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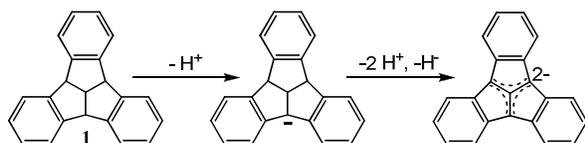
Monometalated Tribenzotriquinacene: *Exo* and *Endo* Coordination of Sodium and Potassium by a Rigid Bowl-Shaped Hydrocarbon Anion[§]Jan Klett^{*,a}

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Treatment of tribenzotriquinacene with trimethylsilylmethyl sodium [NaCH₂SiMe₃] or potassium hydride [KH] leads to the formation of monometalated products. The sodium atom interacts with the carbanion in an *exo* fashion, while the potassium atom is found in an *endo* position inside the rigid bowl-shaped molecule.

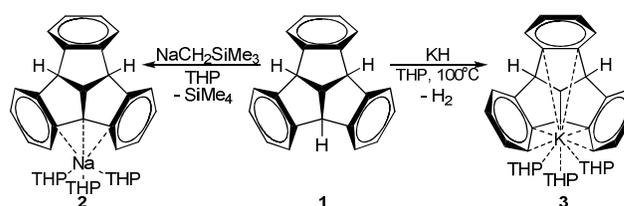
The conformational rigidity of the bowl-shaped polycyclic hydrocarbons such as tribenzotriquinacene¹ (1) makes them attractive units of molecular capsules and molecular receptors.² Similar bowl-shaped molecules, such as sumanene and corannulene, are studied for their electronic properties³ and their similarity to larger systems such as fullerenes, carbon nanotubes, and graphene.⁴ The introduction of electronic charge leads to significant changes in their properties and makes them useful model systems of charged anodes in alkali metal ion batteries. The reduction of corannulene with alkali metals led to the formation of mono-, di- and tetra-anions and was successful with lithium,⁵ sodium,⁶ potassium,^{6a} rubidium and cesium.⁷ In all this anionic forms the corannulene maintains its bowl-shaped form, while the corresponding alkali metal atoms are found in contact (contact ion pair, CIP) or separated (solvent separated ion pair,SSIP)⁸ from the anionic unit. The majority of these CIP structures show a coordination of the alkali metal atom to the convex side (*exo* coordination) or to the edge of the bowl.^{6a} The rarely found *endo* coordination to the concave side of the bowl⁹ with distinct interactions of alkali metal atom and π -electrons of the bowl is only present in the crown ether coordinated cesium compound of the radical mono-anionic corannulene.⁷



Scheme 1. Monometalation of tribenzotriquinacene (1) and the transformation to the tribenzacepentalene dianion by multiple deprotonation.¹⁰

Stalke et al. reported the polymetalation of tribenzotriquinacene¹⁰ by a Lochmann-Schlosser base¹¹ (Scheme 1). The treatment of the hydrocarbon with a mixture of *n*-butyllithium and potassium *tert*-pentoxide led to the formation of the tribenzacepentalene dianion. This reaction is a formal di-deprotonation followed by a subsequent oxidation (by H₂-

elimination); the NMR spectroscopic detection of mono- and di-deprotonated tribenzotriquinacene suggested a stepwise formation of mono-, di- and trianions, followed by a fast hydride elimination from the unstable trianion. Though it was not possible to obtain analytically pure samples of the monoanion, the existence of the monoanion could be confirmed by NMR spectroscopy and the reaction with electrophiles to generate substituted derivatives.



Scheme 2. Synthesis of compounds 2 and 3 by monometalation of tribenzotriquinacene, 1.

This study uses well defined organometallic alkali metal bases in order to achieve metalations of tribenzotriquinacene. Good temperature stability, high reactivity, and high purity make alkali metal trimethylsilylmethyl compounds the reagents of choice. The sodium, potassium, rubidium and cesium compounds (MCH₂SiMe₃, M=Na, K, Rb, Cs) were prepared by a reaction of the corresponding alkali metal with bis(trimethylsilylmethyl)mercury and were successful in metalating benzyltrimethylsilane at the benzylic position.¹² Recently we prepared and isolated these compounds by a reaction of trimethylsilylmethyl lithium and the corresponding alkali metal *tert*-butoxides.¹³

