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- [10] TGA data were obtained on a TGA 2050 thermogravimetric analyser thermobalance using a sample synthesized by using 1,3-diaminopropane.
- [11] BET analysis was performed by using a Micromeritics ASAP2400 porosimeter on a sample activated at 350°C for four days.
- [12] The X-ray powder diffraction data for VSB-5 were collected on a Siemens D5000 diffractometer by using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). To avoid preferred orientation effects, the synthesis was carried out under stirring conditions, keeping the same experimental conditions with the same molar ratio and filling rate. The resulting powder was then loaded in the sample holder. The powder diffraction pattern was scanned over an angular range of 4 – 120° (2θ). The counting times were 27 s per step to 59.98° (2θ) and 54 s per step from 60.00° (2θ) to the end of the scan (to improve the counting statistics of the high-angle region). The full pattern was then scaled to the lower counting time. An accurate determination of the peak positions and relative intensities was carried out by using the software package DIFFRACT-AT.
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- [18] Magnetization measurements were performed in the temperature range 4 – 295 K at 5 kG and 100 G on a Quantum Design Squid magnetometer (MPMS-5).
- [19] The selective hydrogenation of 1,3-butadiene to butenes was carried out in a continuous fixed-bed reactor made of quartz at atmospheric pressure. Before catalytic measurement, the catalyst was reduced with 5% hydrogen in helium at 350°C for 4 – 24 h . The reaction was carried out while introducing mixture of 1,3-butadiene (99.0%) and pure hydrogen under helium. The effluent stream from the reactor was analyzed by an on-line gas chromatograph (HP 5890 Series II) fitted with a capillary column (J&W Alumina) and a flame-ionization detector.
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Spherical Aromaticity of Inorganic Cage Molecules**

Andreas Hirsch,* Zhongfang Chen, and Haijun Jiao

We have shown recently that the icosahedral fullerenes C_{20} , C_{60} , and C_{80} reach maximum spherical aromaticity if their π shells are completely filled.^[1] This is nicely demonstrated, for example, by the very pronounced diatropic character of the $2(N+1)^2$ π systems of the C_{20}^{2+} ($N=2$), C_{60}^{10+} ($N=4$), and C_{80}^{8+} ($N=5$) ions with perfect I_h symmetry. Here we extend this treatment of spherical aromaticity to a set of well-known inorganic cage compounds and demonstrate that they are highly aromatic because of the closed-shell nature of both their σ and π systems.

Tetrahedral clusters P_4 and As_4 form metastable solid allotropes, whereas Sb_4 and Bi_4 are high-temperature modifications existing only in liquid or in the gas phase. Tetrahedral N_4 (T_d), being the most stable singlet N_4 isomer,^[2] was recently generated in a plasma as the first neutral polynitrogen species.^[3] The calculated nucleus-independent chemical shifts (NICS)^[4,5] at the cage centers of these T_d -symmetrical clusters with optimized bond lengths (Figure 1)

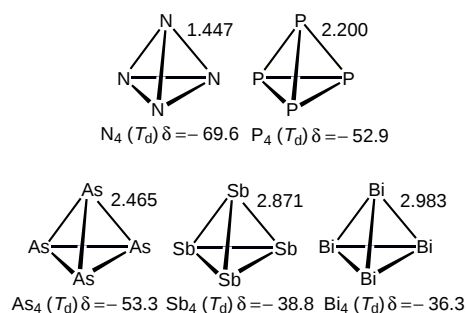


Figure 1. Optimized bond lengths [$\text{\AA}$] and NICS values [δ] for $E_4 (T_d)$ clusters ($E = \text{N, P, As, Sb, Bi}$).

are given in Table 1. The highly negative NICS values of all clusters are a result of pronounced diamagnetic ring currents. The pronounced diatropic character of these clusters is not a result of the addition of four individual increments consisting of three-membered rings, but a new quality of the entire cages. This is clearly reflected by the fact that: 1) the NICS and the NICS per valence electron (NICS/e) values in the center of the cages are considerably more negative than those in the

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Table 1. Calculated NICS values [δ] for E_4 (T_d), E_3H_3 (C_{3v}), and HE_4^+ (C_{3v}).

