex polyhedron containing a single open pentagonal face. Such a *nido* 10-vertex structure would require $2n + 4$ skeletal electrons = 24 for $n = 10$ according to the Wade-Mingos rules.¹⁴⁻¹⁷ In structure **24-5** two of these 24 skeletal electrons are provided by the eleventh

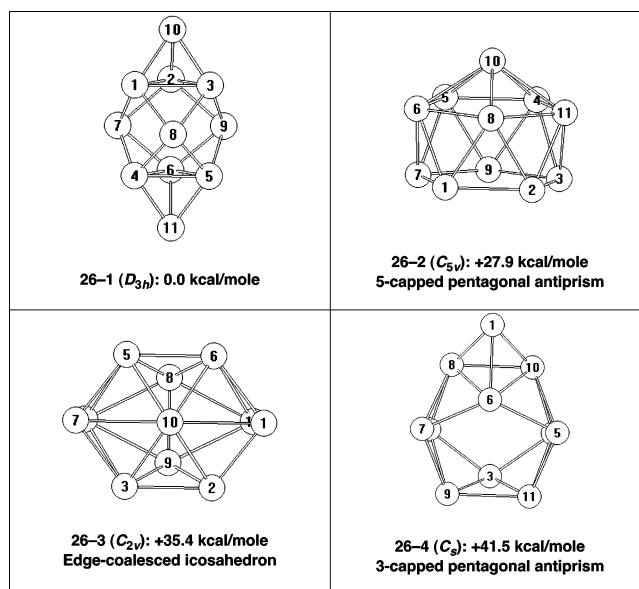


Figure 3. The four optimized structures computed for Ge_{11}^{4-} .

germanium atom, which caps one of the triangular faces of the *nido* polyhedron.

Triplet structures are also found for Ge_{11}^{2-} exhibiting 5-fold symmetry (C_{5v}) in which some of the molecular orbitals are doubly degenerate (e. g., **24-3T** and **24-6T**). A triplet structure thus can be obtained by half-filling a doubly degenerate highest occupied molecular orbital (HOMO). The lower energy of the two triplet structures, namely, structure **24-3T** at +23.9 kcal/mol, is a 5-capped pentagonal antiprism, which can be obtained from an icosahedron by removing a vertex. This structure is related to that of the *nido* carborane $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ with 26 skeletal electrons used as the dicarbollide ligand in transition metal chemistry. Since triplet C_{5v} - Ge_{11}^{2-} has only 24 rather than the 26 skeletal electrons required for a closed-shell singlet 11-vertex *nido* structure, its highest doubly degenerate HOMO is only half full. The other triplet structure, namely, structure **24-6T** at +33.0 kcal/mol, can be derived from structure **24-3T** by rotating the uncapped pentagonal face relative to the capped pentagonal face in a quintuple diamond-square process so that the underlying pentagonal antiprism becomes a pentagonal prism. The higher energy of **24-6T** relative to **24-3T** can be related to the replacement of 10 triangular faces in **24-3T** with five quadrilateral faces in **24-6T**. In most cases replacement of an adjacent pair of triangular faces with a quadrilateral face leads to an increase in energy.

3.2. Electron-Rich Structures. An anion of stoichiometry Ge_{11}^{4-} has the 26 skeletal electrons required by the Wade-Mingos rules¹⁴⁻¹⁷ for a *nido* structure with a single open (nontriangular) face ($26 = 2n + 4$ for $n = 11$). However, the lowest energy structure for this stoichiometry (Figure 3) is not a *nido* structure but instead a prolate D_{3h} structure (**26-1**) derived from the pentacapped trigonal prism by elongating to 3.35 Å the three equivalent “vertical” edges of the underlying prism (distances $\text{Ge1}\cdots\text{Ge4}$, $\text{Ge2}\cdots\text{Ge6}$, and $\text{Ge3}\cdots\text{Ge5}$ in Figure 3). Thus, the resulting polyhedron

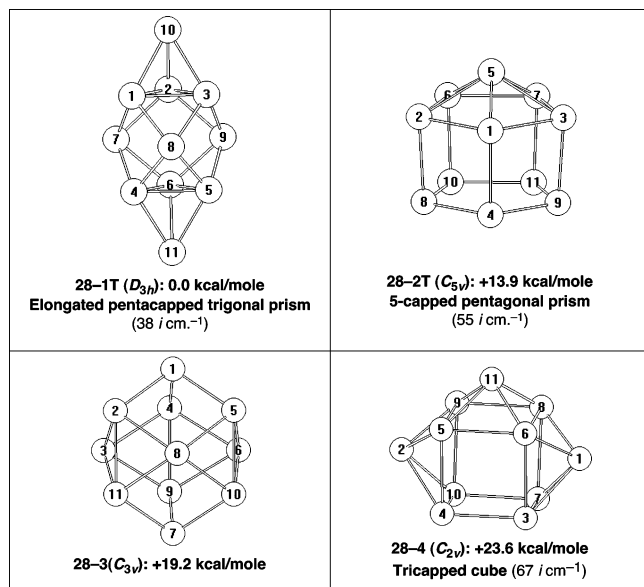


Figure 4. The four optimized structures computed for Ge_{11}^{6-} .

can best be considered to have 12 triangular faces and three bent rhombus faces.

The C_{5v} *nido* structure **26-2** expected from the Wade-Mingos rules¹⁴⁻¹⁷ is also found for Ge_{11}^{4-} but at a considerably higher energy (+27.9 kcal/mol). This is isoelectronic with the $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ “dicarbollide” ligand shown by Hawthorne et al.^{6,7} to form pentahapto transition metal complexes through its open pentagonal face similar to the cyclopentadienyl ligand.

