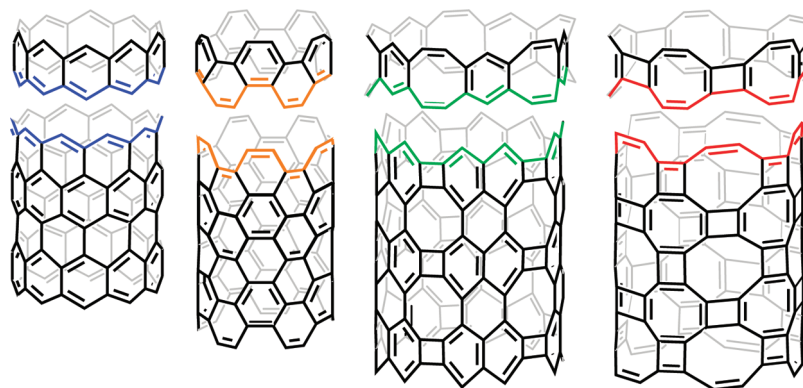


Cyclacenes: Hoop-Shaped Systems Composed of Conjugated Rings

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CONSPECTUS



A carbon nanotube, if it could be cut sideways at the end like a pipe, would yield beltlike structures. These subunits of carbon nanotubes, in their simplest manifestation as the $[6]_n$ cyclacenes, are composed of conjugated six-membered rings that are annelated, that is, made of a series of consecutively fused ring structures. These seemingly simple “one-benzene-thick” slices are of considerable interest as models—for electronic structure and spectroscopic properties, for example—for carbon nanotubes. In the late 1980s Stoddart and co-workers, soon to be followed by other groups, embarked on the synthesis of $[6]_n$ cyclacenes. The necessary curved shape of the belt was achieved with boat-shaped precursors for Diels–Alder reactions, namely, 7-oxanorborene derivatives. The preferred *endo*-addition in Diels–Alder reactions assured an efficient synthesis of beltlike systems containing 12 to 18 six-membered rings. However, the removal of the auxiliary oxygen centers to achieve $[6]_n$ cyclacenes as fully conjugated systems has failed so far: they remain an inaccessible target despite some 25 years of synthetic effort. Concurrently, theoretical studies revealed that $[6]_n$ cyclacenes as linearly annelated systems show small energy gaps between triplet and singlet states; they can thus be expected to be unstable species. Angularly annelated systems, on the other hand, were predicted to have large singlet–triplet splittings. Nakamura and co-workers and our laboratory have found ways around the obstacles to create cyclacenes. Nakamura and co-workers prepared the first angular annelated cyclacene by selective reduction of the north and south poles of C_{60} . We used a cyclic system that is fully conjugated and also adopts a boat conformation: cyclooctatetraene. By following this principle, we synthesized two types of linearly annelated cyclacenes: metal-stabilized four-membered rings alternating with eight-membered rings ($[4.8]_n$ cyclacenes), and six-membered rings alternating with eight-membered rings ($[6.8]_n$ cyclacenes). These new scaffolds, if extended along the molecular axis, would represent as-yet unknown forms of carbon nanotubes and are thus inviting synthetic targets. Calculations show that the incorporation of heteroatoms (S and NH) into these scaffolds is promising, encouraging the synthetic pursuit of thia- and azacyclacenes.

1. Introduction

According to Clar¹ the aromaticity of an annelated system of conjugated six-membered rings can be estimated by the number of aromatic sextets that can be drawn. For linearly annelated systems such

as naphthalene, anthracene (**1**), tetracene etc. only one “aromatic sextet” (symbolized by one circle in Figure 1) results and thus the polyalkene-character grows as the number of rings increases. Hence, larger acenes undergo cycloaddition reaction,

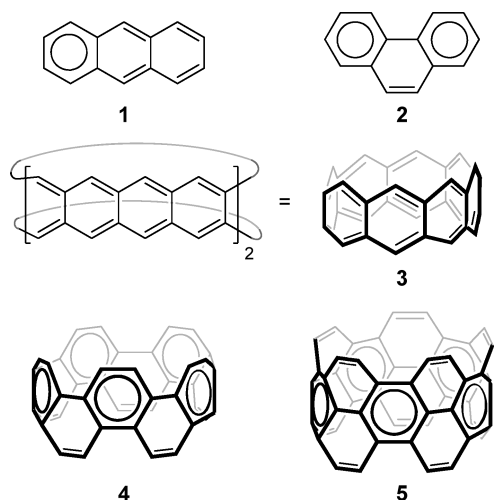


FIGURE 1. Clar's sextets in anthracene (**1**) and phenanthrene (**2**). [6]₈Cyclacene (**3**), showing no sextet, and cyclo[10]phenacenes **4** and **5** consisting of a central belt of cyclo-para-polyphenylene rings with double bonds connecting the ortho-positions on one or both sides, respectively.

thereby gaining more aromatic sextets. In conjugated π -systems, in which six-membered rings are annelated in an angular fashion such as phenanthrene (**2**) or pyrene, more than one "aromatic sextet" is possible, indicating increasing aromatic properties of angular versus linear systems.

