π-extended [12]cycloparaphenylene: from a hexaphenylbenzene cyclohexamer to its unexpected C₂-symmetric congener†

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The synthesis of π-extended [12]cycloparaphenylenes (CPP) derivatives from a kinked triangular macrocycle is presented. Depending on the reaction conditions for reductive aromatization, either a hexaphenylbenzene cyclohexamer or its C₂-symmetric congener was obtained. Their structures were confirmed by NMR spectroscopy or X-ray crystallographic analysis. With the support of DFT calculations, a mechanistic explanation for the unexpected formation of the oval shaped bis(cyclohexadiene)-bridged C₂-symmetric macrocycle is provided. The here employed congested hexaphenylbenzene mode of connectivity in conjunction with a non-strained precursor improves oxidative cyclodehydrogenation toward the formation of ultrashort carbon nanotubes (CNTs). Thus, this strategy can pave the way for new conceptual approaches of a solution-based bottom-up synthesis of CNTs.

Introduction
Carbon nanotubes (CNTs) have gained a great deal of attention over the last decades due to their attractive physical and electronic properties. Special emphasis has been put on the controlled synthesis of CNTs, since their electronic features sensitively depend on size and shape (edge structure, chirality). Cycloparaphenlenes (CPPs) are envisioned as precursors for a concise bottom-up synthesis of carbon nanobelts, i.e., ultrashort CNTs. On surfaces, CPPs besides other templates, have been successfully used for the growth of diameter-defined CNTs, whereas the advancement in solution-based approaches continues to be limited.

To reach this goal, several π-extended CPPs and structurally closely related derivatives have been synthesized over the last years. However, a necessary degree of axial π-extension of these structures, from a CPP to a nanobelt precursor (Fig. 1), was not accomplished to enable a solution-based bottom-up synthesis. In contrast, [9]cyclo-1,4-naphthylene and a [10]CPP dimer, are sufficiently π-extended and can thus be regarded as carbon nanobelt precursors, but dehydrogenation of the products was not reported.

Previously, we attempted a π-extension of CPPs using hexaphenylbenzene (HPB) as the general building block, which can be converted to hexa-peri-hexabenzocoronene (HBC) via oxidative cyclodehydrogenation. This concept has been widely employed for the bottom-up synthesis of 1D- and 2D-structures, such as graphene nanoribbons (GNRs) and nanographenes. To obtain π-lengthened CPPs (3D), HPB was embedded into a macrocycle to give a cyclic hexaphenylbenzene trimer ([3]CHPB) and its corresponding larger homologues. A further addition of phenyl rings afforded polyphenylene cylinders (PPCs), such as 1, following the parallelogram motif (frame A, Fig. 2). A complete cyclodehydrogenation could not be achieved. Thus, the macrocycles have been redesigned with a different connectivity, which is entirely based on the congested HPB motif (frame B, Fig. 2), where one bridging-phenylene moiety is shared by two hexaphenylbenzenes. This structural motif leads to a lower degree of rotational freedom of the attached phenyl groups, which is favorable for the desired cyclodehydrogenation.
Herein, we present the synthesis of PPCs that entirely consist of congested hexaphenylbenzene moieties. A congested cyclic hexaphenylbenzene hexamer ([6]CCHPB$_2$) and its oval-shaped C$_2$-symmetric congener 3 were synthesized via Suzuki coupling and subsequent reductive aromatization. The oxidative cyclo-dehydrogenation of both structures was investigated and a hitherto unprecedented degree of cyclodehydrogenation for PPC systems was achieved.

**Results and discussion**

For the synthesis of the new macrocycles [6]CCHPB 2 and 3 (Scheme 1), we applied a Suzuki-mediated cyclization introduced by Bertozzi and Jasti$^{3a}$ together with a strategy, developed in our group, to convert structurally related, linear polyphenylene (PP) precursors into GNRs,$^{12a,16}$ using oxidative cyclodehydrogenation. The oxidative cyclodehydrogenation of both structures was investigated and a hitherto unprecedented degree of cyclodehydrogenation for PPC systems was achieved.

![Fig. 2](image)

**Fig. 2** Two different modes of connectivity. Previous work (left): CNT synthesis via the parallelogram motif A (left) using [9]PPC 1 and [15]PPC (not shown); in this work (right): CNTs were approached via the congested HPB motif B.

As shown in Scheme 1, the unique “di-kinked” diboronate 7 and its “mono-kinked” counterpart 6 are synthesized via Suzuki coupling. For each approach, a fourfold excess of either diboronate 4 or dibromide 5 was used. Dibromide 6 and diboronate 7 could be obtained in yields of 35%, and 40% respectively. The macrocyclization of these two building blocks was achieved by Suzuki coupling in diluted media (0.1 mmol) to give 8 in 32% yield; side products such as higher linear homologues could be separated by recycling GPC.