The next higher energy structure for Ge_{11}^{4-} (**26-3**) is an edge-coalesced icosahedron similar to that computed for Ge_{11}^{2-} (**24-2** in Figure 2) and found experimentally in $\text{B}_{11}\text{H}_{11}^{2-}$ and $\text{C}_2\text{B}_9\text{H}_{11}$. The fact that this structure is stable for both Ge_{11}^{2-} and Ge_{11}^{4-} can relate to its relatively low C_{2v} symmetry, which means that none of its molecular orbitals are required by symmetry to be degenerate so that closed shell structures are possible for both 24 and 26 skeletal electrons.

The next higher energy structure at +41.5 kcal/mol computed for Ge_{11}^{4-} (**26-4**) is a C_s 3-capped pentagonal antiprism which still has the original two pentagonal faces of the underlying antiprism. This may be regarded as a 10-vertex *arachno* structure capped on one of its triangular faces by an eleventh atom. The Wade-Mingos rules¹⁴⁻¹⁷ require the underlying 10-vertex *arachno* structure to have $(2)(10) + 6 = 26$ skeletal electrons. Two of these skeletal electrons come from the eleventh germanium atom acting as a cap without contributing any new bonding orbitals.

The stoichiometry Ge_{11}^{6-} has the 28 skeletal electron configuration suggested by the Wade-Mingos rules¹⁴⁻¹⁷ to have an *arachno* structure with either two nontriangular faces or one large opening. However, no such *arachno* type structures are found at energies close to those in Figure 4. The lowest energy structure for Ge_{11}^{6-} (**28-1T**) is derived from a D_{3h} pentacapped trigonal prism that is even more elongated than **26-1**. Thus, in this structure the original “vertical” edges of the underlying trigonal prism ($\text{Ge}1\cdots$

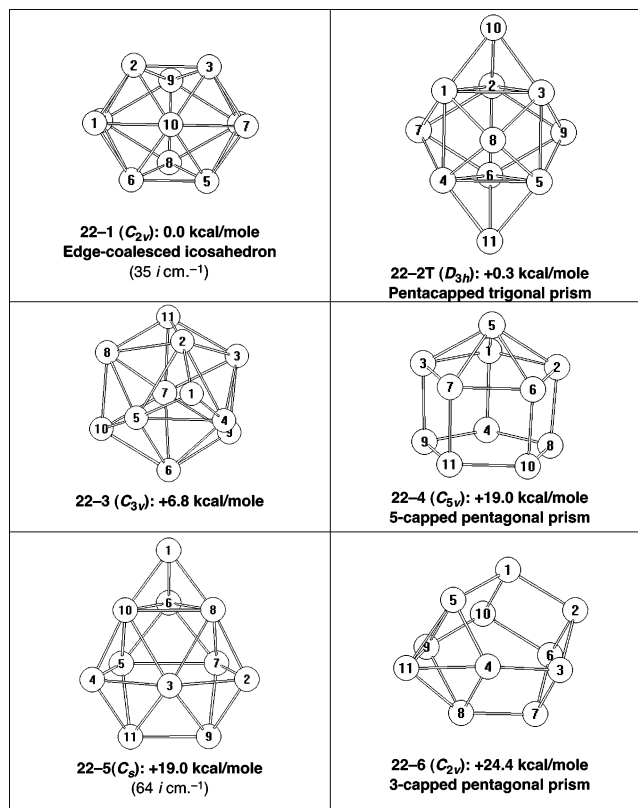


Figure 5. The six optimized structures computed for neutral Ge_{11} .

$\text{Ge}4$, $\text{Ge}2\cdots\text{Ge}6$, and $\text{Ge}3\cdots\text{Ge}5$ in Figure 3) become 3.553 Å and thus are no longer topologically to be considered as edges (see $\text{Ge}1\cdots\text{Ge}4$, $\text{Ge}2\cdots\text{Ge}6$, and $\text{Ge}3\cdots\text{Ge}5$ in Figure 4). A triplet C_{5v} capped pentagonal prism (**28-2T**) is also computed for Ge_{11}^{6-} at only +13.9 kcal/mol above the minimum energy triplet structure (**28-1T**). The next higher energy (+19.2 kcal/mol) structure (**28-3**) is a singlet with C_{3v} symmetry with symmetry-related triplets of quadrilateral faces surrounding the two apical atoms and a belt of six triangles around the “waist.” A still higher energy structure (+26.3 kcal/mol) computed for Ge_{11}^{6-} is a C_{2v} structure (**28-4**) derived from a C_{2v} tricapped cube.

3.3. The 22 Skeletal Electron Neutral Ge_{11} (Figure 5).

A neutral Ge_{11} cluster is certainly unstable with respect to polymerization to bulk germanium metal. However, computations on neutral Ge_{11} are of interest in order to characterize the relative stabilities of various 11-vertex polyhedra in 22 skeletal electron systems. Examples of experimentally known 11-vertex metallaboranes with 22 skeletal electrons include the (arene) $\text{RuB}_{10}\text{H}_{10}$ derivatives¹⁹ (arene = *p*-cymene, hexamethylbenzene, etc.) in which the (arene)Ru unit occupies the unique degree 6 vertex of an edge-coalesced icosahedron. The skeletal bonding in such (arene) $\text{RuB}_{10}\text{H}_{10}$ derivatives has been interpreted as consisting of three-center two-electron (3c-2e) bonds in 11 of the 18 faces of the edge-coalesced icosahedron selected so that each vertex is part of three faces with the 3c-2e bonds.²⁰

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In accord with the experimental work on the 22 skeletal electron (arene) $B_{10}H_{10}$ derivatives,¹⁹ the lowest energy structure **22-1** computed for the 22 skeletal electron neutral Ge_{11} is the same C_{2v} edge-coalesced icosahedron found also in the 24 skeletal electron $B_{11}H_{11}^{2-}$ (ref 18) and computed as low or relatively low energy structures for Ge_{11}^z clusters with 26, 24, or 22 skeletal electrons (i.e., $z = -4, -2, \text{ or } 0$). This indicates the flexibility of this C_{2v} structure to accommodate different numbers of skeletal electron pairs in accord with the absence of degenerate orbitals required by its C_{2v} point group symmetry.