When linear octacene with one aromatic sextet is bent into a belt by self-fusion, a hoop-shaped molecule containing eight six-membered rings results which we name [6]₈cyclacene (**3**)² (Figure 1). In this system no aromatic sextet can be drawn, indicating the properties of a conjugated polyolefin. In the case of angular annelation hoop-shaped molecules such as **4** or **5** result, which consist of central cyclo-paraphenylene belts³ (n]paraphenylenes)—with aromatic sextets—where the benzene rings are further connected by double bonds in the ortho-positions on one or both sides. This indicates a higher stability for **4** and **5** compared to the linearly annelated system **3**.

The interest in cyclacenes was revived when single-walled carbon nanotubes were prepared and their properties were studied.⁴ In Figure 2 we show for the case of $n = 10$ that [6] _{n} cyclacenes represent the smallest subunits of zigzag carbon nanotubes. The cyclacenes **4** and **5** (Figure 1) can be considered the smallest subunits of "armchair" carbon nanotubes (Figure 2).

2. Results of Calculations on [6] _{n} Cyclacenes and Congeners

[6] _{n} Cyclacenes and some angularly annelated congeners have been discussed since 1954 in connection with the conjugation in hoop-shaped π -systems.⁵ With growing accuracy of

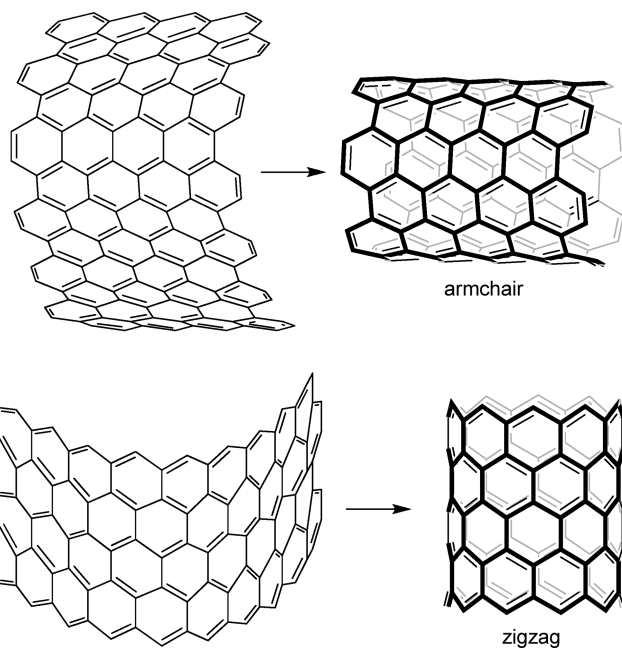


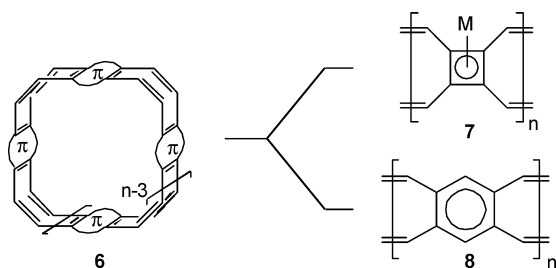
FIGURE 2. Single-walled carbon nanotubes resulting from rolling up of graphite sheets.

quantum chemical calculations more insights into [6] _{n} cyclacenes could be gained since then.⁶ The energy differences between open-shell singlet and triplet states were predicted to be rather small indicating a (bi)radical character for [6] _{n} cyclacenes with even numbers of n .^{6b,f} Another way of looking at [6] _{n} cyclacenes was shown by Houk et al., who pointed out that [6] _{n} cyclacenes can be considered as being composed of two weakly coupled trannulenes.^{6e}

More interesting to synthetic chemists are cyclacenes, in which benzene rings are annelated in a nonlinear fashion, such as **4** or **5** (Figure 1).^{6a,d,g} For both species theoretical investigations predict a singlet ground state with large energy differences between the frontier molecular orbitals (HOMO and LUMO). These predictions were made by Aihara who calculated the topological resonance energy (TRE)^{6a} of so-called cyclophenacenes such as **4**, by Türker using Dewar's AM1 method,^{6d} and by Nakamura based on DFT calculations.^{6g}

Our approach to cyclacenes makes use of different ring sizes apart from six-membered ones by incorporating cyclooctatetraene units in the belt together with six- or four-membered rings (Scheme 1). Calculations on the resulting [6.8] _{n} - and CpCo-capped [4.8] _{n} cyclacenes revealed them to be stable species with only little strain energy induced by the hoop shape.⁷ In the case of **8** the pentameric [6.8]₅cyclacene was predicted to have no strain energy at all compared to an unstrained system, and even the smallest congener with $n = 3$ only showed a destabilization of about 7 kcal/mol per subunit.

SCHEME 1. Construction of $[4.8]_n$ and $[6.8]_n$ Cyclacenes by Annelation of Four- and Eight-Membered Rings (**7**) and Six- and Eight-Membered Rings (**8**), Respectively



3. Synthesis of Unsaturated Belts with Six-Membered Rings as Building Blocks

Stereoregular Diels–Alder Oligomerization: Approach to $[6]_{12}$ Cyclacene.

