Novel Examples of Three-Dimensional Aromaticity: 1,3-Dehydro-silaadamantane Dications. A Theoretical (DFT, GIAO NMR, NICS) Study[†]

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A DFT study of the hitherto elusive 1,3-dehydro-silaadamantane dications $\mathbf{2}^{2+}$−$\mathbf{5}^{2+}$ has been carried out. Computed nucleus independent chemical shift (NICS) values are strongly indicative of three-dimensional heteroaromaticity in the resulting caged dications (via 2-electron, 4-center homoconjugation). In the optimized structures, silicon is pyramidalized. Although charge calculations (NPA and MKS) indicate significant positive charge build-up at silicon(s), the ^{29}Si GIAO NMR chemical shifts are unusually shielded. The latter finding agrees with the recent DFT calculations on 7-silanobornadien-7-ylium monocation $\mathbf{10}^{+}$, suggesting that silicon shielding is a consequence of unusual bonding and homoconjugation in the dications. Both NICS values and silicon shielding decrease in going from $\mathbf{2}^{2+}$ to $\mathbf{5}^{2+}$. Natural bond orbital (NBO) analysis was utilized to shed light on the origin of the three-dimensional heteroaromaticity in these dications.

Introduction

Schleyer's 1,3-dehydro-5,7-adamantanediyl dication $\mathbf{1}^{2+}$ represents a landmark example of three-dimensional aromaticity in a cage structure (see Figure 1).[1] Characteristic of hypercoordinate carbocations, it exhibits shielded bridgehead carbons at δ 6.6 with methylene carbon resonances appearing at δ 35.6. These are in close agreement with the computed chemical shifts (IGLO method).[1] The computed NICS value for dication $\mathbf{1}^{2+}$ is −50.1 at the HF/6-31+G(d)//B3LYP/6-31G(d) level and represents the most aromatic system hitherto reported.[2] The three-dimensional electron delocalization in $\mathbf{1}^{2+}$ was later confirmed by Chan and Arnold employing gradient-corrected correlation (B3PW91) and MP2. They also calculated the radical cation, radical anion, and dianion of **1**.[3] Figure 1 sketches the reported[1,2] experimental and computed NMR chemical shifts, the optimized structure, and NICS for this remarkable dication.

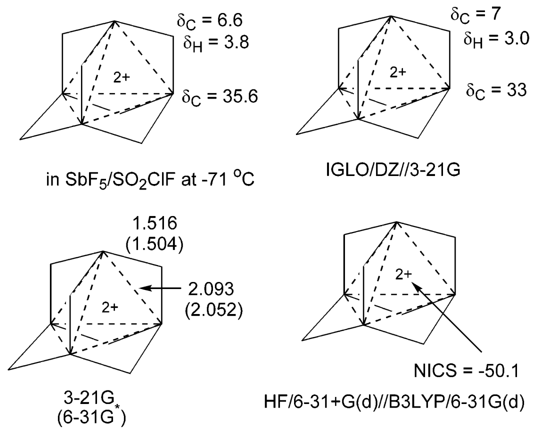
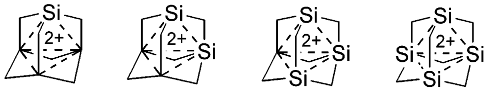


FIGURE 1. Optimized structure, experimental and theoretical NMR chemical shifts, and NICS for $\mathbf{1}^{2+}$.

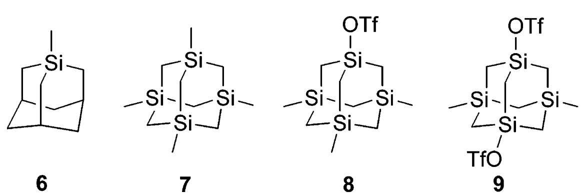
The silicon analogues of dication $\mathbf{1}^{2+}$, namely, dications $\mathbf{2}^{2+}$−$\mathbf{5}^{2+}$ (Figure 2), are hitherto unknown. Their structure, relative aromaticity, and NMR chemical shifts in comparison with $\mathbf{1}^{2+}$ are of substantial structural and mechanistic interest.