Two higher-lying singlet structures for Ge_{11} , namely, **22-3** at +6.8 kcal/mol and **22-5** at +19.0 kcal/mol, can both be derived from a 10-vertex deltahedron by capping one of its triangular faces. Twenty of the $(2)(10) + 2 = 22$ skeletal electrons required by the Wade-Mingos rules¹⁴⁻¹⁷ for a ten-vertex deltahedron can be obtained from its 10 vertex germanium atoms whereas the remaining two skeletal electrons are obtained from the eleventh germanium atom capping one of the triangular faces. The underlying ten-vertex deltahedron in both **22-3** and **22-5** is not the D_{4d} 4,4-bicapped square antiprism found in $B_{10}H_{10}^{2-}$ and related ten-vertex deltahedral boranes and carboranes but a C_{3v} ten-vertex deltahedron similar to the ten-vertex *isocloso* (η^6 -arene) RuB_9H_9 derivative. In **22-3** the vertex capping the C_{3v} ten-vertex deltahedron is on the C_3 axis so that C_{3v} symmetry is maintained. However, in the higher energy **22-5** the capping vertex is not on the C_3 axis so that the symmetry is reduced to C_s . Other computed singlet structures for neutral Ge_{11} are derived from a pentagonal prism capped either on a pentagonal face (C_{5v} **22-4** at +19.0 kcal/mol) or a rectangular face (C_{2v} **22-6** at +24.4 kcal/mol).

In addition to the above five singlet structures for neutral Ge_{11} , this computational study found a D_{3h} triplet structure of energy close to the global minimum, namely, **22-2T** at only +0.3 kcal/mol relative to **22-1**. In **22-2T** the “vertical” edges of the underlying trigonal prism (edges Ge1–Ge4, Ge2–Ge6, and Ge3–Ge5 in Figure 5) are not elongated as in the electron richer D_{3h} structures **24-2**, **26-1**, and **28-1**.

The neutral Ge_{11} cluster system was recently studied computationally by Luo, Li, Zhang, Chen, and Cheng (LLZCC),²¹ who used very different starting points for their optimizations than we used in our work. Thus, in the LLZCC work the starting structures were obtained by adding one atom to stable Ge_{10} clusters or two atoms to stable Ge_9 clusters followed by energetic minimization successively by MM+ molecular mechanics and semiempirical PM3 methods. The resulting intermediate models were then optimized by B3LYP DFT methods closely related to those used in this work but using different basis sets. Since this approach is very different, it is not surprising that the optimized singlet structures found by LLZCC are very different from those found in our work. In general, the optimized singlet structures of LLZCC have symmetries no higher than C_{2v} and many

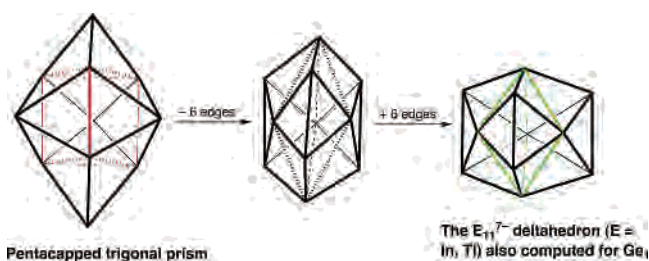


Figure 6. The sextuple diamond-square-diamond process converting a pentacapped trigonal prism to the compressed 11-vertex D_{3h} polyhedron found to be the global minimum for Ge_{11}^{4+} and found experimentally as E_{11}^{7-} ($E = Ga, In, Tl$) in K_8E_{11} . The underlying trigonal prism of the pentacapped trigonal prism is indicated in red and the newly formed edges of a trigonal bipyramid are indicated in green. Edges to be broken or formed are indicated by dashed/hashed lines.

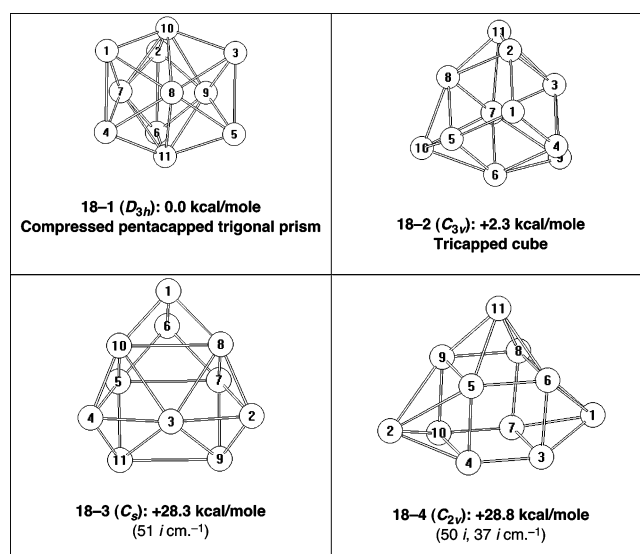


Figure 7. The four optimized structures computed for Ge_{11}^{4+} .

were of only C_s symmetry. However, the lowest energy optimized triplet structure of LLZCC was a pentacapped trigonal prismatic structure closely related to the triplet structure **22-2T** found in our work.