Stoddart and his co-workers were the first to make use of a repetitive Diels–Alder reaction sequence suitable to build up a large beltlike system.^{2a} They took advantage of the π -facial diastereoselectivity observed for reactions of exocyclic *s-cis*-butadiene moieties, such as the 7-oxanorbornene derivative **9**, with dienophiles.⁸ This selectivity had been elucidated by assuming a π/σ mixing in the butadiene moieties leading to a disrotatory tilt of the second highest occupied π -MO (HOMO–1). Thereby the antibonding four-center four-electron interaction in the transition state of the Diels–Alder reaction is reduced.^{9,10} Consequently, the addition of two equivalents of **9** to the bisdienophile **10** (Scheme 2) afforded **11** in good yields.^{10–12} Furthermore, the intrinsic curved shape of the 7-oxanorbornene component is transferred to **11**. Addition of the bisdienophile **10** to **11** afforded system **12**, in which twelve six-membered rings are annelated so as to form a belt.^{10a} To get to $[6]_n$ cyclacene from **12** the six ether bridges have to be removed, and, second, four further double bonds have to be introduced. Stoddart and co-workers succeeded in transforming **12** into the deoxygenated compound **14** in two steps.^{10b} Heating of **12** with $\text{TiCl}_4/\text{LiAlH}_4$

introduced two further π -systems (rings 3 and 9), and from reacting the resulting **13** with Ac_2O and HCl octahydro- $[6]_{12}$ cyclacene (**14**) was gained. However, further experiments to introduce additional double bonds were not performed.^{2a,12}

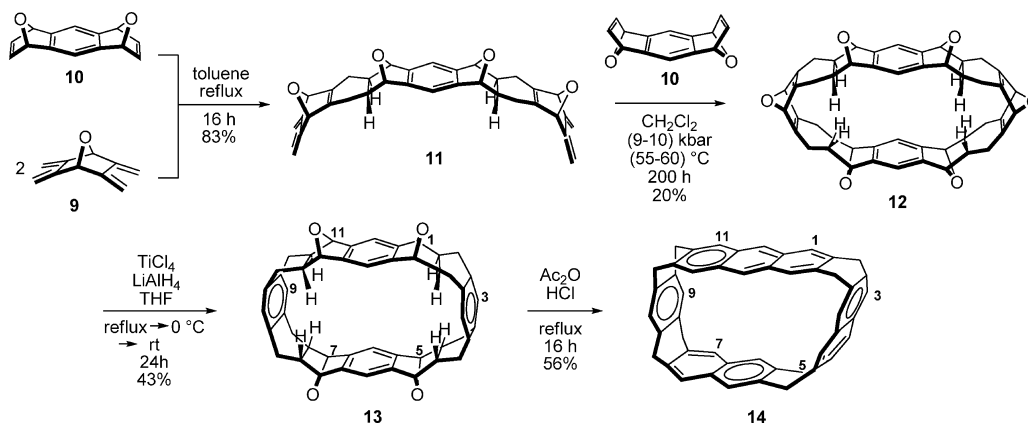
Two Component Diels–Alder Reaction: Approach to $[6]_8$ Cyclacene. A very quick approach to a belt consisting of eight linearly annelated six-membered rings was reported by Cory et al.¹³ The reaction of the bisdiene **15** with 1,4,5,8-anthraquinone (**16**) afforded belt **17** in remarkably good yields (Scheme 3).^{13a} Attempted conversions of **17** to a $[6]_8$ cyclacene failed.^{13b}