Trimethylsilylmethylsodium [NaCH₂SiMe₃] was reacted with tribenzotriquinacene in an *n*-hexane/THP^{14,15} mixture at ambient temperature to produce monometalated tribenzotriquinacene (Scheme 2). The product was isolated as orange crystals suitable for X-ray structural determination from neat THP at -21°C as tris-THP-solvated monomer [(THP)₃Na(C₄H₃(C₆H₄)₃)], 2, with the sodium atom adopting an *exo*-position regarding the curvature of the bowl (Figure 1).[‡] A reaction with KCH₂SiMe₃ was unsuccessful, better result was achieved when potassium hydride¹⁶ [KH] was used in THP at 100°C. Here the product was isolated as orange crystals at -21°C, which also consisted of a monometalated, tris-THP-solvated monomer [(THP)₃K(C₄H₃(C₆H₄)₃)], 3.[‡] However, here the potassium atom was found in an *endo*-position inside the bowl-shaped anionic hydrocarbon (Figure 2).

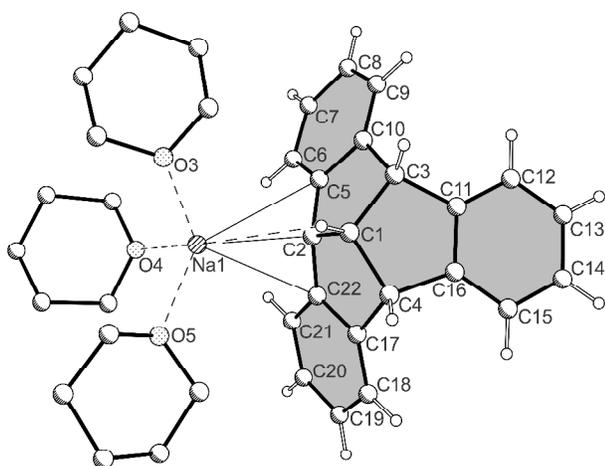


Figure 1. Molecular structure of **2** with selective labeling and selected H atoms omitted for clarity. The bowl framework is shaded for emphasis.

Compound **2** crystallises in the triclinic space group $P\bar{1}$ and was found to be twinned pseudo-merohedrally. The existence of four crystallographic independent molecules makes it reasonable to discuss the molecule including Na1 as reference; significant differences will be discussed.[†] The tribenzotriquinacene is deprotonated at the benzylic (bridgehead) carbon C2; this allows the resulting negative charge to be partially delocalised over the two adjacent aromatic rings. The sodium atom is situated on the convex side of the bowl-shaped molecule next to this benzylic carbon and also shows interactions to the ipso atoms (C5/C22) of the corresponding six-membered rings.

The shortest distance is found to the bridgehead carbon C2 (2.4984(15) Å), the distances to C5 and C22 are 3.148(2) Å and 2.9288(16) Å. The sum of angles involving the three neighbouring atoms of C2 (C1-C2-C5; C1-C2-C22; C5-C2-C22) with values considerably below 360° (Na1: 346.1°; Na2: 347.3°; Na3: 345.4°; Na4: 345.2°) reflects a clear pyramidalization¹⁷ of this carbon next to the sodium atom. Compared to diphenylmethyl sodium¹⁸ with a similar (but planar) carbon framework interacting with a sodium atom, compound **2** shows a shorter bridgehead carbon-sodium distance and no planarity, caused by the structural tension of the attached bowl-shaped framework, therefore leading to a higher localisation of negative charge at C2. This tension also forces the involved six-membered rings to tilt away from the sodium atom and therefore hinders a better interaction with the electron density of the corresponding π -systems.

The alignment of the sodium atom and the proton connected to the central atom C1 next to metalated C2 suggests the possibility of β -hydride elimination which is familiar to alkali metal compounds of aliphatic hydrocarbons.¹⁹ The impossibility of reaching planarity as part of the bowl-shaped framework disfavors this reaction, apparently it is necessary to achieve more than one metalation as it could be shown by Stalke.¹⁰ The coordination sphere of the sodium atom is completed by the additional interaction with three THP molecules (Na1-O3 2.2587(12) Å; Na1-O4 2.2745(12) Å; Na1-O5 2.2818(13) Å), which results in a distorted tetrahedral environment. Additional weak C-H \cdots π intermolecular interactions²⁰ (with minimum H \cdots C distances of 2.7 Å) are observed between the THP molecules with concave and convex surfaces of the bowl fragment.