3.4. The 18 Skeletal Electron Ge_{11}^{4+} (Figures 6 and 7). The 18-skeletal electron Ge_{11}^{4+} is isoelectronic and isolobal with several E_{11}^{7-} ($E = Ga, In, Tl$) anions found experimentally by Corbett and co-workers to have highly oblate structures derived from the D_{3h} pentacapped trigonal prism by such severe compression that the “horizontal” edges of the top and bottom triangular faces of the underlying trigonal prism are stretched far from bonding distances. This compression corresponds to a sextuple diamond-square-diamond process²² converting the original pentacapped trigonal prism into another D_{3h} deltahedron having five degree 6 vertices forming a trigonal bipyramid and six degree 4 vertices forming an oblate trigonal prism missing the six edges of the top and bottom faces (Figure 6). A similar 11-vertex deltahedron is also found in the mixed nickel–rhodium carbonyl cluster anion²³ $Rh_5Ni_6(CO)_{21}^{3-}$ in which the rhodium atoms form the trigonal bipyramid and the nickel atoms

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form the oblate trigonal prism; this Rh/Ni cluster can also be interpreted as an 18 skeletal electron structure.²⁴

In view of these considerations, it is not surprising that the computed global minimum for Ge_{11}^{4+} is this highly compressed D_{3h} deltahedron (**18-1** in Figure 7). This global minimum is reached starting not only from the D_{3h} pentacapped trigonal prism but even from the C_{2v} “edge-coalesced icosahedron.” Furthermore, this computed global minimum for Ge_{11}^{4+} (**18-1**) has the same degree of compression as found experimentally in both the bare E_{11}^{7-} clusters ($\text{E} = \text{In}, \text{Tl}^9$) in the intermetallics K_8E_{11} and the metal carbonyl cluster $\text{Rh}_5\text{Ni}_6(\text{CO})_{21}^{3-}$ (ref 23). This is indicated by the v/h ratio of $2.80/4.43 = 0.63$ computed for Ge_{11}^{4+} as compared with experimental v/h ratios of 0.63 ± 0.01 for the same polyhedron in In_{11}^{7-} in K_8In_{11} ,⁸ $\text{In}_{10}\text{Hg}^{8-}$ in $\text{K}_8\text{In}_{10}\text{Hg}$,²⁵ Tl_{11}^{7-} in K_8Tl_{11} ,⁹ and $\text{Rh}_5\text{Ni}_6(\text{CO})_{21}^{3-}$ (ref 23). The ubiquity of this unusual D_{3h} 11-vertex deltahedron in both computational and experimental work on 11-vertex clusters with 18 skeletal electrons underscores its importance in the chemistry of such systems.

The next higher energy structure for Ge_{11}^{4+} is also of 3-fold symmetry, namely, a C_{3v} tricapped cube (**18-2**, +2.3 kcal/mol). Of much higher energy are two rather unusual structures very close in energy to each other, namely, a C_s structure **18-3** (+28.3 kcal/mol) consisting of a fusion of an octahedron with two trigonal bipyramids and a C_{2v} tricapped cube (**18-4**, +28.8 kcal/mol).

3.5. Other Electron-Poor Structures. The lowest energy structure for the dication Ge_{11}^{2+} with 20 skeletal electrons **20-1** (Figure 8) can be dissected into a tetragonal antiprism with caps on the two quadrilateral and on one of the triangular faces. Above this global minimum in terms of energy (+10.7 kcal/mol) is a C_s symmetry structure which can be viewed as a 10-vertex *nido* polyhedron with one quadrilateral face and a cap on a triangular face (**20-2**). At only slightly higher energy (+11.3 kcal/mol) comes a D_{3h} pentacapped trigonal prism **20-3** followed (at +14.5 kcal/mol) by a compressed pentacapped trigonal prism **20-4**, which is topologically similar to the global minimum **18-1** found for Ge_{11}^{4+} and found experimentally in the isoelectronic and isolobal E_{11}^{7-} ($\text{E} = \text{Ga}, \text{In},^8 \text{Tl}^9$) and $\text{Rh}_5\text{Ni}_6(\text{CO})_{21}^{3-}$ discussed above. Structure **20-4** is slightly more compressed than **18-1** as indicated by a v/h ratio of $2.566/4.298 = 0.60$ for **20-3** as compared with $v/h = 0.63$ for **18-4** as noted above.

From a chemical point of view the most interesting structure found for Ge_{11}^{2+} is the D_{5h} centered pentagonal prismatic structure **20-5** at +23.3 kcal/mol above the global minimum **20-1**. This structure can be considered as a pentagonal prism dianion Ge_{10}^{2-} with a Ge^{4+} cation in the center (Figure 9). The dianion Ge_{10}^{2-} is related to two parallel (eclipsed) C_5H_5^- anions with germanium replacing carbon and the five inter-ring Ge-Ge two-center two-electron bonds (i.e., “vertical” edges of the pentagonal prism) replacing the

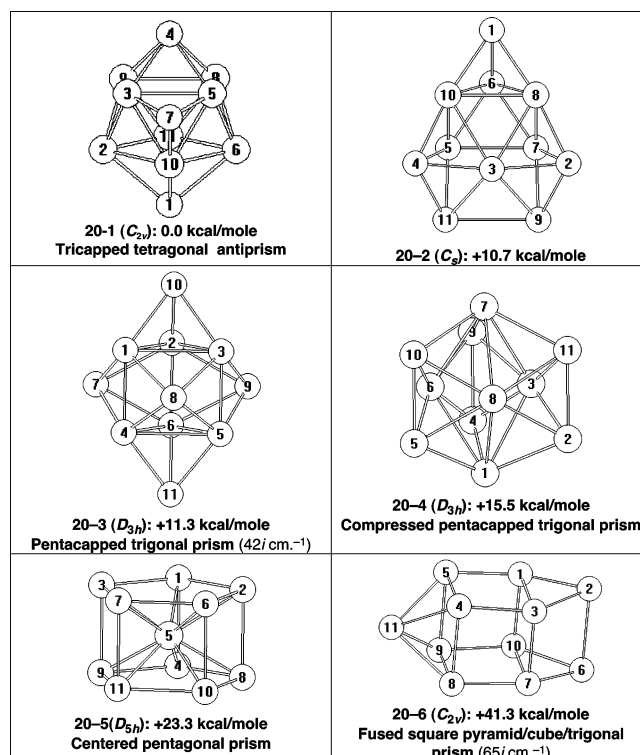


Figure 8. The six optimized structures computed for Ge_{11}^{2+} .



Figure 9. Formation of the centered pentagonal prismatic Ge_{11}^{2+} (20-5) from pentagonal prismatic Ge_{10}^{2-} and a central Ge^{4+} unit (indicated in red).

five external C-H bonds of the C_5H_5^- rings. The idea of encapsulating a relatively high oxidation state metal cation inside a germanium pentagonal prism as exemplified by our computed structure **20-5** is a novel one and suggests some interesting synthetic objectives.