$\mathbf{2}^{2+}$ $\mathbf{3}^{2+}$ $\mathbf{4}^{2+}$ $\mathbf{5}^{2+}$

FIGURE 2. 1,3-Dehydro-silaadamantane dications $\mathbf{2}^{2+}$−$\mathbf{5}^{2+}$.

Synthesis of several derivatives of 1-silaadamantane **6** and symmetrical 1,3,5,7-tetrasilaadamantane **7** (Figure 3) have been reported in the literature,[4−6] and limited structural and solvolytic reactivity studies have been made.[4,7,8] We recently reported on the chemoselective-



6 **7** **8** **9**

FIGURE 3. Synthetically accessible silaadamantanes.

[†] Dedicated with great respect and admiration to Prof. George Olah on the occasion of his 75th birthday.

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(1) Bremer, M.; Schleyer, P. v. R.; Schötz, K.; Kausch, M.; Schindler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 761.

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(3) Chan, M. S. W.; Arnold, D. R. *Can. J. Chem.* **1997**, *75*, 192.

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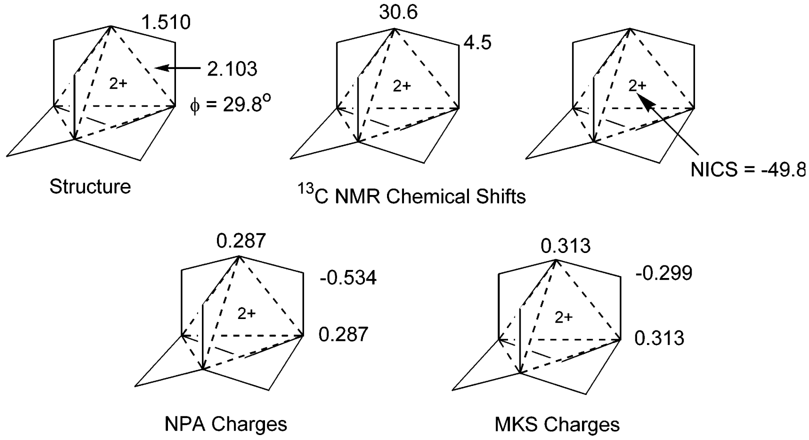
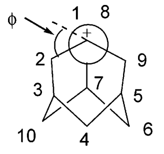


FIGURE 4. Optimized structure, computed NMR chemical shifts, NPA and MKS charges, and NICS for **1**$^{2+}$. The pyramidalization angle (ϕ) is graphically defined in formula 1.

synthesis of the mono- and bis-triflates **8** and **9**, respectively, (Figure 3) from 1,3,5,7-tetramethyl-1,3,5,7-tetrasilaadamantane by reaction with ICl/AgOTf and examined the complexation of **8** with representative super Lewis acids.[9a] In relation to these efforts and because of an ongoing interest in heterocyclic cage compounds and their cations in our laboratory,[9b] we have conducted a theoretical study of the dehydro dications **2**$^{2+}$$-$**5**$^{2+}$.

Results and Discussion

As a starting point and for comparison, we first calculated dication **1**$^{2+}$. Figure 4 summarizes its optimized structure (energies and Cartesian coordinates are given in Supporting Information), the computed GIAO chemical shifts (at the B3LYP/6-31G(d,p)//B3LYP/6-31G (d,p) level), and NICS (at the recommended HF/6-31+G-(d)//B3LYP/6-31G(d) level), as well as NPA and MKS charges. These initial calculations provided excellent overall agreement with the previous results.



$$\phi = 180\text{-}(\angle\, C_2\text{-}C_1^{+}\text{-}C_8\text{-}C_7 + \angle C_7\text{-}C_8\text{-}C_1^{+}\text{-}C_9)$$

Subsequently, attention was focused on the silylated dications **2**$^{2+}$$-$**5**$^{2+}$. Figure 5 summarizes the B3LYP/6-31G(d,p)-optimized structures for the dehydro dications.