Though potassium compound **3** has a similar composition as **2**, it shows a remarkable different arrangement, here the potassium atom K1 interacts with the concave face of the monometalated tribenzotriquinacene. The endo coordination does not only allow an interaction of the potassium atom with the metalated bridgehead carbon C2 and its environment, it also enables an intramolecular interaction with the π -system of the six-membered ring (C11 to C16) opposite of C2 (K1-C11 3.3122(15) Å; K1-C16: 3.4585(16) Å). The distance of K1 to the deprotonated carbon C2 (3.2186(19) Å) is not the shortest interaction, the distances to the ipso- and ortho-carbons (relative to C2) are more evenly distributed compared to compound **2** (K1-C5 2.9973(16) Å; K1-C22 3.1988(18) Å; K1-C6 3.2142(16) Å; K1-C21 3.5003(18) Å). A similar situation is found in 2,4-dimethylpentadienyl-potassium,²¹ where the alkali metal adopts an almost symmetric position over the planar open 5-ring. The more ionic and less covalent interaction with negative charge in compound **3** also manifests itself in the less pronounced pyramidalization of C2 compared to sodium compound **2**; the sum of angles of the three bonds towards C2 (C1-C2-C5; C1-C2-C22; C5-C2-C22) with 353.1° is still significantly below 360°. However, the structural tension of the bowl framework in combination with the endo coordination of K1 leads to an inverted arrangement, with the C2-corner of the distorted trigonal pyramid pointing away from K1. The rotation of the involved six-membered rings towards the potassium atom caused by the structural strain of the bowl arrangement also intensifies the interaction with the π -electrons. The additional interaction with the three THP molecules (K1-O3 2.7370(12) Å; K1-O4 2.6869(14) Å; K1-O5 2.9973(16) Å) and the centroids of the three six-membered rings produces a slightly distorted octahedral environment (X1A-O3 169.0°; X1B-O4 173.5°; X1C-O5 170.3°).

Overall the reduced pyramidalization at atom C2 in compounds **2** and **3** leads to a considerable distortion of the carbon framework in comparison to C_{3v}-symmetrical tribenzotriquinacene **1**, which is reflected in the alternating sum of angles of the bonds toward the bridgehead atoms (**1**: 322.9°; **2**: 346.1°, 321.6°, 319.4°; **3**: 353.1°, 318.1°, 318.6°), and in the angles between the planes formed by the aromatic rings (**1**: 116.8°; **2**: 141.8°, 114.9°, 109.9°; **3**: 147.6°, 106.3°, 105.4°).

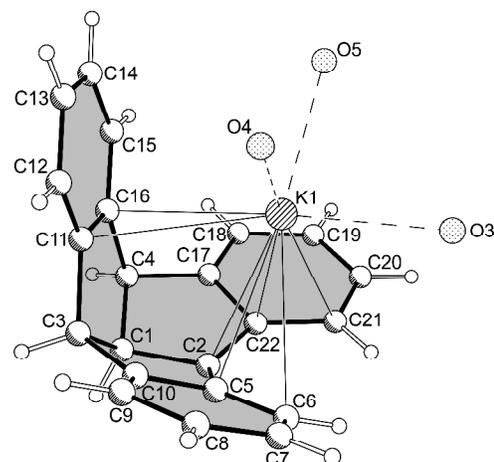


Figure 2. Molecular structure of **3** with selective labeling, selected H atoms, and THP C atoms of THP omitted for clarity. The bowl framework is shaded for emphasis.

Comparison of the experimentally observed structures of **2** and **3** with optimized hypothetical endo (Na) or exo (K) coordinated structures by Density Functional Theory calculations²² (B3LYP/6-31G* level of theory)^{7,23} in gas-phase (based on observed structures of **2** and **3**) revealed that compounds **2** and **3** are energetically in favour compared to their conformationally inverted counterparts (Na-endo +7.7 kJ/mol; K-exo +25.7 kJ/mol).^{10,†}

¹H and ¹³C NMR spectra of **2** and **3** in [D₈]THF solution were consistent with monometalated tribenzotriquinacene.[†] However, **2** lost 1.5 equivalents of THF during the preparation for NMR spectroscopy, **3** lost the solvent almost completely and showed signs of decomposition. The signals of the central and the two bridgehead C-H groups could be clearly identified both in ¹H and ¹³C NMR spectra (**2**: H-C1 4.41 ppm and 58.0 ppm, H-C3/4 4.03 ppm and 55.5 ppm; **3**: H-C1 4.38 ppm and 58.4 ppm, H-C3/4 3.89 ppm and 54.2 ppm). The signals of the protons and carbon atoms of the six-membered rings in positions ortho and para to C2 of both compounds **2** and **3** show a significant upfield shift in comparison with the ipso and meta carbons because of charge delocalisation from C2 into the rings.