Some of the attempts to optimize structures for the 16 skeletal electron Ge_{11}^{6+} led to separation of the 11 atoms into two structures. Thus, starting with the C_{2v} tricapped cube (Figure 1) for Ge_{11}^{6+} gave a monocapped Ge_9 cube and two isolated Ge atoms. Similarly, starting with the D_{3h} pentacapped trigonal prism for Ge_{11}^{6+} gave a D_{3h} tricapped trigonal prism and two isolated Ge atoms.

The lowest energy intact structure found for Ge_{11}^{6+} (**16-1**) consists of a Ge_6 pentagonal pyramid with the remaining five Ge atoms bound as “spikes” to the basal Ge atoms of the pyramid. The other intact structures found for Ge_{11}^{6+} are of much higher energy. The C_{5v} starfish-like structure **16-2** (+45.8 kcal/mol) is closely related to the likewise C_{5v} structure **16-1** in that both have a pentagonal pyramid center. However, in **16-2** the five “extra” Ge atoms bridge the edges of the pyramid base. Next in energy is **16-3** at +56.6 kcal/mol, which consists of a central 4-capped trigonal prism with four symmetry-related edges bridged by the remaining Ge atoms.

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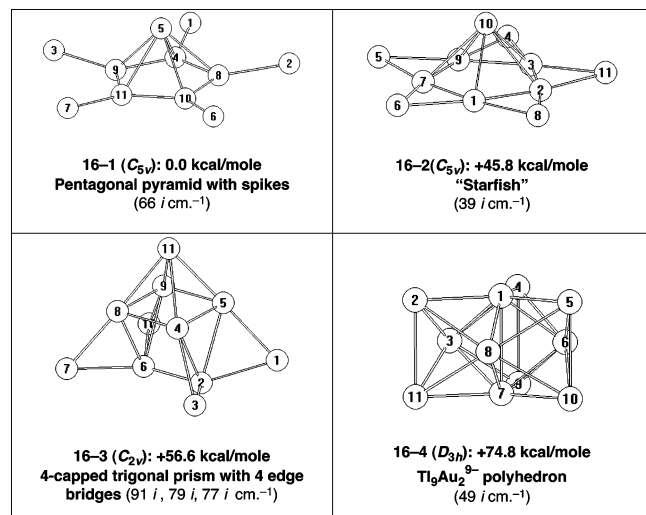


Figure 10. The four optimized structures computed for Ge_{11}^{6+} .

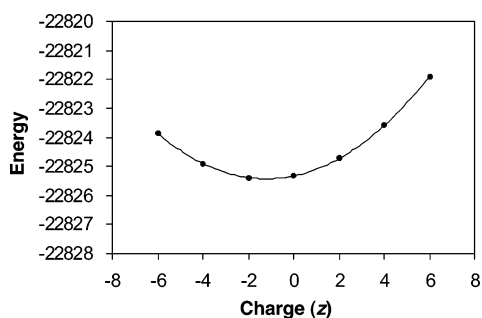


Figure 11. Plot of the total energy of the global minima as a function of charge for the Ge_{11}^z ($z = -6, -4, -2, 0, +2, +4, +6$) clusters.

The lowest energy closed polyhedral structure, namely, the D_{3h} **16-4**, may be derived from the pentacapped trigonal prism by compression so extreme that the two vertices on the C_3 axis, namely, vertices 1 and 7 in Figure 10, are squeezed within the length of an edge. The degree of compression of this polyhedron may be characterized by the ratio a/v , where a is the distance between the two vertices on the C_3 axis and v is the length of the vertical edges of the underlying trigonal prism. This polyhedron is found experimentally in the ion $\text{Tl}_9\text{Au}_2^{9-}$, which occurs in the intermetallic $\text{K}_{18}\text{Tl}_{20}\text{Au}_3$ (ref 10). The ratios a/v and v/h for **16-4** computed in this work are $3.099/3.074 = 1.01$ and $3.074/4.984 = 0.62$, respectively, whereas those found experimentally for $\text{Tl}_9\text{Au}_2^{9-}$ are 0.92 and 0.65, respectively. This small discrepancy may be related to the homoatomic atom nature of Ge_{11}^{6+} and the heteroatomic nature of $\text{Tl}_9\text{Au}_2^{9-}$. Note that $\text{Tl}_9\text{Au}_2^{9-}$ is isoelectronic with Ge_{11}^{6+} with 16 skeletal electrons since the nine Tl vertices are each donors of +1 skeletal electron whereas the two Au vertices are each donors of -1 skeletal electron.

4. Discussion

4.1. Energies. Figure 11 plots the computed energies for the lowest energy structures for the Ge_{11}^z clusters ($z = +6, +4, +2, 0, -2, -4, -6$) against their charges. This plot reflects the instability of the isolated highly charged clusters, either positive or negative. The lowest energy global minimum is found for Ge_{11}^{2-} in accord with its potential

Table 1. Dimensions of the D_{3h} Structures Derived from the Pentacapped Trigonal Prism for Ge_{11}^z ($z = -6, -4, -2, 0, +2, +4, +6$)

structure	"vertical" edge, v , Å	"horizontal" edge, h , Å	v/h
16-4	3.07	4.98	0.62
18-1	2.80	4.44	0.63
20-2	2.50	2.90	0.86
20-3	2.57	4.39	0.59
22-2T	2.69	2.90	0.93
24-1^a	3.02	2.93	1.03
26-1	3.35	2.76	1.21
28-1T	3.55	2.73	1.30

^a An "idealized" D_{3h} structure at an intermediate stage of optimization with an imaginary frequency of $102i$ rather than the final optimized C_{2v} structure is considered here.

three-dimensional aromaticity predicted by the Wade-Mingos rules¹⁴⁻¹⁷ for an n -vertex cluster with $2n + 2$ skeletal electrons.