Type	NICS	Compound				
$E_4^{[a]}$		N_4	P_4	As_4	Sb_4	Bi_4
	NICS ^[b]	−69.6	−52.9	−53.3	−38.8	−36.3
	NICS/e ^[c]	−3.5	−2.6	−2.7	−1.9	−1.8
	NICS ^[d]	−69.4	−52.3	−52.4	−38.7	−36.2
$E_3H_3^{[a]}$		N_3H_3	P_3H_3	As_3H_3	Sb_3H_3	Bi_3H_3
	NICS ^[d]	−51.5	−33.5	−33.8	−26.6	−25.0
	NICS/e ^[c,d]	−2.9	−1.9	−1.9	−1.5	−1.4
$HE_4^{+[a]}$		HN_4^+	HP_4^+	HAs_4^+	HSb_4^+	HBi_4^+
	NICS ^[b]	−64.0	−40.4	−35.8	−22.1	−10.0

[a] All are energy minima. [b] At the cage center. [c] NICS per valence electron (NICS/e). [d] At the center (E_3) of the trigons.

center of the three-membered E_3H_3 -rings (C_{3v}) (Table 1); 2) the NICS values in the center of the three-membered E_3H_3 -rings (C_{3v}) are less negative than those in the center of the trigonal faces of E_4 (Table 1), and 3) the NICS/e values of four E_3H_3 increments at a location corresponding to the cage center of E_4 are considerably lower than those of the E_4 cage centers. For example the sum of the NICS/e values of four P_3H_3 units 0.45 Å away from the center of each plane which corresponds to the middle of the P_4 cage is $\delta = -1.3$ whereas that of P_4 itself is $\delta = -2.6$.

The calculated MO schemes of E_4 are in line with earlier calculations^[6] and clearly reflect the closed-shell nature of both the σ and π subsystems (Figure 2). The σ system contains

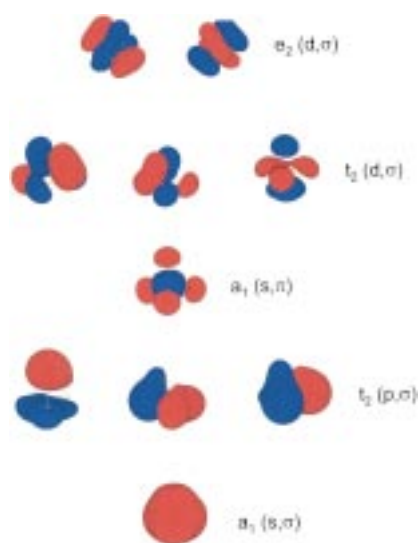


Figure 2. Representation of the MOs of P_4 (HyperChem 5.1). The a_1 (s, π) orbital is a cluster π orbital.^[1, 7] As a result of the pyramidalization of the cluster atoms the endohedral overlap of atomic p orbitals is much more pronounced than the exohedral overlap.

$2(N_\sigma + 1)^2$ σ electrons ($N_\sigma = 2$) and consists of a cluster s orbital, three degenerate cluster p orbitals, and two sets of cluster d orbitals (e and t_2), while the π system contains $2(N_\pi + 1)^2$ π electrons ($N_\pi = 0$).^[7] With respect to the model of the spherical electron gas,^[1, 8] the splitting of the cluster d orbitals of σ systems is a consequence of symmetry lowering from K_h to T_d . With the complete filling of all σ and π shells the angular momenta are symmetrically distributed^[1, 8] and

the clusters are double spherically aromatic.^[9] The HOMOs are the e (d, σ) orbitals (Figure 2). Electrons within the frontier region are the most mobile and contribute predominantly to the ring-current effect. Therefore, the diatropic character of these clusters is mainly determined by the σ electrons. Incomplete filling of the shells, accompanied by asymmetrical distribution of the angular momenta, causes reduction of aromatic character or even establishment of anti-aromaticity. This is shown, for example, with the system P_4^{2-} where one of the three originally degenerate LUMOs of P_4 is occupied causing a symmetry lowering to C_{2v} ($P-P = 2.159$, 2.280, and 3.222 Å) and a NICS value of only $\delta = -23.0$; while the system P_4^{2+} has also lower symmetry (D_2 , $P-P = 2.168$ and 2.670 Å) and a NICS value of $\delta = -15.6$.