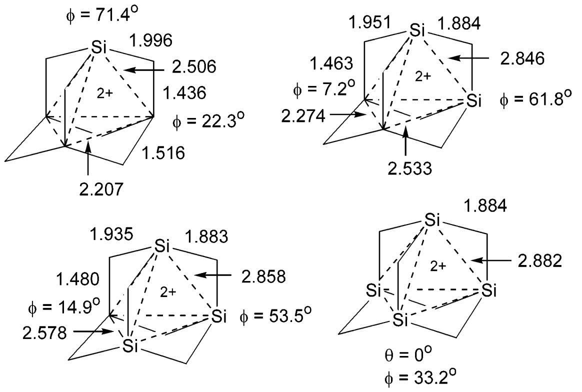


FIGURE 5. Optimized structures of dications **2**$^{2+}$$-$**5**$^{2+}$.

A notable feature is dramatic pyramidalization at silicon with a lesser degree of pyramidalization observed at the cage carbons. In the symmetrical **5**$^{2+}$, the pyramidalization angle is 33.2° and the dihedral angle between the p orbital of the Si atom and the Si(β)$-$C(α) bond is zero.

Figure 6 sketches the GIAO NMR data for **2**$^{2+}$$-$**5**$^{2+}$, calculated at both B3LYP/6-31G(d,p)//B3LYP/6-31G (d,p) and HF/6-31+G(d)//B3LYP/6-31G(d,p) levels, and the NICS data computed at the HF/6-31+G(d)//B3LYP/6-31G(d,p) level. For dication **2**$^{2+}$, the chemical shifts of C_β are close to that of **1**$^{2+}$, but C_α appears significantly more deshielded. The most remarkable are the computed ^{29}Si NMR chemical shifts, which appear extremely shielded! Whereas there are small differences in the magnitude of silicon shielding depending on the basis set, the trends are similar. Shielding at silicon decreases in going from the monosila- to the tetrasila-dehydro dication. This effect is accompanied by deshielding at C_β and sequential shielding at C_α.

As demonstrated in a number of previous theoretical studies, a strongly low-field-shifted ^{29}Si NMR signal is expected in R_3Si^+ species.[10] Interestingly, however, the situation is quite different for 7-silanorbornadien-7-ylium

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(10) See for example: (a) Olsson, L.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1995**, *117*, 7460. (b) Olah, G. A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1999**, *121*, 9615. (c) Olah, G. A.; Rasul G.; Buchholz, H. A.; Li X.-Y.; Prakash, G. K. S *Bull. Soc. Chim. Fr.* **1995**, *132*, 569. (d) Xie, Z.; Manning, J.; Reed, R. W.; Methur, R.; Boyd, P. D. W.; Benesi, A.; Reed C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922.

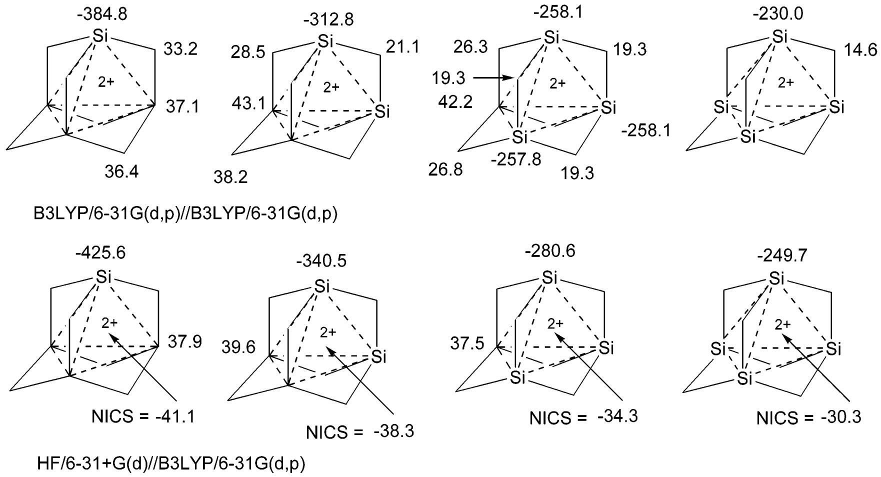
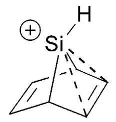


FIGURE 6. Computed NMR chemical shifts using two different basis sets, and NICS for $\mathbf{2}^{2+}-\mathbf{5}^{2+}$.