4.2. Geometry. The two geometries found for Ge_{11}^z with several different skeletal electron counts are various D_{3h} polyhedra derived from the pentacapped trigonal prism and the so-called C_{2v} edge-coalesced icosahedron (also called the octadecahedron from the number of faces) found experimentally¹⁸ in $\text{B}_{11}\text{H}_{11}^{2-}$ and related boranes. Both of these types of polyhedra exhibit significant variations in their geometries as a function of skeletal electron count as discussed below.

4.2.1. D_{3h} Polyhedra. All of the Ge_{11}^z clusters investigated from $z = -6$ to $+6$, i.e., with 28 to 16 skeletal electrons, respectively, gave optimized structures of D_{3h} symmetry of relatively low energies. These structures can be derived from the pentacapped trigonal prism (Figure 1) and are characterized geometrically by their v/h ratios (Table 1), where v and h are the lengths of the "vertical" and "horizontal" edges, respectively, of the underlying trigonal prism. The observed v/h ratios correlate roughly with the number of skeletal electrons with a generally increasing trend as the number of skeletal electrons is increased.

The highly electron-poor clusters Ge_{11}^z ($z = +6, +4, \text{ and } +2$) with 16 to 20 skeletal electrons form highly compressed oblate D_{3h} structures exhibiting v/h ratios in the range 0.60 ± 0.03 . In these oblate structures the six "horizontal" edges of the underlying trigonal prism are so highly elongated (>4.3 Å) that they can be considered to be "broken" in a sextuple diamond-square-diamond process with the formation of six new edges to give another deltahedron of D_{3h} symmetry like the original pentacapped trigonal prism (Figure 6). This new D_{3h} deltahedron is more nearly "spherical" than the original pentacapped trigonal prism since it has no degree 3 vertices but only six degree 4 vertices (the vertices of the original trigonal prism) and five degree 6 vertices (the original capping vertices). As indicated above, this D_{3h} deltahedron is found experimentally in intermetallics as the highly charged anions E_{11}^{7-} ($\text{E} = \text{Ga}, \text{In}, \text{Tl}$)^{8,9} isoelectronic with the 18 skeletal electron Ge_{11}^{4+} .

Intermediate electron counts, i.e., 20 to 24 skeletal electrons in Ge_{11}^z ($z = +2, 0, -2$), lead to more normal pentacapped trigonal prisms with v/h ratios ranging from 0.86 in Ge_{11}^{2+} to 1.03 in Ge_{11}^{2-} . The optimized D_{3h} structure for neutral Ge_{11} , also found by LLZCC,²¹ is a triplet, probably

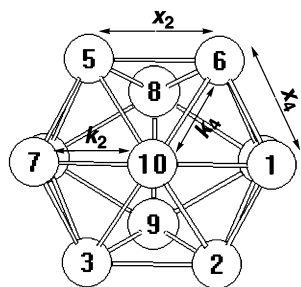


Figure 12. The v_6 -hexagon edges x_4 and x_2 and the v_6 -spoke edges k_4 and k_2 surrounding the unique degree 6 vertex in the edge-coalesced icosahedron.

Table 2. Geometry Surrounding the Unique Degree 6 Vertices in the Edge-coalesced Icosahedra Computed for Ge_{11}^z ($z = -4, -2, 0, +2$) and Found Experimentally in Related Structures

structure	v_6 -hexagon, Å	x_4/x_2	v_6 -spokes, Å	k_4/k_2
22-1	2.61(x_4), 2.43(x_2)	1.07	2.69(k_4), 2.45(k_2)	1.10
(η^6 - <i>p</i> -cymene)RuB ₁₀ H ₁₀	1.76(x_4), 1.71(x_2)	1.03	2.28(k_4), 2.10(k_2)	1.09
24-1	2.61(x_4), 2.60(x_2)	1.00	2.89(k_4), 2.41(k_2)	1.20
[Li(thp) ₂] ₂ B ₁₁ H ₁₁	1.70(x_4), 1.79(x_2)	0.95	2.05(k_4), 1.61(k_2)	1.27
[Et ₃ NCH ₂ Ph][B ₁₁ H ₁₁]	1.66(x_4), 1.85(x_2)	0.90	2.01(k_4), 1.75(k_2)	1.15
26-3	2.61(x_4), 2.59(x_2)	1.01	2.85(k_4), 2.89(k_2)	0.99

with a molecular orbital pattern similar to Ge_{11}^{2-} but with a half-filled doubly degenerate HOMO.

Electron-rich Ge_{11}^z clusters, namely, those with 26 and 28 skeletal electrons (Ge_{11}^{4-} and Ge_{11}^{6-}), give elongated (prolate) optimized D_{3h} structures with v/h ratios in the range 1.25 ± 0.05 (Table 1). In these structures the “horizontal” edges of the underlying trigonal prism are so elongated (>3.3 Å) that they can be considered to be “broken” to give a D_{3h} polyhedron with three rhombus faces and eight triangular faces. Electron-rich metal clusters with this D_{3h} polyhedron do not yet appear to have been realized experimentally.

4.2.2. The C_{2v} Edge-Coalesced Icosahedron. The other 11-vertex polyhedron found in optimized Ge_{11}^z structures with a variety of skeletal electron counts, i.e., 20 to 26 skeletal electrons for $z = +2, 0, -2$, and -4 , is the edge-coalesced icosahedron. As the “most spherical” 11-vertex deltahedron, this deltahedron is found experimentally in 11-vertex deltahedral boranes and carboranes such as $\text{B}_{11}\text{H}_{11}^{2-}$, $\text{CB}_{10}\text{H}_{11}^-$, $\text{C}_2\text{B}_9\text{H}_{11}$, and their derivatives.

The geometries of the edge-coalesced icosahedra can be characterized by the relative lengths of the edges associated with the unique degree 6 vertex (Figure 12 and Table 2). Of interest in this connection are edges of the following two types:

- (1) The six v_6 -spokes emanating from the degree 6 vertex to the six adjacent vertices (k_4 and k_2).
- (2) The six edges of the v_6 -hexagon formed by the six vertices adjacent to the unique degree 6 vertex (x_4 and x_2).