The cluster ions Si_4^{4-} , Ge_4^{4-} , Sn_4^{4-} , and Pb_4^{4-} ^[10, 11] are isoelectronic with P_4 , As_4 , Sb_4 , and Bi_4 , have the same MO structure, and exhibit a comparable pronounced diatropic character and double spherical $2(N+1)^2$ aromaticity (Figure 3).

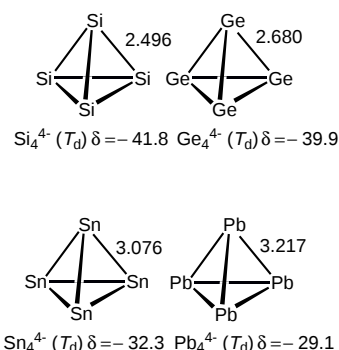


Figure 3. Optimized bond lengths [Å] and NICS values [δ] for E_4^{4-} (T_d) clusters ($E = Si, Ge, Sn, Pb$).

A set of less symmetrical clusters containing nine atoms is represented by the Zintl^[12] ions shown in Figures 4–6 and Table 2. The D_{3h} symmetrical *closo*-cages E_9^{4-} ($E = Si$,^[13] Ge ,^[14] Sn ,^[14c, 15] Pb ^[15e, 16]) and Bi_9^{5+} ^[17] (Figure 4) represent energy minima and do not obey the Wade rules.^[18] A reason for their stability could be the double spherically $2(N+1)^2$ aromatic configuration of their valence-electron system containing 32 σ ($N_\sigma = 3$) and 8 π electrons ($N_\pi = 1$). In contrast to the T_d clusters (Figure 1 and 3) their MO schemes are characterized by a variety of crossovers between the subshells and a considerable decrease in orbital degeneracy of the completely filled σ (s, p, d, f) and π (s, p) levels. However, they still exhibit very high NICS values approaching those of some highly aromatic fullerenes with closed π shells.^[1] The HOMO of these clusters is the $a_2''(f, \sigma)$ orbital which corroborates earlier calculations.^[19]

The corresponding *nido* structures with C_{4v} symmetry are slightly less stable (Figure 5, Table 2).^[19] They are also double spherically $2(N+1)^2$ aromatic. Their HOMOs (f, σ), however, are two-fold degenerate.^[19] E_9^{4-} clusters are known to be fluxional on the NMR time scale.^[20] The D_{3h} cages can smoothly rearrange into the corresponding C_{4v} cages. Most of the corresponding Wade rule obeying *closo* cages E_9^{2-} ($E = Sn, Pb$)^[21] and Bi_9^{7+} are unknown (Figure 6, Table 2), while

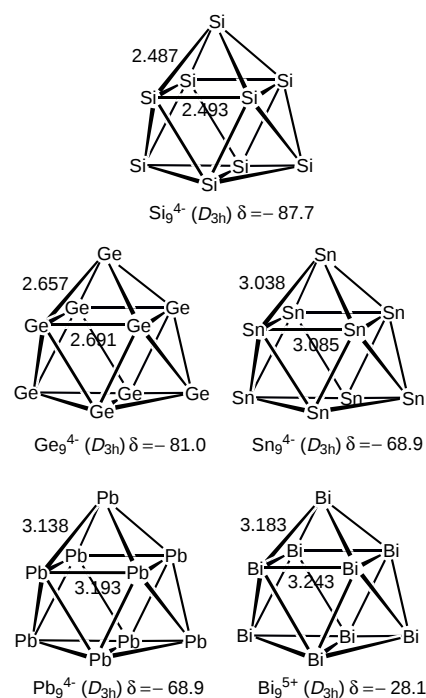


Figure 4. Optimized bond lengths [Å] and NICS values [δ] for E_9^{4-} (D_{3h}) clusters (E = Si, Ge, Sn, Pb) and Bi_9^{5+} (D_{3h}).