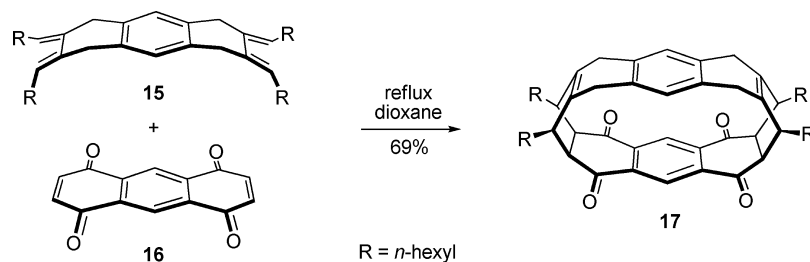
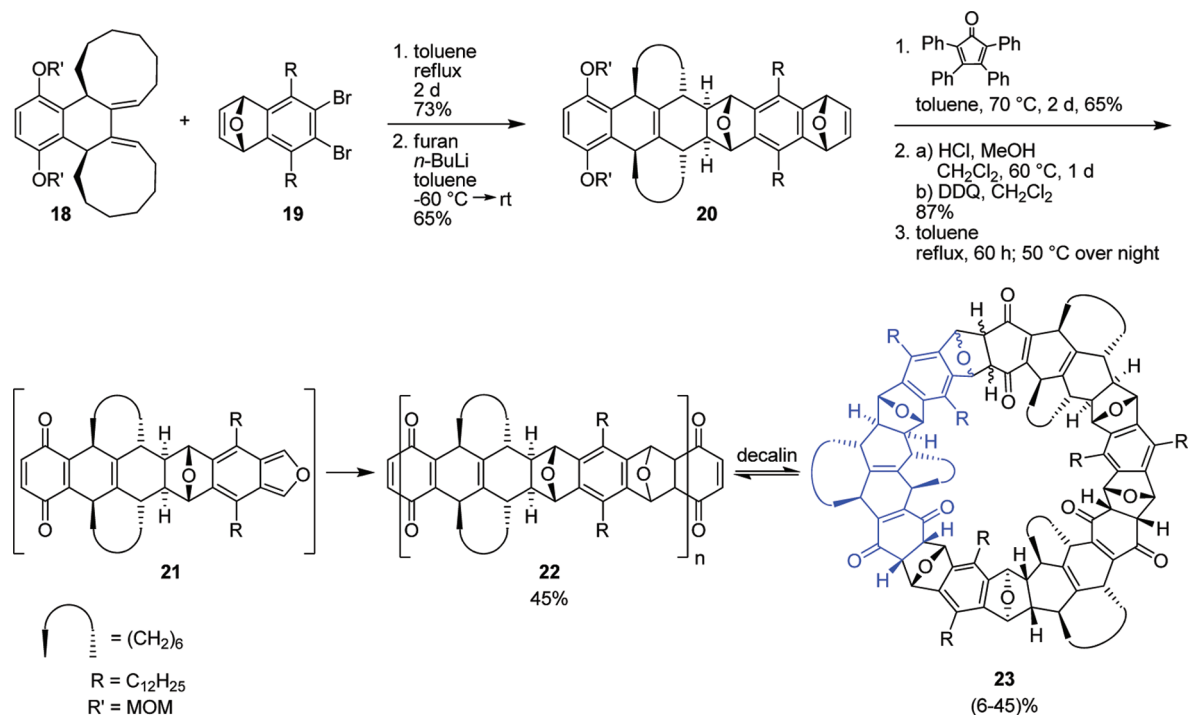
Synthesis of a Double-Stranded Cycle: Approach to $[6]_{18}$ Cyclacene.

Schlüter and co-workers used a three component Diels–Alder reaction to build up a beltlike system.^{14a} The starting point of the sequence given in Scheme 4 was the diene **18**, which is available from the dimer of cyclonona-1,2-diene and *p*-benzoquinone in three steps.^{14b} Reaction of **18** with the dienophile **19** followed by elimination of bromine in the presence of furan afforded **20**. A four-step sequence of heating with tetraphenylcyclopentadienone (tetracyclone), deprotection and oxidation of the hydroquinone moiety and final thermolysis in refluxing toluene led to **21**.^{14a} The linear system **21** comprises an electron rich diene on one end and a dienophilic double bond on the other and thus oligomerized under self-addition to **22** and the cyclic trimer **23**. The latter can be looked at as a precursor of $[6]_{18}$ cyclacene (Scheme 4).

The examples shown so far reveal that there are very efficient procedures available, which allow assembling beltlike scaffolds with various numbers of six-membered rings. But these experiences have also shown that there are two main obstacles in the synthesis of $[6]_n$ cyclacenes. The first of these requires bending a linear chain of annelated benzene rings into a hoop shape, which has been overcome by the prepa-

SCHEME 2. Synthesis of Octahydro $[6]_{12}$ cyclacene (**14**) by Stoddart and Co-Workers¹⁰



SCHEME 3. Synthesis of [6]₈Cyclacene Precursor **17** by Cory and Co-Workers.¹³SCHEME 4. Synthesis of [6]₁₈Cyclacene Precursor **23** by Schlüter and Co-Workers¹⁴

ration of beltlike precursors through Diels–Alder reactions with 7-oxanorbomadiene or 1,4-cyclohexadiene derivatives. The second obstacle is the high reactivity of [6]_{*n*}cyclacenes due to small singlet–triplet gaps predicted by quantum chemical calculations.^{6b,f} This latter fact might very well be one of the reasons for the failure to convert the beltlike precursors into fully conjugated systems so far.