An initial demethoxylation of 8 was achieved under reductive conditions that had previously been applied in our group: low-valent titanium was generated *in situ* and reacted with the triangular macrocycle 8 to give 2 in 46% (Scheme 2). The applied conditions are very effective at inducing reductive aromatization, but require elevated temperatures (80 °C). To unambiguously characterize cyclohexamer 2, 2D NMR experiments (Section 4.1, ESI†) were carried out. Single crystals of 2 were obtained after slow diffusion of MeCN into DCM. However, the obtained crystals did not yield sufficient reflections to resolve the structure.

Therefore, we performed density functional theory (DFT) calculations of 2 with the B3LYP hybrid functional$^{18}$ and the 6-31G(d) Pople basis set.$^{19}$ The fully optimized geometry revealed a torsional angle between neighboring phenylene units of about 90° (Fig. 3, right), in an alternating fashion within the CPP ring. Interestingly, in comparison to PPC 1 (Fig. 2, left), which is...
based on an odd membered CPP ring with an ellipsoidal structure, cyclohexamer 2 exhibits a circular-shaped structure.

In the second approach, a milder reduction of compound 8 with sodium naphthalenide (NaNp) (−78 °C vs. 80 °C) was attempted (Scheme 3). To our surprise, we did not obtain the expected [6]CCHPB, but rather a macrocycle containing four additional hydrogen atoms (Scheme 3). This was first indicated by the blue color of the reaction solution, hinting at the formation of anionic species, which can stem from an over-reduction of the cyclohexadiene moieties, as reported in the literature. Therefore, the reaction was quenched with a proton source (MeOH) to trap the charged intermediate, while the use of iodine to quench the reaction or lowering the temperature did not afford any characterizable product. By mass spectrometry, we inferred that the obtained structure possesses four additional hydrogen atoms in comparison to [6]CCHPB. We expected that the reductive aromatization had not overcome ring strain at temperatures of −78 °C, but rather came to a halt after in situ formation of a tetraanionic species, which was then preserved by protonation. For this structure, only one of the three 3,6-dimethoxycyclohexadienes was reduced, when applying the above described conditions to give one phenylene moiety instead of the expected three, as shown in Scheme 3. Astonishingly, single crystal X-ray crystallography (Fig. 5) revealed the formation of 3 instead of the expected structure 9.

The formation of 3 can be explained by taking into account the mechanistic details of the aromatization: a stepwise two-electron reduction is proposed in the literature, forming a radical under loss of one methoxy group. After the second one-electron transfer, a monoanion is formed, which leads to an expulsion of the remaining methoxy group under concomitant aromatization, affording a phenylene moiety from the previous 3,6-dimethoxycyclohexadiene. Based on the obtained product 3, we propose a mechanism via a tetraanionic species with subsequent charge migration. For this structure, only one of the three cyclohexadiene moieties was reduced, when applying the above described conditions to give one phenylene moiety instead of the expected three, as shown in Scheme 3. Interestingly, the tetraanion 10 was not found as a stable

![Scheme 3 Proposed reaction mechanism for the synthesis of 3. (a) NaNP, 1 h, −78 °C (THF); (b) −78 °C, H⁺.

Fig. 3 Optimized geometry of 2 top (left) and side (right) view, as calculated at the B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.
intermediate, but rather spontaneously evolved into the \( \text{C}_4^* \)
symmetric tetraanion \( 10c \). On the other hand, the neutral
counterpart of the anionic structures (namely \( 8a, 9 \), and \( 3 \); for all
structures the methoxy groups are substituted by hydrogen
atoms to reduce computational cost) were obtained as stable
structures. To account for the observed charge migration, we
compared the relative strain energies of structures. To account for the observed charge migration, we
compared the relative strain energies of structures the methoxy groups are substituted by hydrogen
atoms. Hydrogen atoms are omitted for clarity.

Fig. 4 Comparison of strain energies of \( 8a, 9 \), and \( 3 \), using DFT
calculations at the B3LYP/6-31G(d) level of theory. For all structures,
methoxy groups are substituted by hydrogen atoms. Hydrogen atoms
are omitted for clarity.

neutral structure) and \( 10c \) (tetraanionic intermediate) were
studied. The computed geometry optimization suggests an
increase of the oval opening from \( 8.2 \, \text{Å} \) to \( 12.2 \, \text{Å} \), respectively
(opening of the neutral structure \( 9 \) is \( 13 \, \text{Å} \)), which is shown in
Fig. 5. Thus, the equilibrium structure of the tetraanionic intermediate \( 10c \) is shifted toward \( 3 \) in comparison to \( 9 \). To
understand whether the strain release is accompanied by a
redistribution of charge over the entire aromatic system, a
charge analysis for \( 11 \) (2e\(^-\)) and \( 10c \) (4e\(^-\)) was performed: the
dianionic structure \( 11 \) is considered as a starting point and
shows that the charges are mainly localized over the cyclo-
hexadiene moieties where the hydrogen atoms have been
removed. For \( 10c \), the calculations reveal that the main part of the
charges (~2e\(^-\)) is strongly localized over the cyclohexadiene moieties of the macrocycle, while the remaining partial charges
(~2e\(^-\)) are delocalized over the substituted phenyl rings of the
belt (Fig. S16, ESI†), leading to an oval shaped macrocycle.
These findings additionally corroborate the postulated form of the
tetraanionic intermediate \( 10c \) in opposition to \( 10a \). The
proposed charge migration based on DFT calculations is also
supported for a dianionic species after formation of one phen-
ylene moiety (Fig. S10 and S15, ESI†). An over-reduction of [6]
CCHPB 2 to give the tetraanion \( 10c \), which can be trapped by a
proton source, has not been observed experimentally.

