



Stepwise Reduction of Azapentabenzocorannulene

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Abstract: Mono- and dianions of 2-*tert*-butyl-3a²-azapentabenzocorannulene (**1a**) were synthesized by chemical reduction with sodium and cesium metals, and crystallized as the corresponding salts in the presence of 18-crown-6 ether. X-ray diffraction analysis of the sodium salt, $[\{Na^+(18\text{-crown-6})(THF)_2\}_3\{Na^+(18\text{-crown-6})(THF)\}-(1a^{2-})_2]$, revealed the presence of a naked dianion. In contrast, controlled reaction of **1a** with Cs allowed the isolation of singly and doubly reduced forms of **1a**, both forming π -complexes with cesium ions in the solid state. In $[\{Cs^+(18\text{-crown-6})\}(1a^-)]\cdot THF$, asymmetric binding of the Cs^+ ion to the concave surface of **1a**⁻ is observed, whereas in $[\{Cs^+(18\text{-crown-6})\}_2(1a^{2-})]$, two Cs^+ ions bind to both the concave and convex surfaces of the dianion. The present study provides the first successful isolation and characterization of the reduced products of heteroatom-containing buckybowl molecules.

Curved carbon π -surfaces exhibit unique reactivity for metal coordination because of their distorted framework of conjugated sp^2 carbon atoms. In particular, buckybowl molecules, bowl-shaped polycyclic aromatic hydrocarbons (PAHs) that have a partial structure of fullerenes,^[1] are interesting as both of their faces, concave and convex, are amenable to metal coordination.^[2] Furthermore, the binding properties of buckybowls can be enhanced and tuned through stepwise electron addition.^[3] For example, corannulene ($C_{20}H_{10}$), the most representative buckybowl, has a doubly degenerate LUMO, which enables it to accept up to four electrons upon treatment with alkali metals^[4] and to form a variety of supramolecular aggregates with different metal binding patterns.^[5] In the case of sumanene ($C_{21}H_{12}$), deprotonation takes place at its benzylic CH_2 groups to generate the corresponding mono-

di-, and trianions, which behave as cyclopentadienyl ligands for metal coordination.^[6] The unique multi-electron reduction properties and metal coordination abilities of buckybowls are of great potential for applications in energy storage and supramolecular materials.^[7]

Despite the significant progress on the chemical reduction and coordination chemistry of buckybowls composed of carbon and hydrogen atoms, no studies have focused on those of heteroatom-containing buckybowls.^[8] In this context, our group^[9] and Shinokubo^[10] and co-workers independently reported the synthesis of 3a²-azapentabenzocorannulene (**1**), a nitrogen-containing corannulene derivative (Figure 1).^[11] The Shinokubo group intensively studied

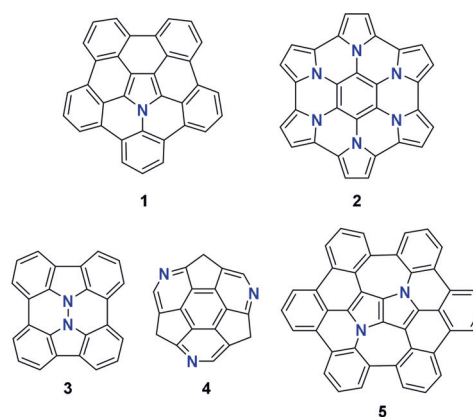


Figure 1. Azapentabenzocorannulene **1** and related nitrogen-containing PAHs.

the oxidation of **1** and related molecules to reveal the characteristic reactivity of the π -radical cations.^[10a,c] These examples as well as the isolation of oxidized products of azacoronene **2**^[12] and hydrazinobuckybowl **3**^[13] reflect the electron-rich character of pyrrole-fused PAHs. In contrast, the chemical reduction of nitrogen-containing buckybowls has not been studied, although electrochemical measurements of triasumanene **4**^[14] and scanning tunneling spectroscopy of nitrogen-containing bowl-shaped PAH **5**^[15] have recently been reported.