In both cases the C_{2v} overall symmetry of the edge-coalesced icosahedron partitions each of the above sets of six edges into four symmetry-related edges of one type (k_4 and x_4) and two symmetry-related edges of a second type (k_2 and x_2) (Figure 12). The ratio k_4/k_2 indicates the deviation from equivalence of the six distances from the degree 6 vertex to the adjacent vertices (the v_6 -spokes). Similarly the

ratio x_4/x_2 indicates the deviation from regularity of the hexagon surrounding the unique degree 6 vertex (the v_6 -hexagon).

The electron-poor C_{2v} edge-coalesced icosahedron structures computed for Ge_{11} with 22 skeletal electrons have x_4/x_2 and k_4/k_2 ratios of 1.07 and 1.10, respectively. An almost identical k_4/k_2 ratio of 1.09 is found experimentally for the “spokes” in (η^6 -*p*-cymene)RuB₁₀H₁₀, which has 22 skeletal electrons such as the neutral Ge_{11} . The x_4/x_2 ratio of 1.03 found experimentally¹⁹ for (η^6 -*p*-cymene)RuB₁₀H₁₀ deviates more significantly from that of 1.07 computed for Ge_{11} but this could be an effect of the d orbitals of the ruthenium atom in the center of the v_6 -hexagon.

The “edge-coalesced” icosahedron geometry computed for Ge_{11}^{2-} with 24 skeletal electrons is appreciably different from that computed for the electron-poorer clusters. Particularly significant is the high k_4/k_2 “spoke” ratio of 1.20 for Ge_{11}^{2-} . A similar nonequivalence of the spoke lengths is found experimentally in the isoelectronic $\text{B}_{11}\text{H}_{11}^{2-}$ salts with the k_4/k_2 “spoke” ratios of [Li(thp)₂]₂B₁₁H₁₁ and [Et₃NCH₂Ph][B₁₁H₁₁] of 1.27 and 1.15, respectively, bracketing the computed 1.20 value for Ge_{11}^{2-} . The four long spoke lengths in the isoelectronic 11-vertex carborane $\text{CB}_{10}\text{H}_{11}^-$ have been interpreted²⁶ to mean that they are no longer polyhedral edges. This would imply that the so-called 11-vertex polyhedra found in the 24-skeletal electron systems obeying the Wade-Mingos¹⁴⁻¹⁷ $2n + 2$ rule for $n = 11$ are not really deltahedra but have several nontriangular faces.

The most nearly regular “edge-coalesced icosahedron,” at least around the degree 6 vertex, is computed for the electron-rich cluster Ge_{11}^{4-} with 26 skeletal electrons, where both the x_4/x_2 and k_4/k_2 ratios are essentially unity, i.e., 1.00 ± 0.01 . No examples of 26 skeletal electron edge-coalesced icosahedron clusters have yet been synthesized.

4.3. Electron Count versus Geometry: Relevance of the Wade-Mingos Rules. The edge-coalesced icosahedron (Figure 1) is the “most spherical” *closo* deltahedron with 11 vertices.⁵ The Wade-Mingos rules¹⁴⁻¹⁷ therefore suggest that it should be the preferred deltahedron for an 11-vertex cluster with $2n + 2 = 24$ skeletal electrons, namely, Ge_{11}^{2-} , which is isoelectronic with the known borane anion $\text{B}_{11}\text{H}_{11}^{2-}$. Thus, Ge_{11}^{2-} with a C_{2v} edge-coalesced icosahedron structure should exhibit three-dimensional aromaticity²⁷ and be particularly stable. The skeletal bonding in an n -vertex deltahedron exhibiting such three-dimensional aromaticity can be viewed as a combination of bonds of the following two types:

- (1) A single n -center core bond analogous to the π -bonding in benzene but using only two skeletal electrons;
- (2) A total of n 2c-2e surface bonds analogous to the σ -bonding in benzene and using $2n$ skeletal electrons.

This skeletal bonding model for deltahedral structures exhibiting three-dimensional aromaticity requires a total of $2n + 2$ skeletal electrons in accord with the Wade-Mingos rules.¹⁴⁻¹⁷ In this connection the edge-coalesced icosahedron

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24–2 (Figure 2) was computed to be very close (+5.2 kcal/mol) to the lowest energy singlet structure found for Ge_{11}^{2-} .

Electron-rich Ge_{11}^z clusters, i.e., those with more than 24 skeletal electrons, would be expected by the Wade-Mingos rules to have polyhedral structures with one or more nontriangular faces. The C_{5v} 5-capped pentagonal antiprism **26–2** (Figure 3) with one nontriangular face is an example of such a *nido* structure for Ge_{11}^{4-} with $2n + 4 = 26$ skeletal electrons for $n = 11$. The carborane analogue of Ge_{11}^{4-} is well-known as the dicarbollide ligand $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ in transition metal complexes.^{6,7}

The even more electron-rich cluster Ge_{11}^{6-} with $2n + 6 = 28$ skeletal electrons would be expected by the Wade-Mingos rules^{14–17} to have an *arachno* structure with two nontriangular faces or one large opening in a polyhedron with otherwise triangular faces. None of the optimized structures for Ge_{11}^{6-} (Figure 4) appears to fit this description.

Electron-poor Ge_{11}^z clusters, i.e., those with less than 24 skeletal electrons, have a number of structural options including the following:

(1) An edge-coalesced icosahedron but with skeletal bonding consisting of 3c-2e bonds in 11 of the 18 faces thereby requiring only 22 rather than the 24 skeletal electrons for an edge-coalesced icosahedron exhibiting full three-dimensional aromaticity with an 11-center core bond and n 2c-2e surface bonds. This more localized bonding model has been postulated for the so-called *isocloso* metallaboranes^{28–31} as exemplified by the 11-vertex (η^6 -arene) $\text{RuB}_{10}\text{H}_{10}$ (ref 19) discussed in this paper. The lowest energy structure **22–1** (Figure 5) computed for Ge_{11} , isoelectronic with (η^6 -arene)- $\text{RuB}_{10}\text{H}_{10}$, is an example of such a structure.