Single crystals of \( 3 \) were obtained after slow vapor diffusion
of MeCN into a solution of DCM. The crystal structure
confirmed the oval-shaped nature (Fig. 6) of \( 3 \). Pentaphenylene
units (labeled in red) are bridged by two 3,6-substituted

Fig. 5 Geometric analysis of structures \( 9, 10c, 11 \) and \( 3 \) to understand
the equilibrium structure of tetraanion \( 10c \), using DFT calculations at
the B3LYP/6-31G(d) level of theory. Structure \( 11 \) is twice negatively
charged at one cyclohexadiene moiety, whereas the other contains
two hydrogen atoms, analogously to the other structures.

Fig. 6 Crystal structure of \( 3 \). ORTEP drawing at 50% probability level.
All hydrogen atoms and solvent molecules are omitted for clarity.
Phenylene moieties are labelled in red. 3,6-Bridging cyclohexa-1,4-
dienes are labelled in blue. Front view (a) and top view (b).
cyclohexa-1,4-dienes (labeled in blue). The pentaphenylen moieties are slightly bent (Fig. 6b) as the sp²-carbons cannot be fully torn out of plane due to angle constraints (Fig. 3, ESIF). Additionally, the crystal structure reveals the inherent design pattern: tetraphenyl and tetraakis -(4-t-butylphenyl) substituents are attached to the central ring in an alternating fashion.

As compounds 2 and 3 were designed in order to serve as direct precursors for a solution-based bottom-up synthesis of CNTs, we subjected both molecules to oxidative cyclodehydrogenation conditions using FeCl₃ at room temperature.† For 2, a loss of 20 hydrogen atoms of a possible 96 was observed by MALDI-MS, at which the cyclodehydrogenation came to a halt, despite prolonged reaction times. In contrast to our previous results, here we could, for the first time, determine the degree of cyclodehydrogenation due to isotopically resolved mass peaks. For the barely strained C₂-symmetric congener 3, of the 96 hydrogen atoms to obtain a CNT a loss of 60 could be observed (see Scheme S3, † p. S92). The detailed analysis of the mass spectra hints at the formation of ribbon-like sidewall structures (Section 7.2, ESIF), rendering cyclodehydrogenation of the pentaphenylen sidewalls reasonable. However, since the structural analysis is based on mass spectrometry, well known side reactions for Scholl reactions, such as rearrangements, cannot be ruled out. Prolonged reaction times led to chloro-deuteriation (ESI†).

In summary, we presented the bottom-up synthesis of a [12]CPP based nanobelt precursor [6]CCHPB 2 and its unexpected weakly-strained C₂-symmetric congener 3. Their structural features are based on congested hexahyphenylene benzene units, i.e., two hexa-phenylenebenzenes are bridged by one shared phenylene unit. The surprising synthesis of 3 occurred due to the use of the milder reducing agent NaNp, whereas low valent titanium was applied for the synthesis of the congested HPB 2. We assume that two different products were obtained because of the high difference of thermal energy (ΔT 160 °C), giving rise to a kinetic control of the reaction. The mechanistic explanation for the astonishing charge migration during reductive aromatization of 3 was confirmed by DFT calculations. The inherent congested HPB structural feature leads to reduced rotational freedom for both macrocycles in comparison to the previously prepared PPCs such as 1. Finally, we attempted oxidative cyclodehydrogenation which resulted in a loss of 20 H and 60 H for 2 and 3, respectively. The higher loss for 3 may be assigned to the barely strained pentaphenylenebenzenes. The above discussed findings suggest that the oxidative cyclodehydrogenation runs more smoothly if (a) the congested HPB structural motif in comparison to the parallelogram approach is applied, as this mode of connectivity restricts rotation of the π-extended macrocycle, thus avoiding mismatched structural arrangements possible for 1 (parallelogram vs. trapezoid); and (b) a minimum of strain is present in the cyclic system, observed for 3 in comparison to 2. Thus, the synthesis of such non-strained precursors to 2, which is the base of cyclodehydrogenated close to the target structure and are then being converted to strained geometries could open up new concepts for a concise bottom-up synthesis of carbon nanobelts.

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