Based on density functional theory (DFT) calculations with the B3LYP/6-311 + G(2d,p) method, the core of **1** has almost degenerated LUMO and LUMO + 1 orbitals (-1.95 and -1.94 eV, respectively). These could be similar to those of corannulene, which has two degenerate LUMOs (-1.66 eV). These characteristics of azapentabenzocorannulene **1** attract special interest in studying its reactivity upon stepwise electron acquisition. Herein, we report on the first chemical reduction and the coordination chemistry of 2-*tert*-butyl-3a²-

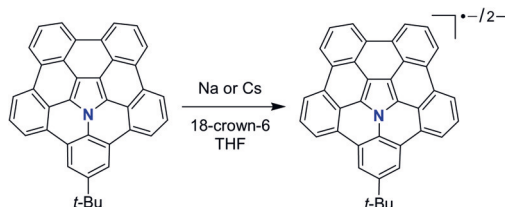
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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201906748>.

azapentabenzocorannulene (**1a**). By using alkali metals such as sodium and cesium as the reducing agents, we are able to synthesize the first mono- and dianions of **1a** and crystallize them with the corresponding alkali metal counterions (Scheme 1). This allowed us to reveal the consequences of adding one and two electrons to the N-containing bowl for the first time.



Scheme 1. Chemical reduction of **1a** with Na and Cs metals.

Azapentabenzocorannulene **1a** was prepared according to the procedures reported previously^[9] and purified by gas-phase sublimation in vacuo at elevated (300 °C) temperature prior to use. Notably, this procedure produced good-quality single crystals of **1a**, and their X-ray structural analysis showed a new structural polymorph (monoclinic space group, $P2_1/n$), which differs from that prepared from a solution at room temperature (orthorhombic, $Pbca$).^[9a] Detailed structural analysis revealed that the volume per molecule has increased from 574(2) Å³ to 585(1) Å³ in the high temperature (HT) polymorph. In the solid-state structure (Figure 2

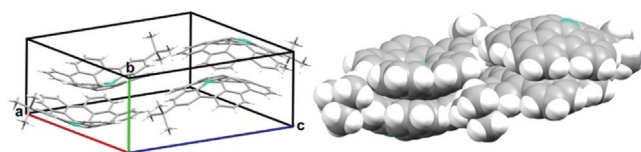


Figure 2. Solid-state packing of **1a** in a unit cell, capped-stick model (left) and space-filling model (right).

and Figure S15 in the Supporting Information), the molecules of **1a** are packed into 1D columns through $\pi \cdots \pi$ interactions (3.417(5) Å) with a rotation angle of 180° and a bowl slip distance of 0.885(5) Å (Figure S16). This differs from the rotation angle of 90° observed in the room temperature (RT) polymorph. The bowl slip also allows for the intercolumn C–H $\cdots\pi$ interactions (2.789(5) Å) that are responsible for the formation of an extended 2D network in the new crystal structure of **1a**. In contrast, no strong interactions are found between the adjacent aligned 1D columns in the previously reported structure.

The chemical reduction of **1a** with two selected Group 1 metals of different ionic sizes and different metal binding abilities, namely sodium and cesium, was then investigated. Sodium metal is known to facilitate the formation of the doubly reduced carbanions of planar^[16] and curved PAHs, often isolated in their “naked” forms.^[17] The reduction of **1a** with 2 equivalents of sodium in THF in the presence of 18-crown-6 resulted in the preparation of the dianion of **1a**,

which was isolated as the corresponding sodium salt. The structure was elucidated by X-ray diffraction to be a solvent-separated ion product, $[\{\text{Na}^+(\text{18-crown-6})(\text{THF})_2\}_3\{\text{Na}^+(\text{18-crown-6})(\text{THF})\}(\mathbf{1a}^{2-})]$ (Figure 3). Surprisingly, ¹H NMR

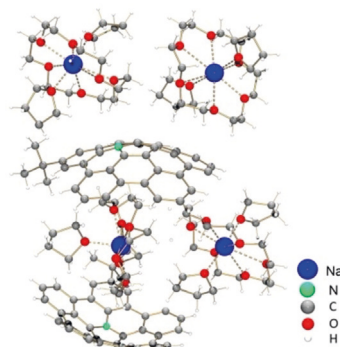


Figure 3. Molecular structure of $[\{\text{Na}^+(\text{18-crown-6})(\text{THF})_2\}_3\{\text{Na}^+(\text{18-crown-6})(\text{THF})\}(\mathbf{1a}^{2-})]$.

studies revealed that the doubly reduced product is NMR-silent in solution even at low temperature (Figure S9). DFT calculations at the B3LYP/6-31+G(d) level of theory suggested that for compound **1**, the triplet state is more stable than the singlet state by 7.5 kcal mol⁻¹. This trend is totally different from that of the parent corannulene, where the NMR-active singlet state is more stable than the triplet state.^[4c] Notably, the addition of two electrons is reversible according to a DART-MS study of the reduced and air-quenched products (Figure S13).