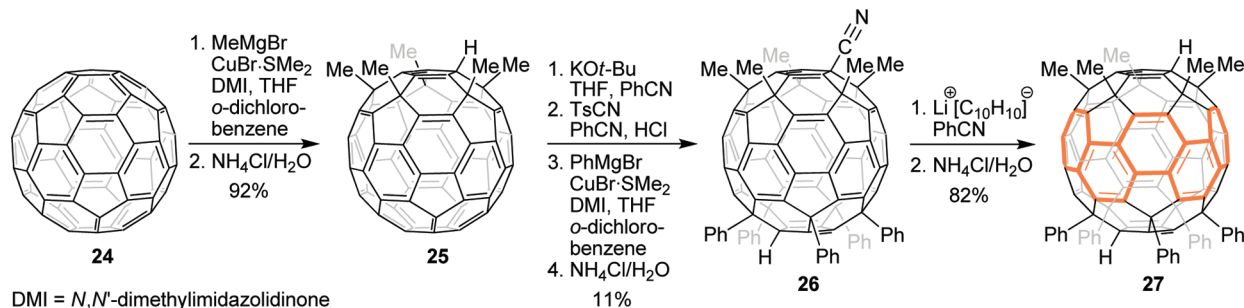
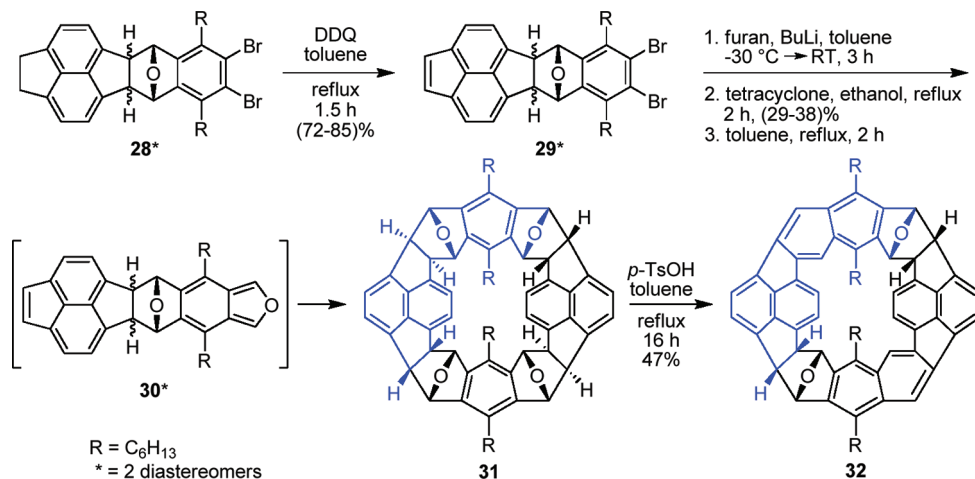
These obstacles can be circumvented in two ways: either a cage molecule containing an angular cyclacene as substructure is used as a starting point or such conjugated ring moieties are introduced in the belt that naturally adopt a boatlike conformation.

Synthesis of C₆₀-Embedded Cyclo[10]phenacene. The first approach was successfully carried out by Nakamura and co-workers¹⁵ who explored methods to reduce the north and south poles of C₆₀ (**24**). These attempts led to a cyclo[10]phenacene along the equator of C₆₀. The reduction of the north pole of C₆₀ was accomplished by reaction of

24 with an organocopper reagent generated from MeMgBr and CuBr · SME₂ (Scheme 5).

Before the south pole of the resulting **25** could be reduced, the acidic proton in the generated cyclopentadiene unit had to be replaced by a CN group. Afterwards an organocopper reagent prepared from PhMgBr and CuBr · SME₂ could be applied. Reductive removal of the cyano group yielded **27** having a cyclo[10]phenacene belt incorporated into the C₆₀ scaffold. The bond lengths determined in a derivative of **27** revealed only a small bond alternation in the [5]paraphenylene part of the cyclacene moiety.

Synthesis of a Double-Stranded Cycle: Approach to the Belt Region of C₈₄. Schlüter and co-workers also tried to circumvent the expected instability of a linear [6]_{*n*}cyclacene in a later work in which they aimed for the central belt of D₂-symmetrical C₈₄.¹⁶ In contrast to C₆₀, the belt region of C₈₄ contains both five- and six-membered rings. Scheme 6 summarizes this approach. For **28** as the starting material dihy-

SCHEME 5. Synthesis of C_{60} -Embedded Cyclo[10]phenacene **27** by Nakamura and Co-Workers¹⁵SCHEME 6. Synthesis of **32** as a Precursor for the Central Belt of D_2 -Symmetrical C_{84} by Schlüter and Co-Workers¹⁶

dropyracylene had to be prepared in a five-step synthesis and was reacted with 5,6-dibromoisobenzofuran in a Diels–Alder reaction (Scheme 6).^{16a}

Oxidation of the diastereomeric mixture (*endo*, *exo*) yielded **29**. This was then—analogously to the sequence in Scheme 4—converted to intermediate **30** by generating a dehydrobenzene intermediate in the presence of furan, followed by reaction with tetracyclone. The subsequent thermolysis yielded **30** as an *endo*–*exo* mixture of two diastereomers with an electron rich diene on one end and a dienophilic double bond on the other end. As anticipated **30** dimerized to **31**, whose structure was confirmed by an X-ray structural analysis. Aromatization experiments on **31** led to the removal of two equivalents of H_2O ; further experiments to convert **32** into a fully conjugated system failed.^{16a–d}

