In the last quarter century, the concept of aromaticity\textsuperscript{1,2} has been expanded from its origins in benzene and two-dimensional arenes to three-dimensional clusters, exemplified by the \textit{closo} $B_nH_{2n}^2$ borane dianions.\textsuperscript{3,4} The large, diatropic (negative, shielded) nucleus-independent chemical shifts in their cage centers, NICS(0),\textsuperscript{5} along with other criteria, establish all members of the deltahedral $B_nH_{2n}^2$ 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,\textsuperscript{6,7} may be likened to that of planar molecules obeying the well-known Hückel $4N + 2$ electron rule. Hirsch’s $2(N + 1)^2$ spherical aromaticity rule is a recent refinement.\textsuperscript{8} It applies to the highest symmetry and most aromatic clusters, like octahedral $B_6H_{12}^2$ and icosahedral $B_{12}H_{22}^2$, 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 cag\textsuperscript{e} to the isoelectronic $E_n^2$ (E = Si, Ge, Sn, Pb) bare main group element clusters (e.g., “Zintl ions”)\textsuperscript{9} systematically.\textsuperscript{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 differences. Remarkably and completely different from their \textit{closo} borane counterparts (Figure 1), the most symmetrical octahedral $Si_6^2$- and icosahedral $Si_{12}^2$- clusters have paratropic NICS(0) values characteristic of antiaromaticity. This behavior can be explained by analyzing the dissected NICS(0) contributions to the total NICS(0) values from the individual bonding molecular orbitals (MOs).\textsuperscript{11}

Figures 2 and 3 show that most of the individual MO-NICS(0) contributions of the bonding MOs of $B_nH_{2n}^2$ and $Si_n^2$- are diatropic (the core orbital contributions are minor). However, the effect of the very paratropic 3-fold degenerate $t_{1u}$ orbitals offsets the diatropicity, partially in $B_6H_{12}^2$, but more than completely in $Si_6^2$. The mixing of the external hydrogen orbitals with the symmetry adapted skeletal MOs of $B_6H_{12}^2$ lowers their energies relative to the corresponding lone pair-dominated $Si_6^2$ MOs. This affects the magnitude of the $t_{1u}$ orbital contributions sufficiently to change the sign of total NICS(0) from negative (diatropic) in $B_6H_{12}^2$ to positive (paratropic) in $Si_6^2$.

The contrast between isoelectronic $B_{12}H_{22}^2$ and $Si_{12}^2$- is even more pronounced: the antiaromaticity of $Si_{12}^2$- also is much greater than that of $Si_6^2$ (Figure 1). The highly paratropic 5-fold degenerate $h_g$ MO set of $Si_{12}^2$- has a larger effect on the total NICS(0) than the 3-fold degenerate $t_{1u}$ orbitals in $Si_6^2$, as well as the $h_g$ MO set of $B_{12}H_{22}^2$ (Figures 4 and 5).

<table>
<thead>
<tr>
<th>n, point group</th>
<th>$B_6H_{12}^2$</th>
<th>$Si_6^2$-</th>
<th>NICS(0)</th>
<th>NICS(0)</th>
<th>$\Delta B_6H_{12}^2$</th>
<th>$\Delta Si_6^2$</th>
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<tr>
<td>5, $D_{3h}$</td>
<td>-25.9</td>
<td>-38.5</td>
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<td>41.6</td>
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<td>6, $O_h$</td>
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<td>+17.7</td>
<td>118.7</td>
<td>+685.9</td>
<td>63.1</td>
<td>70.0</td>
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<tr>
<td>7, $D_{3d}$</td>
<td>-21.7</td>
<td>+2.9</td>
<td>107.4</td>
<td>+159.9</td>
<td>70.0</td>
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<tr>
<td>8, $D_{5d}$</td>
<td>-17.7</td>
<td>+4.8</td>
<td>104.8</td>
<td>+290.8</td>
<td>53.8</td>
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<td>$D_2$</td>
<td>+3.9</td>
<td>+5.2</td>
<td>109.0</td>
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<td>48.4</td>
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<td>+54.6</td>
<td>112.7</td>
<td>-992.2</td>
<td>117.4</td>
<td>62.4</td>
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</table>

* NMR data (in ppm) at the GIAO-PW91/IGLOIII level with additional s and p diffuse functions for silicon. The $B_nH_{2n}^2$- NICS values differ minimally from those in ref 4. \textsuperscript{6} Data from ref 4.

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\textsuperscript{1} University of Georgia.
\textsuperscript{2} Technische Universität Dresden.
\textsuperscript{3} University of Geneva.
their unusually deshielded average $^{29}$Si values. The HOMO–LUMO gap of $\text{Si}_3^{2-}$ is much lower than that of $\text{B}_3\text{H}_5^{2-}$. We relate the antiaromaticity of $\text{Si}_3^{2-}$ and $\text{Si}_5^{2-}$ 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 $\text{Si}_{12}^{2-}$ 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 $\text{E}_{12}^{2-}$ ($\text{E} = \text{Ge, Sn, Pb}$) Zintl clusters among the alkali metal reduction products of group 14 elements.9 This contrasts with the prevalence of icosahedral $\text{B}_{12}^{2-}$ units, not only in the highly stable $\text{B}_{12}\text{R}_{12}^{2-}$ ($\text{R} = \text{H, Cl, CH}_3$, etc.), $\text{CB}_{11}\text{R}_{12}$, and $\text{C}_2\text{B}_{10}\text{R}_{12}$ ($\text{R} = \text{H, Cl, CH}_3$, etc) single molecules, but also as building blocks in highly refractory solid-state materials including boron carbide, [B$_4$C], and elemental boron. In contrast, the nine-vertex $\text{D}_{3d}^{12}$ dodecahedra, single tricapped $\text{E}_{9}^{2-}$ trigonal prisms ($\text{E} = \text{Ge, Sn}$), are prevalent in Zintl ion chemistry.9

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Supporting Information Available: Gaussian archive entries of $\text{Si}_n^{2-}$ 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


(10) Related neutral tetrahedra and nine vertex species with different charges were studied in ref 8.
