

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 aromaticity^{1,2} has been expanded from its origins in benzene and two-dimensional arenes to three-dimensional clusters, exemplified by the *closo* $B_nH_n^{2-}$ 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 $B_nH_n^{2-}$ 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 $4N + 2 \pi$ electron rule. Hirsch's $2(N + 1)^2$ spherical aromaticity rule is a recent refinement.⁸ It applies to the highest symmetry and most aromatic clusters, like octahedral $B_6H_6^{2-}$ and icosahedral $B_{12}H_{12}^{2-}$, 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 cages⁴ to the isoelectronic E_n^{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_{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).¹¹

Figures 2 and 3 show that most of the individual MO-NICS(0) contributions of the bonding MOs of $B_6H_6^{2-}$ and Si_6^{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 $B_6H_6^{2-}$, but more than completely in Si_6^{2-} . The mixing of the external hydrogen orbitals with the symmetry adapted skeletal MOs of $B_6H_6^{2-}$ 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 $B_6H_6^{2-}$ to positive (paratropic) in Si_6^{2-} .

The contrast between icosahedral $B_{12}H_{12}^{2-}$ 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 $B_{12}H_{12}^{2-}$ (Figures 4 and 5).

Table 1. Data for Si_n^{2-} and $B_nH_n^{2-}$ Species: NICS(0), Averaged $\sigma^{11}B$, $\delta^{29}Si$, Δ HOMO–LUMO Gaps at B3LYP/6-311+G**, in kcal/mol

n , point group	$B_nH_n^{2-}$ NICS(0)	Si_n^{2-} NICS(0)	$\langle\sigma\rangle^{11}B$	$\langle\delta\rangle^{29}Si$	$\Delta^b B_nH_n^{2-}$	ΔSi_n^{2-}
5, D_{3h}	-25.9	-38.5	122.2	-87.7	41.6	65.7
6, O_h	-27.5	+17.7	118.7	+695.9	63.1	70.0
7, D_{5h}	-21.7	+7.9	107.4	+159.8	70.0	55.0
8, D_{2d}	-17.7	+4.8	104.8	+290.8	53.8	49.8
D_2		+3.9		+163.0		48.4
9, D_{3h}	-22.7	-40.8	115.5	-263.9	64.7	51.3
10, D_{4d}	-27.0	-61.9	123.9	+39.3	83.7	68.9
11, C_{2v}	-25.6	+2.2	115.6	+300.3	76.1	51.1
12, I_h	-27.3	+56.4	112.7	+982.2	117.4	62.4

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

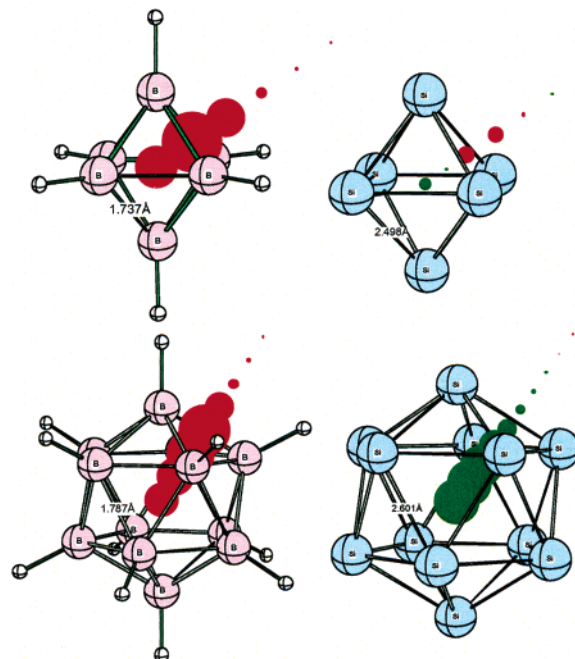


Figure 1. NICS points (red = diatropic; green = paratropic) for the isoelectronic cluster pairs $B_6H_6^{2-}/Si_6^{2-}$ and $B_{12}H_{12}^{2-}/Si_{12}^{2-}$. Magnitudes are given by the sizes of the dots.

While all of the $B_nH_n^{2-}$ ($n = 5-12$) NICS(0) are diatropic (Table 1),⁴ 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. Si_6^{2-} and especially Si_{12}^{2-} are exceptional in having appreciably positive NICS(0)s (Figure 1). Table 1 also documents

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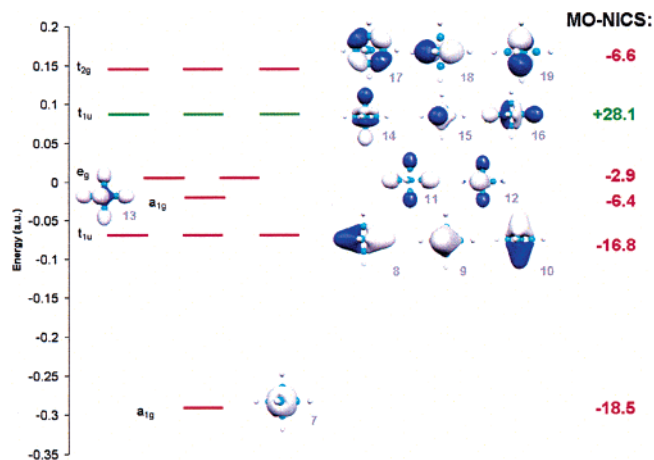


Figure 2. MO-NICS for $B_6H_6^{2-}$ at the GIAO PW91/IGLOIII level (in ppm). Molecular orbital energies are given in hartree.