The controlled reduction of **1a** with cesium metal in the presence of 18-crown-6 in THF allowed the isolation of two products as good-quality single crystals suitable for X-ray diffraction analysis. The first one contains the singly reduced anion coordinated by a cesium ion capped by an 18-crown-6 molecule, $[\{\text{Cs}^+(\text{18-crown-6})\}(\mathbf{1a}^-)] \cdot \text{THF}$ (Figure 4a). The cesium ion coordinates to the concave face of **1a**⁻ (Figure 5a); such a selective concave coordination of a cesium ion has also been seen in the reduction of corannulene and its methylated derivatives.^[18] The shortest Cs $\cdots\pi$ contacts are observed to the C17 and C18 atoms (3.502(3) and 3.354(3) Å, respectively). The distances to the adjacent C16, C19, and C22 atoms are longer and span over the range of 3.595(3)–3.707(3) Å.

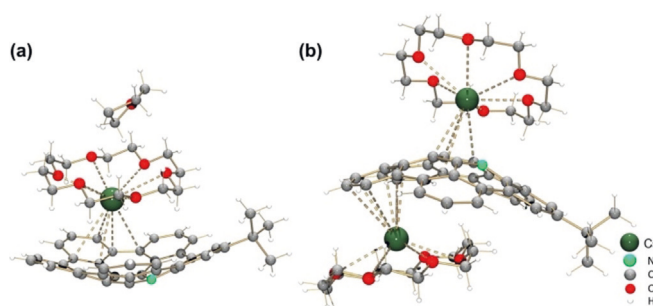


Figure 4. Molecular structures of a) $[\{\text{Cs}^+(\text{18-crown-6})\}(\mathbf{1a}^-)] \cdot \text{THF}$ and b) $[\{\text{Cs}^+(\text{18-crown-6})\}_2(\mathbf{1a}^{2-})]$.

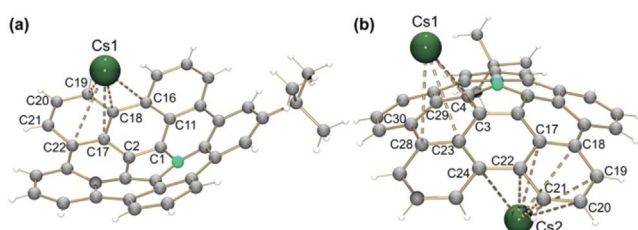


Figure 5. Metal coordination in a) $\text{Cs}/1\text{a}^-$ and b) $\text{Cs}_2/1\text{a}^{2-}$.

The second cesium product, $[\{\text{Cs}^+(18\text{-crown-6})\}_2(1\text{a}^{2-})]$, is formed by the doubly reduced anion with two cesium cations bound to the convex and concave surfaces of 1a^{2-} (Figure 4b). In both cases, the metal binding to the six-membered rings of 1a^{2-} is asymmetric (Table S3). For Cs1, the shortest distances are measured at 3.363(6) and 3.451(6) Å to the C3 and C4 sites, respectively, with other Cs– π distances ranging from 3.638(6) to 3.771(6) Å (Figure 5b). For Cs2, the Cs–C distances to the six-membered ring range over 3.275(6)–3.729(6) Å.

As both cesium products are NMR-silent, DART-MS was used to confirm the formation of the singly and doubly reduced products. By quenching with D_2O , $[\text{C}_{38}\text{H}_{24}\text{ND}_2^+]$ and $[\text{C}_{38}\text{H}_{24}\text{ND}_2^{2+}]$ species were separately detected for $\text{Cs}/1\text{a}^-$ and $\text{Cs}_2/1\text{a}^{2-}$, respectively (Figures S10 and S11).

The first X-ray structural characterization^[19] of the singly and doubly reduced states of 1a allowed us to analyze the changes in bowl depth upon one- and two-electron acquisition (Table 1). It is especially informative to compare 1a with the “naked” dianion isolated with sodium counteranions, as metal binding effects are excluded in this case. A curvature increase of both the exterior and interior core can be clearly detected in $\text{Na}_2/1\text{a}^{2-}$, and both are further affected by cesium binding in $\text{Cs}_2/1\text{a}^{2-}$.