$\mathbf{10}^{+}$

FIGURE 7. 7-Silanobornadien-7-ylium monocation $\mathbf{10}^{+}$.

cation $\mathbf{10}^{+}$, in which the electron-deficient silicon is intramolecularly stabilized by π-participation.[11]

For this monocation, the computed ^{29}Si NMR chemical shift is −149.7 ppm at GIAO/B3LYP/6-311+G(2df,p) (Si) level.[11] For the dehydro-dications, homoconjugation and three-dimensional aromaticity must amplify silicon shielding. It is also noteworthy that the silicon in $\mathbf{10}^{+}$ is pyramidalized as is found for $\mathbf{2}^{2+}-\mathbf{5}^{2+}$ dications in the present study.

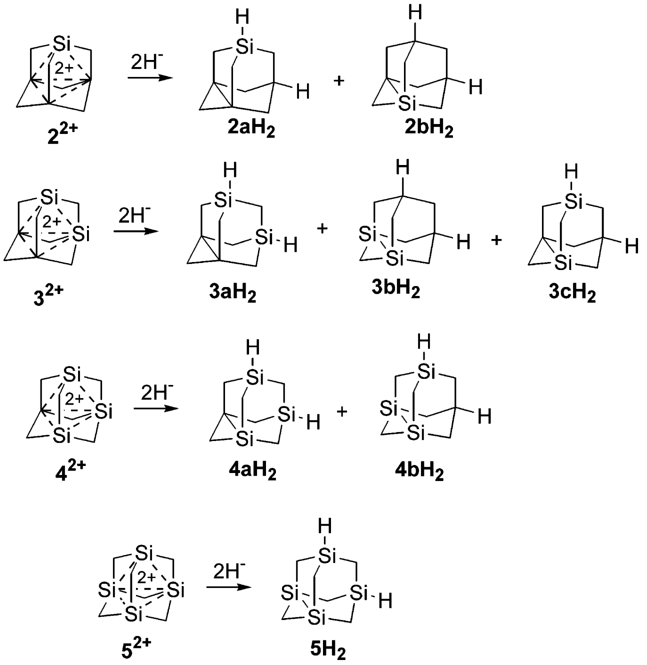
Computed NICS values for $\mathbf{2}^{2+}-\mathbf{5}^{2+}$ dications are strongly indicative of three-dimensional heteroaromaticity, with $\mathbf{2}^{2+}$ predicted to be somewhat less aromatic than $\mathbf{1}^{2+}$. The observed trend in the NICS values reflects reduced three-dimensional aromaticity as more silicon atoms are introduced into the bridgehead positions, and this seems to correlate with reduced shielding at silicon.

To obtain a charge delocalization pattern based on changes in charges upon dication formation, the neutral silanes **2a**H_2, **2b**H_2, **3a**H_2, **3b**H_2, **4a**H_2, **4b**H_2, and **5**H_2 (Scheme 1), which can be considered logical precursors to the dications via double-hydride abstraction, were computed at the B3LYP/6-31G(d,p) level. These were all shown to be minima, with **2a**H_2, **3a**H_2, **4a**H_2, and **5**H_2 estimated to be more stable within each group (see Table S7 in Supporting Information).

Figures 8a and 8b provide a summary of the computed NPA and MKS charges in the dications as well as changes in charges (relative to **2a**H_2, **3a**H_2, **4a**H_2, and **5**H_2). The overall pattern is consistent with predominant positive charge localization on the bridgehead silicon and carbon atoms.