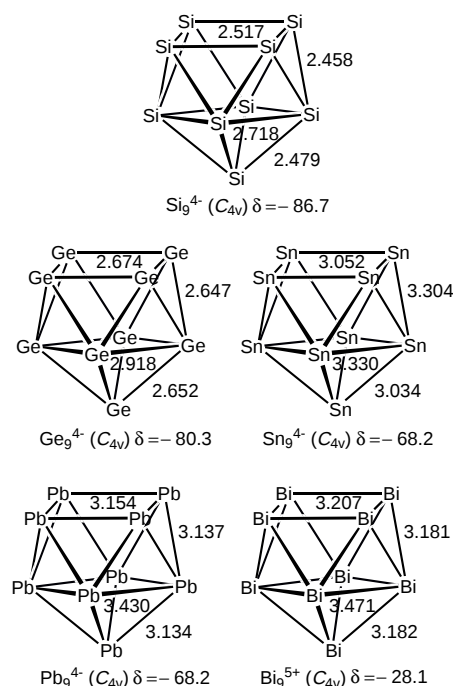


Figure 5. Optimized bond lengths [Å] and NICS values [δ] for E_9^{4-} (C_{4v}) clusters (E = Si, Ge, Sn, Pb) and Bi_9^{5+} (C_{4v}).

Ge_9^{2-} was reported.^[14b] Noteworthy is that their σ shells are not completely filled, since the $a_2''(f, \sigma)$ orbital is now empty leaving the $a_2'(f, \sigma)$ as the HOMO.^[19] As a consequence, the NICS values are considerably lower than those of the corresponding double $2(N+1)^2$ aromatic systems (Figure 4, Table 2). In all cases the HOMOs are σ orbitals and the π levels are inner-shell states.^[19]

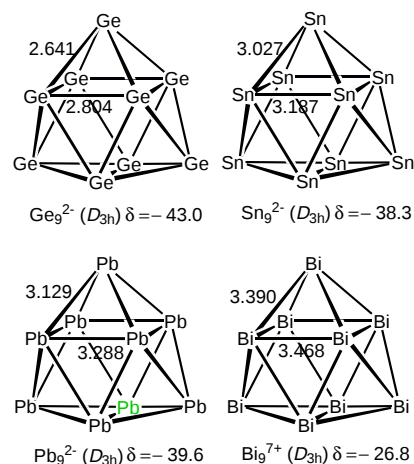


Figure 6. Optimized bond lengths [Å] and NICS values [δ] for E_9^{2-} clusters (D_{3h}) (E = Ge, Sn, Pb) and Bi_9^{7+} (D_{3h}).

Table 2. Calculated NICS values [δ] and relative energies E_{rel} [kcal mol⁻¹] for E_9^{4-} , E_9^{2-} , Bi_9^{5+} , and Bi_9^{7+} .

Species	symmetry	NICS	E_{rel}	Reference
Si_9^{4-}	<i>closo</i> (D_{3h})	-87.7	0.0	[13]
	<i>nido</i> (C_{4v})	-86.7	1.1	[13]
Ge_9^{4-}	<i>closo</i> (D_{3h})	-81.0	0.0	[a]
	<i>nido</i> (C_{4v})	-80.3	0.8	[14]
Sn_9^{4-}	<i>closo</i> (D_{3h})	-68.9	0.0	[a]
	<i>nido</i> (C_{4v})	-68.2	0.8	[14c, 15]
Pb_9^{4-}	<i>closo</i> (D_{3h})	-68.9	0.0	[16]
	<i>nido</i> (C_{4v})	-68.3	1.0	[15e, 16]
Bi_9^{5+}	<i>closo</i> (D_{3h})	-28.1	0.0	[17]
	<i>nido</i> (C_{4v})	-28.1	0.4	[a]
Ge_9^{2-}	<i>closo</i> (D_{3h})	-43.0	—	[14b]
Sn_9^{2-}	<i>closo</i> (D_{3h})	-38.3	—	[a]
Pb_9^{2-}	<i>closo</i> (D_{3h})	-39.6	—	[a]
Bi_9^{7+}	<i>closo</i> (D_{3h})	-26.8	—	[a]

[a] Unknown experimentally.

