Highly Strained [6]Cycloparaphenylene: Crystallization of an Unsolvated Polymorph and the First Mono- and Dianions

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Highly Strained [6]Cycloparaphenylene: Crystallization of an Unsolvated Polymorph and the First Mono- and Dianions

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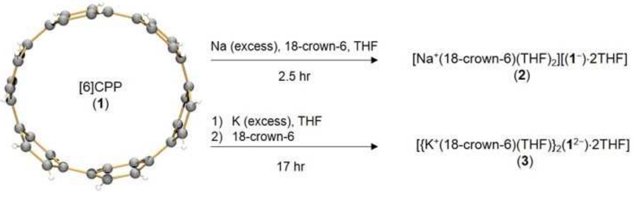
The X-ray diffraction study of [6]cycloparaphenylene (1), crystallized under solvent-free conditions, revealed a unique solid state structure with tight packing of individual molecules that minimizes empty internal space. The controlled chemical reduction of this highly strained nanohoop with Group 1 metals resulted in the first isolation and structural characterization of its mono- and dianions, allowing for the evaluation of core transformations for the series ranging from 1^0 to 1^{1-} and 1^{2-}.

Polycyclic aromatic hydrocarbons (PAHs) with radially-oriented π-systems are of fundamental interest due to their unique structure and conjugation pathways,[1] providing new opportunities in the design of optoelectronic materials and novel supramolecular architectures. Recently, [*n*]cycloparaphenylenes ([*n*]CPPs, where n = number of phenyl units) have burst onto the scene as a new and intriguing structural type with radially-oriented π-systems.[2] These molecules, coined “carbon nanohoops” due to their structural relationship to carbon nanotubes, had long been sought since their early conceptualization in 1934[3] and Vögtle’s pioneering synthetic efforts in the 1990s.[4] Following the first [*n*]CPPs in 2008,[5] scalable[6] and selective syntheses of numerous sizes[7] have led to extensive studies of the size-dependent optoelectronic properties,[8,2b,7c] unique crystal packing[2b,9,7e] and supramolecular behavior[10] of the [*n*]CPPs. Particularly noteworthy, the HOMO-LUMO gaps of the strained nanohoops narrow with decreasing size, a trend exactly opposite to typical PAHs.[8a] Thus, the oxidation[11] and reduction chemistry[12] of the macrocyclic [*n*]CPPs as a function of size is of significant interest for a variety of applications, including lithium ion storage.[13] Our crystallographic characterization of the tetrareduced [8]CPP in 2014 remains the only study of a highly reduced CPP.[12b] In this work, we set to explore the reduction behavior of a smaller and more rigid cycloparaphenylene, [6]CPP (**1**, Scheme 1), in order to gain some insight into the size dependent behavior of multireduction processes for the nanohoops. Herein, we report crystallographic characterization of mono- and doubly-reduced states of **1**, allowing us to evaluate the effect of one and two electron acquisition by the carbon framework of [6]CPP. We also provide evidence that the tri- and tetrareduced states are accessible with this small nanohoop, highlighting the potential of these materials for multielectron storage.



Scheme 1 Chemical reduction of [6]CPP (**1**) to afford mono- and dianions isolated as the corresponding alkali metal salts **2** and **3**.

Bulk quantities of [6]CPP (**1**) were prepared using the synthetic procedures reported previously.[14] A slow sublimation of this solid *in vacuo* at 220 °C produced crystals of **1** (*See ESI for more details*) suitable for X-ray structural characterization. Notably, the sublimation-deposition crystallization[15] excludes an encapsulation of any solvent molecules into the crystal lattice and is known to afford novel high-temperature polymorphs.[16] Indeed, the unit cell parameters of crystals obtained by the solvent-free deposition method differ from those previously grown from solution,[7e] indicating a new crystal packing motif. The detailed structural analysis revealed that the molecular structures and core parameters of [6]CPP are very similar in both crystal types (See Fig. S7 for C–C bond distance comparison). However, the solid state packing of [6]CPP molecules is completely different. In contrast to the cylinder-like alignment reported previously, a herringbone pattern is observed in the new structural polymorph of **1** (Fig. 1, left). Interestingly, the neighbouring [6]CPP molecules are stacked in a concave-convex fashion, thus minimizing an open internal space inside their cavities (Fig. 1, right). These cavities have been filled with disordered solvent molecules, either *n*-hexane or dichloromethane, in the crystals grown from solution. Solvent exclusion during crystallization of **1** in this work results in a very tight packing with the accessible void inside each [6]CPP molecule reduced from 134 Å^3 to only 42 Å^3, as estimated with the help of PLATON.[17]

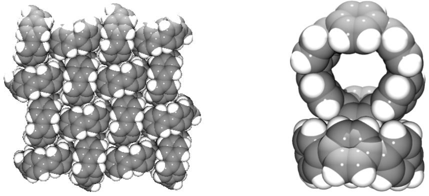


Fig. 1 Crystal packing along with the view of two inserted molecules of **1** (space-filling models).