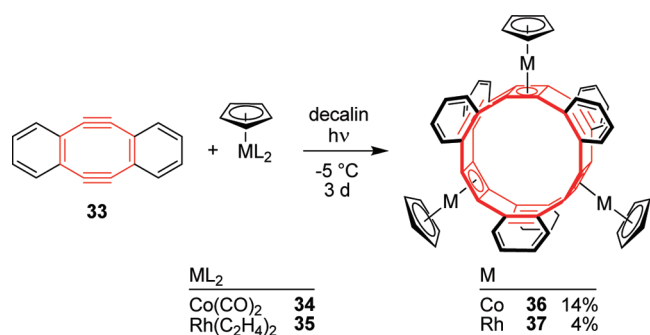
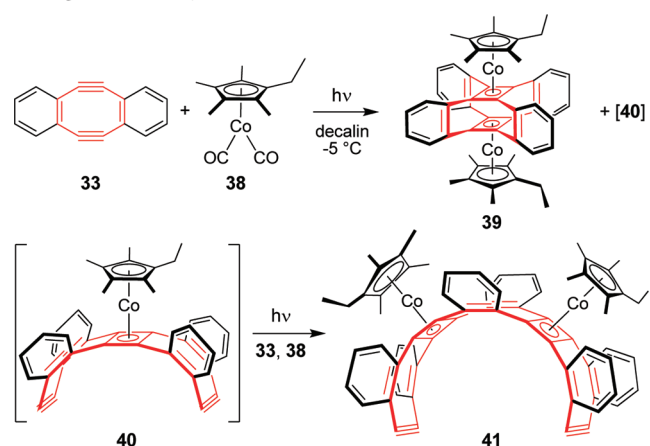
4. Syntheses and Properties of [4.8]_n- and [6.8]_nCyclacenes

In our approach to synthesize linearly annelated conjugated belts we incorporated a cyclooctatetraene moiety as building block utilizing the observation that cyclooctatetraene prefers a boat conformation. Our concept of combining eight-mem-

bered with four- and six-membered rings is shown in Scheme 1 leading to cyclic oligomers of **7** and **8**.^{2e}

[4.8]₃Cyclacenes: Composed of Four- and Eight-Membered Rings. In view of earlier results on oligomerization reactions with cycloocta-1,5-diyne derivatives and $CpCo(CO)_2$ ¹⁷ we first tried to prepare 1,5-cyclooctadiyne derivatives with one leaving group in each of the aliphatic bridges. However, so far we were not successful with this strategy. In our second approach we irradiated tetrahydrodibenzo-*[a,e]*cyclooctatetraene (**33**) in the presence of $CpCo(CO)_2$ (**34**) and received the cyclacene **36** in a one-pot reaction (Scheme 7). By varying the substituents in the Cp ring (CO_2Me , $SiMe_3$, $(CH_3)_5$, $(CH_3)_4C_2H_5$) further derivatives were obtained.^{18a}

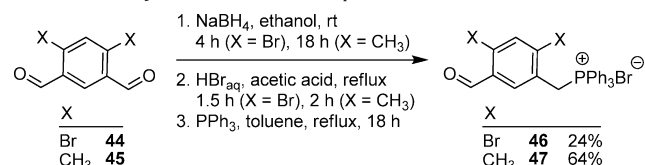
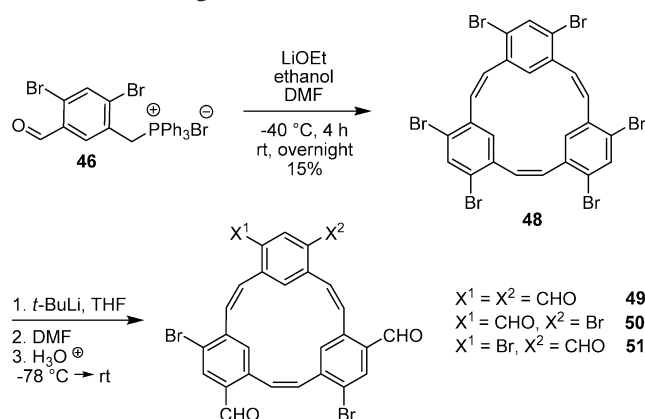
The reaction could also be extended to the corresponding $CpRh$ -capped [4.8]₃cyclacene derivatives.^{18b} In the case of the rhodium species the cyclopentadienyl ring was substituted by $SiMe_3$, $COCH_3$, CO_2CH_3 , $(CH_3)_5$, and Cl . X-ray crystallographic investigations on **36**, **37**, and their substitution products revealed a central scaffold with a diameter of 4.5 Å (average). The mean angle between the plane of the CpM-capped cyclobutadiene rings and the adjacent phenyl rings amounts to 63°–65°. Neglecting the bending of the cyclobutadiene

SCHEME 7. Synthesis of Cyclacenes **36** and **37** by Gleiter and Co-Workers¹⁸**SCHEME 8.** Intermediates in the Trimerization Reaction of **33** Leading to a [4.8]₃Cyclacene^{18b}

ring and assuming that the overlap of the p-orbitals between the benzene units and the adjacent cyclobutadiene centers is directly proportional to the cosine of the angle between them, 40% to 45% conjugation can be expected for the cyclacene torus.

To unravel the reaction mechanism of the one-pot reaction shown in Scheme 7 the crude product of the reaction between [(*η*⁵-tetramethylethyl)cyclopentadienyl]cobalt (**38**) and **33** was investigated by means of mass spectrometry (Scheme 8).