Figure 9 (Supporting Information) sketches the forms of HOMO, LUMO, LUMO + 1, and LUMO + 2 orbitals for dications $\mathbf{1}^{2+}-\mathbf{5}^{2+}$, computed at B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level. For $\mathbf{1}^{2+}$, these orbitals are composed of p orbitals and the LUMOs are degenerate because the molecular point group is T_d. Since Si atoms are strongly pyramidalized, orbitals that contribute to the formation of a 4-center, 2-electron bond should be rehybridized 3s and 3p orbitals. Dication $\mathbf{5}^{2+}$ has a similar HOMO and three degenerate LUMO orbitals; however, the latter contain partial methylene carbon orbitals. Dications $\mathbf{2}^{2+}-\mathbf{4}^{2+}$ have rather similar HOMOs, but their LUMOs contain greater participation by C-orbitals.

SCHEME 1



The observed trends in the NICS values and computed NMR chemical shifts for $\mathbf{2}^{2+}-\mathbf{5}^{2+}$ are analogous to those of 1,3-dehydro-boroadamantyl systems, namely, $C_9H_{12}B^+$ (**11**), $C_8H_{12}B_2$ (**12**), $C_7H_{12}B_3^-$ (**13**), and $C_6H_{12}B_4^{-2}$ (**14**), from studies by Schleyer,[12] Olah,[13] and their associates.

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[11] Schuppan, J.; Herrschaft, B.; Müller, T. *Organometalics*, **2001**, *20*, 4584.

[12] Fokin, A. A.; Kiran, B.; Bremer, M.; Yang, X.; Jiao, H.; Schleyer, P. v. R.; Schreiner, P. R. *Chem. Eur. J.* **2000**, *6*, 1615.

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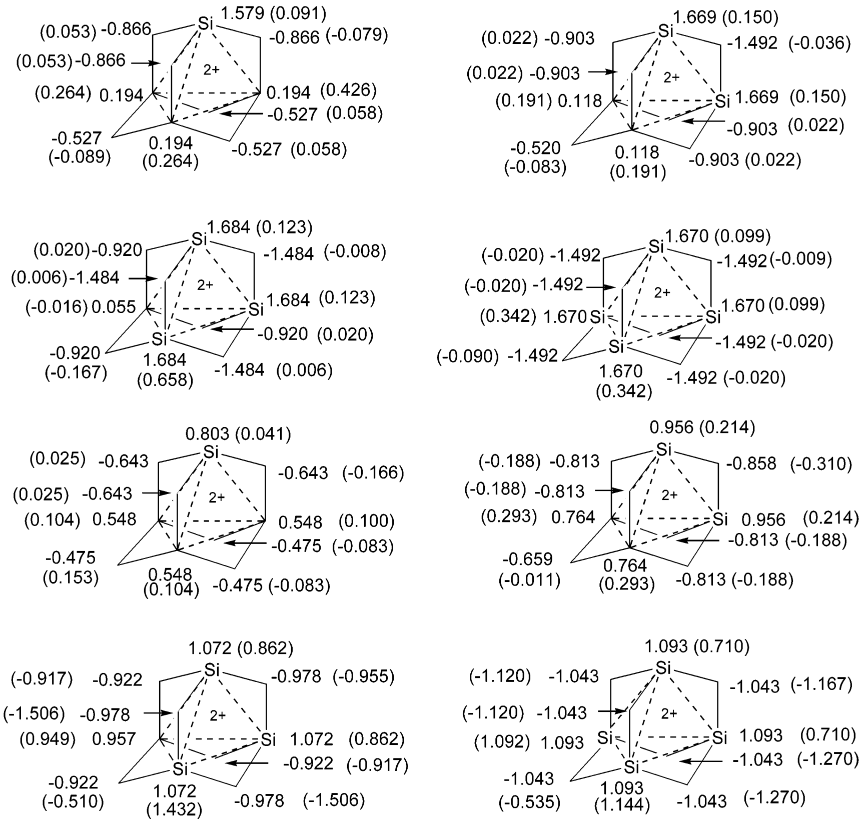

FIGURE 8. (a) Computed NPA charges and changes in charges (in parenthesis) in dications. (b) Computed MKS charges and changes in charges (in parenthesis) in dications.