For the next step, the controlled reduction of **1** with alkali metals in THF has been investigated. We observed that the use of sodium and potassium metals readily generates a red-brown solution followed by the formation of a purple-red colour, assigned to the mono- and doubly reduced states of **1**, respectively (See Figs. S1-S4 for UV-vis spectroscopy data). Specifically, the reduction of **1** with an excess of sodium metal in THF in the presence of 18-crown-6 ether over a short reaction time (*ca*. 2.5 hours) allows the controlled preparation of the monoanion of **1** (Scheme 1). The resulting product was isolated as dark air- and moisture sensitive crystals, [Na$^+$(18-crown-6)(THF)$_2$][($\mathbf{1}^-$)·2THF] (**2**). Their X-ray diffraction study revealed the formation of the monoreduced [6]CPP^{1-} anion crystallized as a solvent-separated ion pair (SSIP) with sodium counterion fully wrapped by one 18-crown-6 ether and two THF molecules (Fig. 2, left). The corresponding Na···O$_{\mathrm{THF}}$ and Na··O$_{\mathrm{crown}}$ bond length distances of 2.3407(19) Å and 2.7362(13)–2.7909(12) Å are comparable with the reported values.[18] Interestingly, two THF molecules occupy the small inner cavity of the monoreduced [6]CPP (Fig. 2 right). Notable changes in the C–C bond lengths of the carbon core of $\mathbf{1}^{1-}$ can be detected in comparison with $\mathbf{1}^0$ (Table 1). Therefore, the preparation of the higher reduced states of **1** was targeted next.

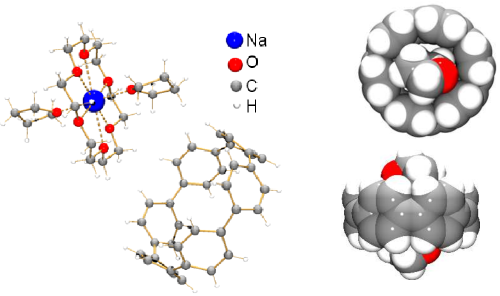


Fig. 2 Molecular structure of **2** (left, ball-and-stick model. THF inside the cavity of [6]CPP has been removed for clarity). Space-filling models of encapsulated THF molecules inside [6]CPP^{1-} (right).

The chemical reduction of **1** to the doubly-reduced state required a longer reaction time (*ca*. 17 hours) and an excess of potassium metal in THF (Scheme 1). Again, the addition of 18-crown-6 ether was used to facilitate crystallization of the resulting product from a THF/hexanes mixture to yield dark air- and moisture sensitive crystals of [{K$^+$(18-crown-6)(THF)}$_2$($\mathbf{1}^{2-}$)·2THF] (**3**). The X-ray diffraction study revealed the formation of the dianion of [6]CPP crystallized as a contact-ion complex with two potassium counterions (Fig. 3). The external K$^+$ ions bind to the opposite six-membered rings of [6]CPP^{2-} with the K···C$_{\mathrm{centroid}}$ distance of 3.177(2) Å. It can be noted here that exterior binding of potassium ions to the highly reduced [8]CPP^{4-} ring was accompanied by a shorter K···C$_{\mathrm{centroid}}$ distance of 3.059(6) Å.[12b] The coordination sphere of each K$^+$ ion is completed by one axial 18-crown-6 ether and one apical THF molecule. The corresponding K···O$_{\mathrm{THF}}$ and K··O$_{\mathrm{crown}}$ bond length distances of 2.7555(16) Å and 2.7808(13)–2.8799(13) Å are comparable with the previously reported values.[12b] Similar to **2**, two THF molecules occupy the inner cavity of the doubly-reduced [6]CPP anion (Fig. 3), showing propensity of its core for solvent encapsulation upon charging.

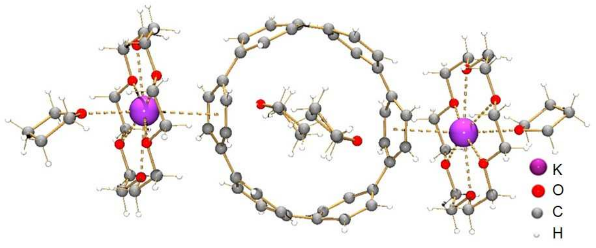
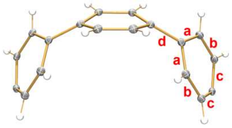


Fig. 3 Molecular structure of **3**, ball-and-stick model.