To elucidate the nature of the anionic species, DFT calculations were performed at the B3LYP/6–31 + G(d) level of theory. According to its MO diagram, 1 has two almost degenerated LUMOs (Figure S26), which can potentially accept up to four electrons. Upon the first reduction, one electron is introduced into the LUMO of 1 to form the radical anion 1^- (Figure S27). The second electron is placed into the LUMO of 1^- to form 1^{2-} as a triplet diradical species. This two-step reduction is in full agreement with the electrostatic potential (ESP) maps shown in Figure 6, where the negative charge in 1^- and 1^{2-} is increased in a stepwise manner over the molecular orbitals where the electrons are located.

In summary, we have synthesized the mono- and dianions of azapentabenzocorannulene 1a by chemical reduction with sodium and cesium metals in THF in the presence of 18-crown-6. X-ray diffraction analysis of the sodium salt, $\text{Na}_2/1\text{a}^{2-}$, revealed the presence of the naked dianion. On the other hand, the controlled reduction of 1a with cesium metal allowed the isolation of singly and doubly reduced anions complexed with cesium ions, $\text{Cs}/1\text{a}^-$ and $\text{Cs}_2/1\text{a}^{2-}$. The former complex shows selective binding of the Cs^+ ion to the concave surface of 1a^- , whereas in the latter, two Cs^+ ions bind to both the concave and convex surfaces of 1a^{2-} . This structural

Table 1: Bowl depth (BD) in the X-ray structures of 1a , $\text{Cs}/1\text{a}^-$, $\text{Na}_2/1\text{a}^{2-}$, and $\text{Cs}_2/1\text{a}^{2-}$ along with the calculated values in 1 , 1^- , and 1a^{2-} (in Å).

		BD average exterior (green) ^[a]	BD average interior (red) ^[b]
X-ray	1a (RT) ^[9a]	1.588(8)	0.879(8)
	1a (HT)	1.581(5)	0.871(5)
	$\text{Cs}/1\text{a}^-$	1.615(5)	0.897(5)
	$\text{Na}_2/1\text{a}^{2-}$	1.646(9)	0.887(9)
	$\text{Cs}_2/1\text{a}^{2-}$	1.657(12)	0.908(12)
DFT	1 (singlet)	1.528	0.853
	1^- (doublet)	1.562	0.886
	1^{2-} (triplet)	1.530	0.858

[a] Determined by averaging the distances between the plane including the central pyrrole ring and C8, C14, C20, C26, and C34. [b] Determined by averaging the distances between the plane including the central pyrrole ring and the midpoints of C10–C12, C16–C18, C22–C24, C28–C30, and C34–C6.

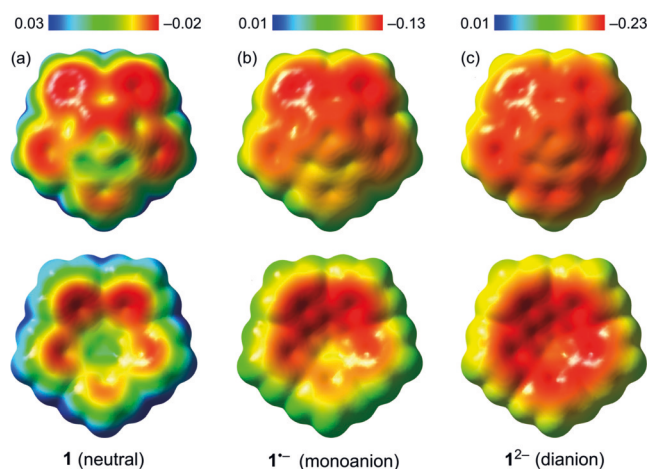


Figure 6. Electrostatic potential maps of azapentabenzocorannulenes a) 1 , b) 1^- , and c) 1^{2-} calculated at the B3LYP/6–31 + G(d) level of theory.

characterization of anionic species of azapentabenzocorannulene represents the first example of the chemical reduction of heteroatom-containing buckybowls, and thus provides new perspectives for the chemistry and application of non-planar and heteroatom-doped PAH molecules.

Acknowledgements

This work was supported by the U.S. National Science Foundation, NSF-CHE 1608628 and NSF-MRI 1726724 (M.A.P.); the Japan Society for the Promotion of Science (JSPS) via KAKENHI grant 16H06030 (S.I.); and Nanyang Technological University and the Singapore Ministry of Education via Academic Research Fund Tier 1: 2018-T1-002-021 (S.I.). Y.T. would like to thank the JSPS for a Research Fellowship for Young Scientists.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkali metals · buckybowl · chemical reduction · corannulenes · X-ray diffraction

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 12107–12111
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Manuscript received: May 30, 2019
Accepted manuscript online: June 28, 2019
Version of record online: July 10, 2019