(2) A structure based on a smaller central polyhedron with one or more capped *triangular* faces. The central polyhedron determines the skeletal electron requirement for this structure with the additional capping atom(s) contributing additional skeletal electrons but no new bonding molecular orbitals. Structure **22–3** (Figure 5) computed for Ge_{11} is an example of such a structure where the central 10-vertex deltahedron requires $(2)(10) + 2 = 22$ skeletal electrons with two of these skeletal electrons being provided by the capping eleventh vertex. The 24 skeletal electrons in structure **24–5** computed for Ge_{11}^{2-} (Figure 2) also arise from this principle where a 10-vertex *nido* structure with a single pentagonal face and requiring $24 = 2n + 4$ skeletal electrons for $n = 10$ is capped on one of its triangular faces.

(3) Flattening degree 4 vertices of deltahedra with bare vertices so that otherwise external electron pairs are drawn into the skeletal bonding.³² In this connection the highly oblate D_{3h} deltahedron in structure **18–1** (Figure 7) can be derived from the pentacapped trigonal prism by flattening

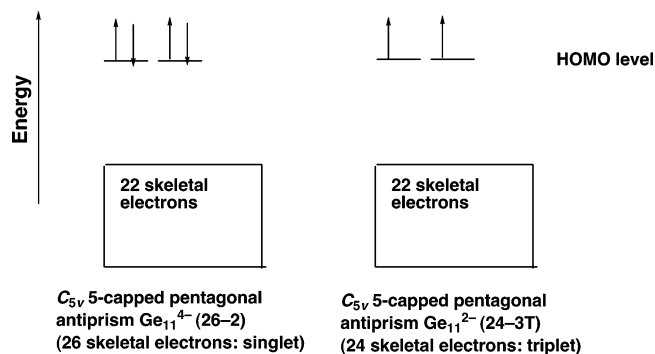


Figure 13. A comparison of the electron occupancy in the doubly degenerate HOMO in the C_{5v} 5-capped pentagonal antiprism clusters Ge_{11}^{4-} (**26–2** singlet) and Ge_{11}^{2-} (**24–3T** triplet).

the three caps on the rectangular faces of the underlying prism (compare Figure 6). This provides three extra electron pairs in the formally 18-skeletal electron system Ge_{11}^{4+} isoelectronic with the known E_{11}^{7-} ($\text{E} = \text{Ga}, \text{In},^8 \text{Ti}^9$) and $\text{Rh}_5\text{Ni}_6(\text{CO})_{21}^{3-}$ (ref 23) to make it a system with $18 + (3)(2) = 24$ effective skeletal electrons corresponding to the $2n + 2$ ($n = 11$) skeletal electrons for a globally delocalized three-dimensional aromatic system. The even more electron-poor structure **16–4** computed for Ge_{11}^{6+} with 16 apparent skeletal electrons and found experimentally¹⁰ in $\text{Tl}_9\text{Au}_2^{9-}$ can formally be considered to combine flattening of the three vertices capping the rectangular faces of the underlying trigonal prism with an “internal” metal–metal bond between the two axial vertices located on the C_3 axis.

This work led to the discovery of several triplet structures for the Ge_{11}^z clusters, mainly structures with C_{5v} symmetry such as **24–3T** and **24–6T** for Ge_{11}^{2-} and **28–2T** for Ge_{11}^{6-} . The C_{5v} point group has two two-dimensional irreducible representations conventionally designated as E_1 and E_2 corresponding to doubly degenerate molecular orbitals (MOs). If one of these doubly degenerate MO sets is half-filled as the highest occupied MOs, then a triplet structure would arise. The geometry of this triplet structure would be expected to be the same as a singlet structure with two more skeletal electrons (Figure 13). Thus the triplet C_{5v} capped pentagonal antiprism structure **24–3T** for Ge_{11}^{2-} with 24 skeletal electrons is essentially the same as the singlet C_{5v} structure **26–2** for Ge_{11}^{4-} with 26 skeletal electrons.

5. Summary

The 11-vertex Ge_{11}^z systems studied in this work are considerably more complicated than the systems discussed in previous papers having a smaller number of vertices.^{1–4} Nevertheless, all of the experimentally known 11-vertex cluster structures having vertices isolobal with germanium vertices have been found in this work as optimized structures without significant imaginary frequencies. Such structures include the C_{2v} edge-coalesced icosahedron found in $\text{B}_{11}\text{H}_{11}^{2-}$ and related 11-vertex carboranes,¹⁸ the C_{5v} 5-capped pentagonal prism of the “dicarbollide” ion $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ found as a ligand in transition metal chemistry,^{6,7} and the unusual 11-vertex D_{3h} polyhedra found in electron-poor intermetallics containing the ions E_{11}^{7-} ($\text{E} = \text{Ga}, \text{In},^8 \text{Ti}^9$) and $\text{Tl}_9\text{Au}_2^{9-}$

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(ref 10) as well as the related metal carbonyl cluster $\text{Rh}_5\text{Ni}_6(\text{CO})_{21}^{3-}$ (ref 23). The success of this DFT computational approach in generating known 11-vertex structures suggests that some of the currently unknown structures found in this DFT study will be realized experimentally in the future. Particularly interesting targets suggested by this work are centered pentagonal prismatic structures related to the computed structure **20–4** for Ge_{11}^{2+} .

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Supporting Information Available: Figure S1 (initial Ge_{11} geometries used for the optimizations), Table S1 (energies of the optimized Ge_{11}^z structures ($z = 0, \pm 2, \pm 4, \pm 6$)), and Table S2 (details of the optimized Ge_{11}^z structures ($z = 0, \pm 2, \pm 4, \pm 6$), structures including all interatomic distances (Å)). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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