The sensitivity of the ¹³C signal of C2 towards changes in charge density makes it a useful instrument to study the behaviour of ion pairs in solution at different temperatures.²⁴ Sodium compound **2** showed a large upfield shift (Figure 3) over a temperature range from -75°C to 65°C (from 89.0 to 79.3 ppm). This indicates that **2** exist at higher temperatures as contact ion pair (CIP) and is transformed to an energetically favoured solvent separated ion pair (SSIP) at low temperatures. On the other hand, **3** shows a small downfield shift in the same temperature range (from 86.8 to 88.9 ppm); this different behaviour can be attributed to a reversal of the CIP/SSIP equilibrium caused by the chelating effect of the bowl molecule. However, the influence of the less polarising nature of potassium on the anion, or the unusual bonding situation concerning C2 cannot be ruled out completely.

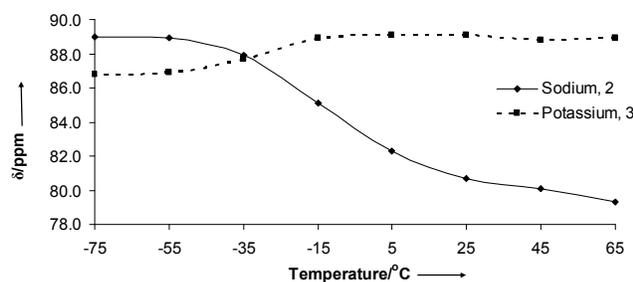


Figure 3. ¹³C NMR spectroscopic shift of the benzydrylic carbon C2 resonance of compounds **2** and **3** in a temperature range from -75°C to 65°C in [D₈]THF.

Conclusions

In summary, this study has shown that monometallic bases can achieve monometalation of the rigid bowl-shaped tribenzotriquinacene, the sodium and potassium compounds could be isolated as highly air- and moisture sensitive orange crystals. The structures of the tris-THP complexes were determined by X-ray diffractometry as exo-bound (sodium, **2**) and endo-bound (potassium, **3**) complexes. Simple theoretical gas phase calculations revealed these structures are energetically

favoured in comparison to their inverted counterparts. In solution sodium compound **2** was observed as contact ion pair which is converted into a solvent separated ion pair at low temperature, as revealed by NMR spectroscopic studies. The same investigation with **3** turned out to be less conclusive, which originates from the unusual bonding situations enabled by the possible endo interaction with a rigid bowl-shaped framework. The absence of bowl-to-bowl inversion enables configurationally stable interactions of metal atoms with the convex or concave face of the bowl, leading to new properties and structural motifs. This research was supported by the German Academic Exchange Service DAAD (*Rückgewinnung deutscher Wissenschaftler aus dem Ausland*). We are also very grateful to Professor Dietmar Stalke and his coworkers for their very generous support.

Notes and references

⁶⁵ *In memory of Ken Wade.*

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[†] Electronic Supplementary Information (ESI) available: Details on structural data, NMR spectroscopic data, and DFT calculations. See DOI: 10.1039/b000000x/

[‡] Crystal data for **2**: C₃₇H₄₅NaO₃, M = 560.72 g mol⁻¹, triclinic, space group P $\bar{1}$, a = 10.364(2), b = 18.028(2), c = 33.590(3) Å, α = 90.01(2), β = 90.01(2), γ = 93.40(2)°, V = 6265.0(15) Å³, Z = 8, μ (CuK α) = 0.691 mm⁻¹, 197816 reflections, 22618 unique (R_{int} = 0.0289), R_1 (all data) = 3.12%, wR_2 [$I > 2\sigma(I)$] = 8.30 %, GooF = 1.037, largest diff. peak and hole 0.225 and -0.153 e⁻³. Crystal data for **3**: C₃₇H₄₅KO₃, M = 576.83 g mol⁻¹, monoclinic, space group Cc, a = 16.783(2), b = 12.416(2), c = 15.368(2) Å, β = 102.75(2)°, V = 3123.4(8) Å³, Z = 4, μ (CuK α) = 1.750 mm⁻¹, 27313 reflections, 4682 unique (R_{int} = 1.96 %), R_1 (all data) = 2.02 %, wR_2 [$I > 2\sigma(I)$] = 4.85 %, GooF = 1.020, largest diff. peak and hole 0.163 and -0.093 e⁻³. CCDC 978138 (**2**) and 978139 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request. Single crystals were mounted in inert oil under protective atmosphere by applying the X-Temp2 device.²⁵

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