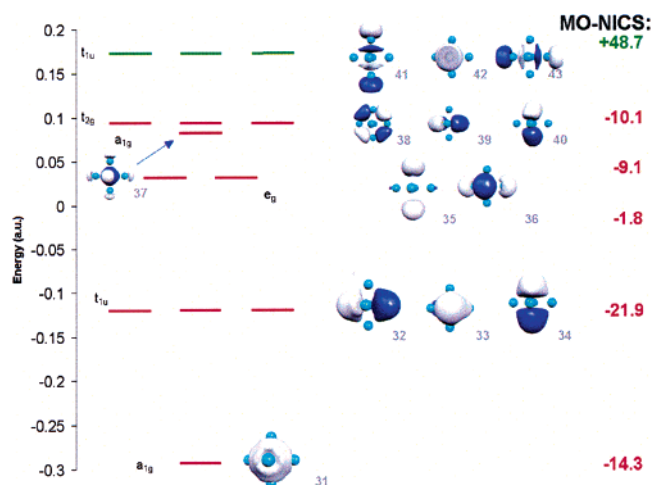


Figure 3. MO-NICS for Si_6^{2-} . Details are as in Figure 2 with additional s and p diffuse functions.

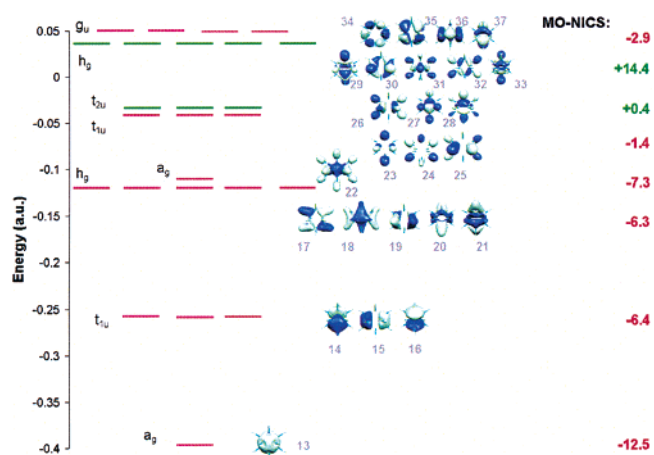


Figure 4. MO-NICS for $B_{12}H_{12}^{2-}$. Details are as in Figure 2.

their unusually deshielded average $\delta^{29}Si$ values. The HOMO–LUMO gap of Si_{12}^{2-} is much lower than that of $B_{12}H_{12}^{2-}$. We relate the antiaromaticity of Si_6^{2-} and Si_{12}^{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

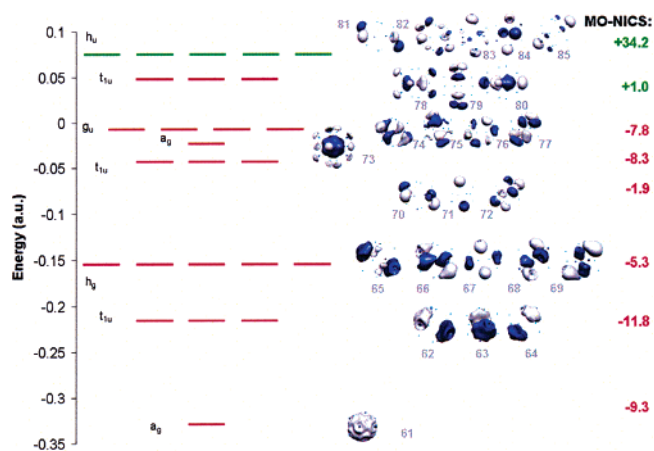


Figure 5. MO-NICS for Si_{12}^{2-} . Details are as in Figure 3.

The remarkable antiaromaticity of 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 E_{12}^{2-} ($E = Si, Ge, Sn, Pb$) Zintl clusters among the alkali metal reduction products of group 14 elements.⁹ This contrasts with the prevalence of icosahedral B_{12} units, not only in the highly stable $B_{12}R_{12}^{2-}$ ($R = H, Cl, CH_3, \text{etc.}$), $CB_{11}R_{12}^-$, and $C_2B_{10}R_{12}$ ($R = H, Cl, CH_3, \text{etc.}$) single molecules, but also as building blocks in highly refractory solid-state materials including boron carbide, $[B_4C]$, and elemental boron. In contrast, the nine-vertex D_{3h} dodecahedra, single tricapped E_9^{2-} trigonal prisms ($E = Ge, Sn$), are prevalent in Zintl ion chemistry.⁹

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Supporting Information Available: Gaussian archive entries of 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>.

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