The inner tetrahedral bonds in 1,3-dehydro-boroadamantyl systems are considerably shorter than those of 1,3-dehydro-silaadamantyl dications. For the boraadamantyl systems, the computed NICS values decrease in going from **11** to **14** (from −37.8 to −33.3)[12] and IGLO NMR predicts unusual δ ^{11}B NMR shielding for **11** and **12**.[13]

To understand the nature of the nonclassical interactions present in the silaadamantane dications, a natural bond orbital (NBO) analysis was performed for dications **1**$^{2+}$–**5**$^{2+}$. There appear to be only a few studies in the literature that deal with analysis of the wave function as a means to reveal the origin of homoconjugative interactions. Werstiuk and associates studied the 2-norbonyl cation by atoms in molecules (AIM) and electron localization function (ELF) and concluded that there is an electrostatic interaction between C(6) and the C(1)–C(2) π-bond.[14] But similar studies on 1,2,4,7-*anti*-tetramethyl-2-norbonyl and 6-tricyclo[3.2.1.0^{2,4}]octyl cations led to the conclusion that they do not present nonclassical structures.[15]

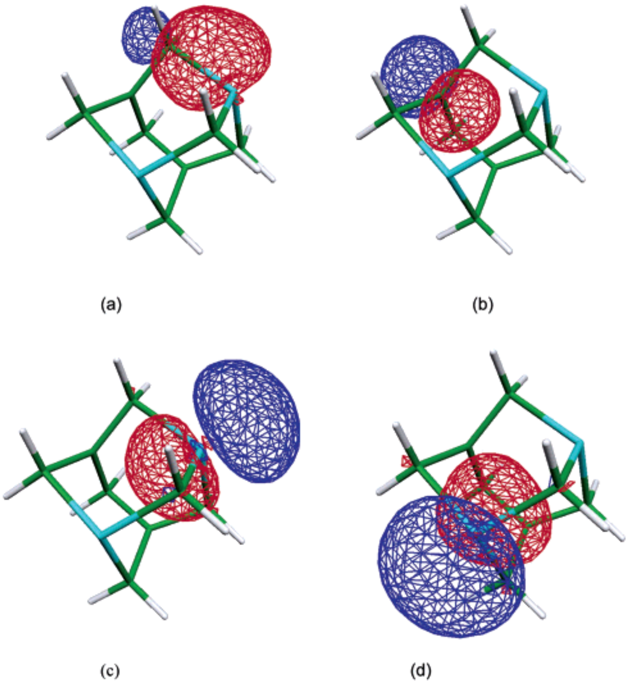

FIGURE 10. (a) σ(X−C); (b) β π(X); (c) α π(X); and (d) remote π(X) natural bond orbitals. The orbital in panel a is donating electron density to formally empty orbitals in panels b−d.

The NBO analysis in the present work indicates that the interaction that contributes the most to the stability of **1**$^{2+}$–**5**$^{2+}$ is electron donation from a σ(X−C) bonding orbital to a formally empty β π(X) (X = Si, C) (Figure 10). This interaction follows the order σ(Si−C) → π(C) > σ(Si−C) → π(Si) > σ(C−C) → π(C) > σ(C−C) → π(Si). This type of interaction is similar to the well-established β-silyl effect in carbocations.[16] There is also an α-interaction between a σ(X−C) and a π(X), but with a smaller

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[14] (a) Werstiuk, N. H.; Muchall, H. M. *J. Phys. Chem. A* **2000**, *104*, 2054. (b) Werstiuk, N. H.; Muchall, H. M.; Noury, S. *J. Phys. Chem. A* **2000**, *104*, 11601.

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contribution compared to the former interaction. For silicon-containing cations there is a very small donation from σ(X−C) to a p orbital of a remote Si atom (Figure 10).