Evidence (HRMS data) was found for the existence of **39** and **41** besides the cyclacene. To separate intermediate **41** from the cyclacene (equal *R_f* values) the mixture was reacted with two equivalents of methylrhenium trioxide, complexing both triple bonds of **41**. The resulting complex was isolated and fully characterized. An X-ray structural analysis confirmed the *syn*-configuration of both triple bonds as shown in the formula. The distance between the triple bonds in the (methyl-dioxo)rhenium adduct amounts to 4.1 Å.^{18b} This close proximity of the complexed triple bonds is due to a strong bending of the central COT unit and almost planar conformations of the peripheral COT units. The short distance between

SCHEME 9. Retrosynthetic Approach to [6.8]₃Cyclacene (**42**)**SCHEME 10.** Synthesis of the Phosphonium Bromides **46** and **47**¹⁹**SCHEME 11.** Synthesis of Bromo-Substituted Metacyclophanetriene **48** and Br/Li Exchange^{19b}

the complexed triple bonds explains why the formation of the trimeric cyclacene is favored over that of the tetrameric congener although the latter was calculated to be less strained (9 kcal/mol per subunit compared to 18 kcal/mol for the trimeric cyclacene).⁷

[6.8]_nCyclacenes: Composed of Six- and Eight-Membered Rings. To select a reasonable synthetic path to [6.8]_ncyclacenes we were spoiled for choice between a multi-component one-pot reaction and a stepwise procedure. Looking for ways to accomplish a one-pot reaction we explored routes to synthesize 1,2,4,5-substituted benzenes with differently functionalized groups at the 1,2- and 4,5- or 1,5- and 2,4-positions.^{19b} Our experience was that the overall yields for such starting materials were low. Therefore we concentrated on a stepwise procedure. On this route we took benefit from the work of Wennerström and co-worker,^{20a} Oda and co-workers,^{20b} and Iyoda and co-workers^{20c} from their studies on *meta*- and *ortho*-cyclophanetrienes and higher oligomers. Our retrosynthetic concept is illustrated in Scheme 9 with [6.8]₃cyclacene (**42**) as target.

In a first retrosynthetic step we disconnected three double bonds leading to a metacyclophanetriene derivative with two

functional groups at each benzene ring, *ortho*-positioned to the double bonds, e.g. **43**. The latter system might be prepared from the isophthalic aldehydes **44** or **45** with differently functionalized groups at the 1,5-positions as shown in Scheme 9. For X we chose either Br or CH₃, because both substituents can be transformed into an aldehyde at a later stage of the synthesis. Starting materials for our synthesis of *o,o'*-hexabromo[2₃]metacyclophanetriene (**48**) and *o,o'*-hexamethyl[2₃]metacyclophanetriene (**53**) were 4,6-dibromoisophthalic aldehyde (**44**) and 4,6-dimethylisophthalic aldehyde (**45**) (Scheme 10).¹⁹

The selective reduction of one aldehydic group in **44** and **45** to the corresponding alcohols was achieved with less than one equivalent of NaBH₄. Subsequent treatment with HBr followed by reaction with triphenylphosphane yielded the desired phosphonium bromides **46** and **47**, respectively (Scheme 10).

A self-Wittig reaction of **46** at low temperature yielded the desired product **48** in the *all-Z* configuration as the main product. Br/Li exchange with *tert*-butyllithium followed by quenching with dry DMF did not yield the desired hexaformyl substituted **43** but a mixture of **49–51** (Scheme 11).^{19b} Therefore an alternative path to **43** was explored. Utilizing an intermolecular Wittig reaction of **47** afforded the *E,Z,Z* configured *o,o'*-hexamethyl[2₃]metacyclophanetriene (**52**) as main product, and the *all-Z* configured **53** as minor product. The isomerization of **52** into the desired *all-Z* product was accomplished by irradiation (Scheme 12).¹⁹

NBS bromination transformed **53** into hexakis(bromomethyl)[2₃]metacyclophanetriene (**54**) in 40% yield (Scheme 13). To modify **54** into the hexaformyl[2₃]metacyclophanetriene (**43**) we first hydrolyzed **54** to the hexahydroxy derivative which was then oxidized by 2-iodoxybenzoic acid (IBX) to **43**. This route was abridged by a direct oxidation of **54** with IBX.

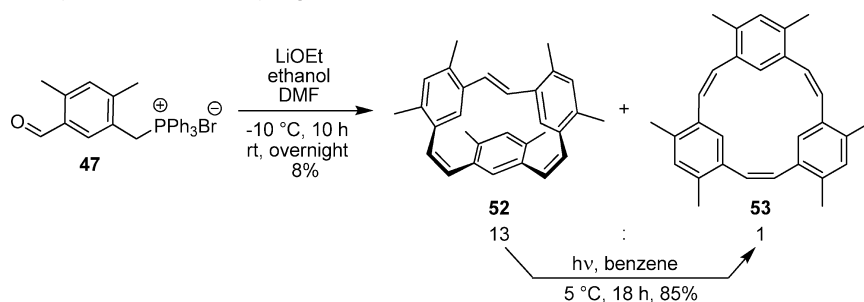
Now the stage was set for the ring closure of **43** to cyclacene **42**. In this step a McMurry coupling reaction using low valent titanium in refluxing DME was successful and yielded [6.8]₃cyclacene (**42**).¹⁹

