Antiaromaticity in Bare Deltahedral Silicon Clusters Satisfying Wade's and Hirsch's Rules: An Apparent Correlation of Antiaromaticity with High Symmetry

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Abstract

Entirely unlike the aromatic closo B[n]H[n][2-] borane dianions, isoelectronic Si[6][2-] and Si[12][2-] are antiaromatic. Their O[h] and I[h] symmetries are responsible, as the other deltahedral silicon dianion clusters do not exhibit this behavior. These high symmetries prevent mixing among the degenerate lone pair and skeletal orbitals, leading to paratropic behavior.

Reference


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Antiaromaticity in Bare Deltahedral Silicon Clusters Satisfying Wade’s and Hirsch’s Rules: An Apparent Correlation of Antiaromaticity with High Symmetry

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In the last quarter century, the concept of aromaticity1,2 has been expanded from its origins in benzene and two-dimensional arenes to three-dimensional clusters, exemplified by the closo B$_6$H$_6$~2~ borane dianions.$^3$,$^4$ The large, diatropic (negative, shielded) nucleus-independent chemical shifts in their cage centers, NICS(0),$^5$ along with other criteria, establish all members of the deltahedral B$_n$H$_n$~2~ series ($5 \leq n \leq 12$) to be strongly aromatic. Consequently, the aromatic stabilization of deltahedral boranes, which follow Wade’s 2n + 2 skeletal electron rule,$^6$,$^7$ may be likened to that of planar molecules obeying the well-known Hückel 4N + 2 π electron rule. Hirsch’s (2N + 1)$^2$ spherical aromaticity rule is a recent refinement.$^8$

It applies to the highest symmetry and most aromatic clusters, like octahedral B$_6$H$_6$~2~ and icosahedral Si$_6$H$_6$~2~, with total electron counts of 26 (18 first shell + 8 second shell) and 50, respectively.

We are now extending our NICS aromaticity studies of the boron cages$^9$ to the isoelectronic E$_6$~2~ (E = Si, Ge, Sn, Pb) bare main group element clusters (e.g., “Zintl ions”)$^9$ systematically.$^{10}$ Some of the most startling results are described here.

With minor variations, members of the corresponding Si$_n$~2~ series have similar diatropic NICS(0) values (Table 1), except for two completely unexpected exceptions. Remarkably and completely different from their closo borane counterparts (Figure 1), the most symmetrical octahedral Si$_6$~2~ and icosahedral Si$_6$H$_6$~2~, with total electron counts of 26 (18 first shell + 8 second shell) and 50, respectively, have large diatropic NICS(0) values, whereas those of n = 7, 8, and 11 are small. The Si$_6$~2~ and especially Si$_6$H$_6$~2~ are exceptional in having appreciably positive NICS(0)s (Figure 1). Table 1 also documents

<table>
<thead>
<tr>
<th>Table 1. Data for Si$_n$<del>2</del> and B$_n$H$_n$<del>2</del> * Species: NICS(0), Averaged $^\sigma$ B, $^\delta$ Bl, $^\Delta$ HOMO–LUMO Gaps at B3LYP/6-31+G**, in kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>n, point group</td>
</tr>
<tr>
<td>5, D$_{3h}$</td>
</tr>
<tr>
<td>6, O$_h$</td>
</tr>
<tr>
<td>7, D$_{5h}$</td>
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<tr>
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<tr>
<td>10, D$_{5d}$</td>
</tr>
<tr>
<td>11, C$_{2v}$</td>
</tr>
<tr>
<td>12, I$_h$</td>
</tr>
</tbody>
</table>

$^\sigma$ NMR data (in ppm) at the GIAO-PW91/IGLOIII level with additional s and p diffuse functions for silicon. The B$_n$H$_n$~2~ NICS values differ minimally from those in ref 4. $^\delta$ Data from ref 4.

Figure 1. NICS points (red = diatropic; green = paratropic) for the isoelectronic cluster pairs B$_n$H$_n$~2~/Si$_n$~2~ and B$_n$H$_n$~2~/Si$_n$~2~. Magnitudes are given by the sizes of the dots.

While all of the B$_n$H$_n$~2~ (n = 5–12) NICS(0)s are diatropic (Table 1), the Si$_n$~2~ NICS(0) behavior is more variable: n = 5, 9, and 10 have large diatropic values, whereas those of n = 7, 8, and 11 are small. The Si$_6$~2~ and especially Si$_6$H$_6$~2~ are exceptional in having appreciably positive NICS(0)s (Figure 1). Table 1 also documents

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their unusually deshielded average δ²⁹Si values. The HOMO–LUMO gap of Si₆⁻ is much lower than that of B₆H₆⁻. We relate the antiaromaticity of Si₆⁻ and Si₁₂²⁻ to their high octahedral and icosahedral symmetry. The resulting highly degenerate MOs preclude mixing of the external Si lone pair MOs with the tangential surface skeletal orbitals on the vertex atoms.¹²

The remarkable antiaromaticity of Si₁₂²⁻ revealed by the NICS method and by its relatively low Coulomb repulsion-corrected per vertex energy (see Supporting Information) may be related to the failure to find empty icosahedral E₁₂²⁻ (E = Ge, Sn, Pb) Zintl clusters among the alkali metal reduction products of group 14 elements.⁹ This contrasts with the prevalence of icosahedral B₁₂ units, not only in the highly stable B₁₂R₁₂⁻ (R = H, Cl, CH₃, etc.), CB₁₁R₁₂, and C₂B₁₀R₁₂ (R = H, Cl, CH₃, etc) single molecules, but also as building blocks in highly refractory solid-state materials including boron carbide, [B₄C], and elemental boron. In contrast, the nine-vertex D₃h dodecahedra, single tricapped trigonal prisms (E = Ge, Sn), are prevalent in Zintl ion chemistry.⁹

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Supporting Information Available: Gaussian archive entries of Siₙ⁻ minima at B3LYP/6-311+G*, MO-NICS analysis, and Figures 2–5 at a larger scale (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References