The bond orders for nonclassical bonds, calculated by natural resonance theory (NRT), are in the range 0.1−0.2, indicating relatively strong interactions. These bonds are polar, presenting ca. 50% ionic character, as deduced from the ionic contribution of bond orders, and they present the same ionic character as the Si−C bonds. These results indicate that the resulting homoconjugative bond is partially polar and originates from electron donation from a localized σ occupied orbital to a formally empty p orbital. The most important effects are from β-interactions.

In summary, the present DFT study of hitherto elusive 1,3-dehydro-silaadamantane dications $\mathbf{2}^{2+}$−$\mathbf{5}^{2+}$ has provided insight into their structure, charge distribution modes, aromaticity, and NMR chemical shifts. The three-dimensional heteroaromaticity in these dications are clearly indicated by NICS calculations. The computed highly shielded ^{29}Si NMR chemical shifts for these dications are unprecedented but are in line with previous calculations on cation $\mathbf{10}^{+}$. The NBO method has indicated that homoconjugation originates from β-interaction between an occupied σ orbital and a formally empty p orbital. While the generality of silicon NMR shielding in homoconjugated and heteroaromatic silyl cations remains open to further theoretical scrutiny, synthesis of suitable 1,3-dehydro derivatives of silaadamantanes and attempts at their ionization constitute challenging problems for experimentalists.

Computational Methods. Structures were optimized using molecular point groups T_d for $\mathbf{1}^{2+}$, C_{3v} for $\mathbf{2}^{2+}$, C_{2v} for $\mathbf{3}^{2+}$, C_{3v} for $\mathbf{4}^{2+}$, and T_d for $\mathbf{5}^{2+}$ by the DFT method at the B3LYP/6-31G(d,p) level using the Gaussian 98 package.[17] Computed geometries were verified by frequency calculations. NMR chemical shifts were calculated by the GIAO methods at B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) and at HF/6-31+G(d)//B3LYP 6-31G(d,p) levels. NICS calculations were performed at the HF/6-31+G(d)//B3LYP/6-31G(d,p) level. Natural bond orbital (NBO),[18] natural population analysis (NPA),[19] and natural resonance theory (NRT)[20] analyses were performed with NBO 5.0 software.[21] Orbital illustrations were generated using the Molekel 4.1 software.[22]

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Supporting Information Available: (Table S1) Electronic energies (E), Zero point energies (ZPE), and Gibbs free energies (G) obtained from DFT calculations for $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$, and $\mathbf{5}^{2+}$ at the B3LYP/6-31G(d, p) level; (Tables S2−S6) Cartesian coordinates for $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$, and $\mathbf{5}^{2+}$ at the B3LYP/6-31G(d, p) level; (Table S7) point broups, electronic energies (E), zero point energies (ZPE), and Gibbs free energies (G) obtained from DFT calculations at the B3LYP/6-31G(d, p) level for $\mathbf{1}$H$_2$, $\mathbf{2a}$H$_2$, $\mathbf{2b}$H$_2$, $\mathbf{3a}$H$_2$, $\mathbf{3b}$H$_2$, $\mathbf{3c}$H$_2$, $\mathbf{4a}$H$_2$, $\mathbf{4b}$H$_2$, and $\mathbf{5}$H$_2$; (Tables S8−S16) Cartesian coordinates of the optimized structures for $\mathbf{1}$H$_2$, $\mathbf{2a}$H$_2$, $\mathbf{2b}$H$_2$, $\mathbf{3a}$H$_2$, $\mathbf{3b}$H$_2$, $\mathbf{3c}$H$_2$, $\mathbf{4a}$H$_2$, $\mathbf{4b}$H$_2$, and $\mathbf{5}$H$_2$ at the B3LYP/6-31G(d, p) level; (Figure 9) forms of the HOMO, LUMO, LUMO + 1, and LUMO + 2 for $\mathbf{2}^{2+}$−$\mathbf{5}^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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