The addition of two electrons to [6]CPP along with the coordination of potassium ions resulted in a notable core transformation compared to $\mathbf{1}^0$ (Table 1). There are clear and systematic trends in the C–C bond length changes going from neutral [6]CPP to its mono- and doubly-reduced forms (in **2** and **3**, respectively). For example, the C–C bond connecting the six-membered rings shortens from 1.4897(18) in **1** to 1.440(3) in **3**. This result is consistent with enhanced quinoidal character similar to what is observed in the case of radical cations and dications for CPPs.[11a]

Table 1. Key C–C bond length distances in **1**–**3**



	[6]CPP **1**	[6]CPP^{1-} **2**	[6]CPP^{2-} **3**
a	1.4042(18)	1.416(3)	1.424(3)
b	1.3856(18)	1.378(3)	1.371(3)
c	1.4036(18)	1.415(3)	1.426(3)
d	1.4897(18)	1.463(3)	1.440(3)

In order to further follow the molecular structure transformation, three inner diameters of [6]CPP rings were measured for **1**–**3** (See ESI). The calculated deformation is systematically increasing from [6]CPP to the [6]CPP^{2-} form (Table 2, Fig. 4).

Table 2. Inner diameters of [6]CPP ring in **1**–**3** (see Fig. S8 for labeling)

	[6]CPP **1**	[6]CPP^{1-} **2**	[6]CPP^{2-} **3**
A (Å)	8.049	8.009	7.848
B (Å)	8.050	8.105	8.156
C (Å)	8.117	8.296	8.374
DP[a]	1.008	1.036	1.067

[a] DP (deformation parameter) = maximum/minimum diameter ratio

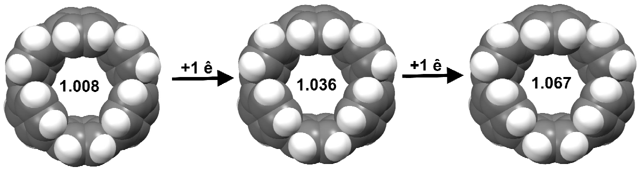


Fig. 4 Core transformation of **1** upon addition of one and two electrons, space-filling models of [6]CPP, [6]CPP^{1-}, and [6]CPP^{2-}.

Higher reduction states of **1** have been detected by UV-vis spectroscopy upon prolonged reaction time (see ESI for details). The quenching of the resulting solution with D_2O affords the tri- and tetradeuterio derivatives (*m/z* = 463.6 and 465.6, respectively) as the major products (ESI, Fig. S6), pointing out to the formation of tri- and tetraanionic states of **1** in the THF solution. So far, multiple attempts to crystallize the corresponding products have failed, as only non-diffracting precipitates were observed. Nevertheless, the first reported X-ray crystal structures of mono- and doubly-reduced products of [6]CPP allowed the first evaluation of core transformation upon reduction.

Conclusions

In summary, we have isolated and structurally characterized the first negatively charged forms of [6]CPP as well as crystallized the parent molecule under solvent-free conditions without any extraneous molecules. The latter exhibits unique crystal packing with decreased internal volume of the [6]CPP cavities, which were found to be filled by THF molecules in both reduced products. The structural analysis of the products ranging from [6]CPP to [6[CPP^{2-} revealed the carbon framework changes upon addition of one and two electrons, consistent with an increased quinoidal structure. We also demonstrated that the tri- and tetrareduced states can be generated for such a small cycloparaphenylene, highlighting its potential for multielectron storage. This study expands on the reduction, coordination and supramolecular limits of cyclic aromatic receptors and opens new perspectives for investigation of their highly reduced forms as novel π-ligands and hosts.

Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, X-ray diffraction data and refinement details, UV-vis and mass spectra. CCDC 1841065, 1841066 and 1841067. For ESI and crystallographic data in CIF or other electronic format, see DOI: /

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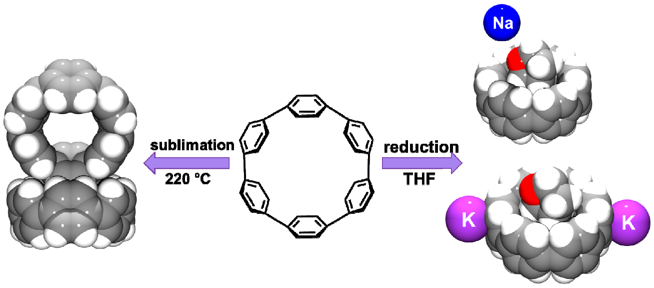

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