Protonation of E_4 (E = N, P, As, Sb, Bi) leading to the isoelectronic C_{3v} -symmetrical cages HE_4^+ causes a reduction of the NICS values (i.e. becomes less negative) because of a reduction of electron mobility (Table 1). However, especially the clusters HE_4^+ (E = N, P, As) are still highly aromatic. The corresponding cluster σ and π orbitals^[7] are closely related to those of the parent E_4 cages. The only difference is the presence of the exohedral protons, making the H–E fragments *pseudo* cluster atoms.^[7] The complete protonation of all cluster atoms is realized in the *closo*-boranes $B_nH_n^{2-}$ ($n = 5–12$). As reported by Schleyer and Najafian,^[22] the *closo*-boranes $B_nH_n^{2-}$ are highly diatropic with NICS values of the cluster centers ranging from $\delta = -24.5$ to -34.4 . The closed-shell nature of $O_h B_6H_6^{2-}$, for example, is realized with $2(N_\pi + 1)^2$ π electrons ($N_\pi = 1$) and $2(N_\sigma + 1)^2$ σ electrons ($N_\sigma = 2$; Figure 7). The I_h -symmetrical $B_{12}H_{12}^{2-}$ ion contains $(N_\pi + 1)^2$ π electrons ($N_\pi = 2$) and $2(N_\sigma + 1)^2$ σ electrons ($N_\sigma = 3$). Note that these two highly symmetrical systems are double spherical aromatic and exhibit the highest NICS values in this series.^[22]

In contrast to the carbon-based fullerene clusters the HOMOs within the highly symmetrical inorganic cage com-

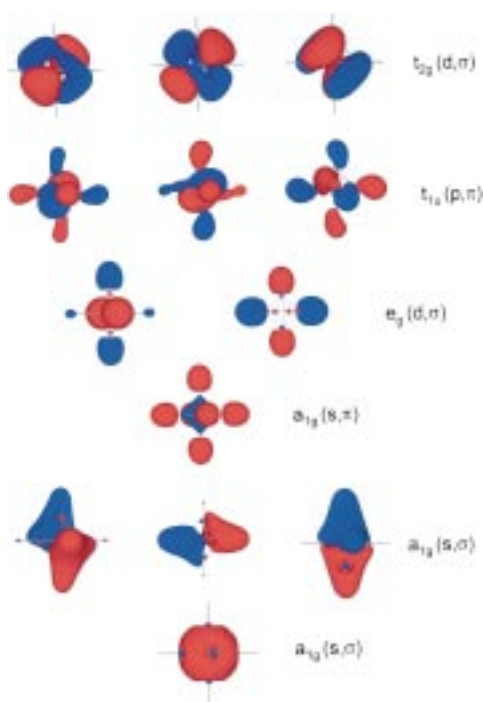


Figure 7. Representation of the MOs of $B_6H_6^{2-}$ (HyperChem 5.1).

pounds investigated here are σ orbitals. Like the spherical $2(N_\pi + 1)^2$ aromaticity of the fullerenes the double spherical aromaticity of inorganic cage compounds involving both the whole π and σ system is a consequence of complete filling of the corresponding shells that can be deduced with group theory from molecular s, p, d, ... shells of a spherical electron gas by reduction of the K_h symmetry to the cluster symmetry under consideration. As we will show in an forthcoming publication small and less symmetrical clusters such as Bi_5^{3+} do not obey the $2(N + 1)^2$ rule and their aromaticity is reduced compared to systems with completely filled shells. However, we will also demonstrate that the spherical electron gas model^[1, 8] that we used to deduce the $2(N + 1)^2$ count rule forms the basis to treat any cluster type with a closed-cage structure. It can even be used by symmetry lowering to deduce the Hückel count rule for the cyclic annulenes. This leads to a unified picture of aromaticity and understanding of the special stability and reactivity of nonorganic molecules.^[23]

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