An X-ray crystal structure confirmed the anticipated *D*_{3h} symmetry of **42** (Figure 3). In **42** the mean angle between the plane of the double bonds and that of the adjacent aromatic rings amounts to 72°. This indicates about 31% conjugation for the cyclacene torus.²¹ The crystal packing of [6.8]₃cyclacene (**13**) in the solid state is shown in Figure 3. The molecules are stacked in piles on top of each other building molecular tubes. We found that CH/π interactions contribute to the molecular arrangement in the solid state. Cyclacene **42** represents the smallest and most strained member of the [6.8]_ncyclacene family. Smaller bending angles are predicted for larger [6.8]_ncyclacenes.⁷ The synthetic principle of a stepwise ring closure should be applicable in their syntheses.^{19b}

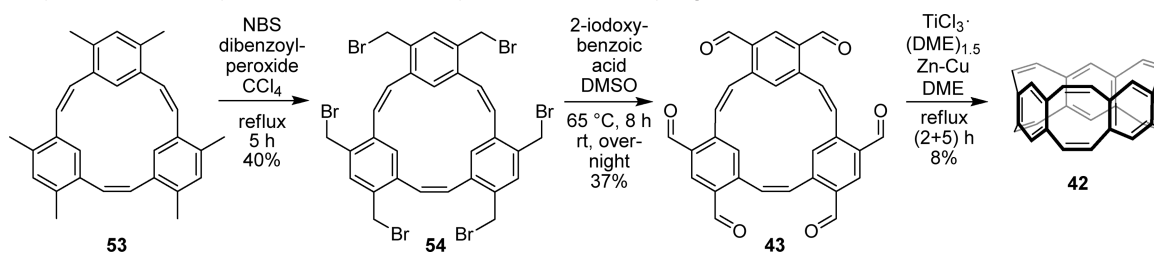
5. Heterocyclacenes

The concept of incorporating eight-membered rings into cyclacene structures can be widened to heteroanalogous systems.

SCHEME 12. Synthesis of Methyl Substituted Metacyclophanetriene **53**¹⁹



SCHEME 13. Synthesis of [6.8]₃Cyclacene (**42**) from Methyl Substituted Metacyclophanetriene **53**¹⁹



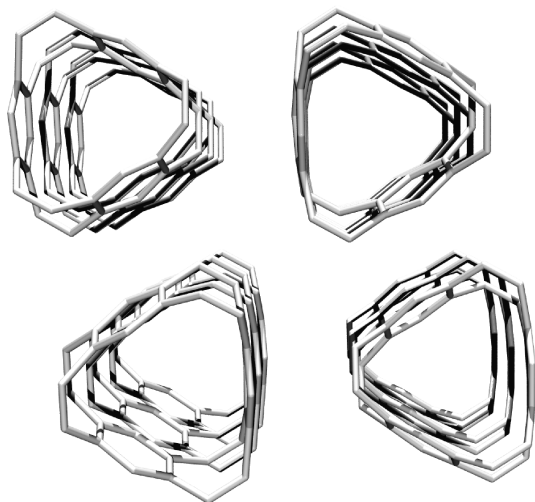


FIGURE 3. Molecular structure and packing of [6.8]₃cyclacene (**42**) in the solid state. Hydrogen atoms are omitted for clarity.¹⁹

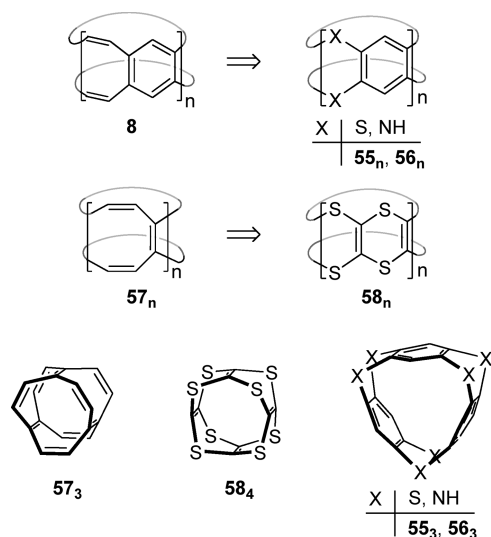


FIGURE 4. Replacement of double bonds in **8** and **57_n** by S and NH-groups: **55_n**, **56_n**, and **58_n**, [8]_ncyclacenes **57_n**, and schematic drawings of **57₃**, **58₄**, **55₃**, and **56₃**.²²

We recently carried out model calculations on novel types of cyclacenes which incorporate thia- and aza-atoms.²² Divalent sulfur atoms or NH-groups provide an electron pair, and thus cyclooctatetraene rings can be replaced by 1,4-dithiin or 1,4-dihydropyrazine units without the π -electron count being altered. This concept is illustrated in Figure 4 where we have also shown **57_n** as a cyclacene composed of annelated eight-membered rings only.

Our model calculations on **55_n**, **56_n**, **57_n**, and **58_n** revealed them to be electronically stable species. The structures have little strain energy and provide large cavities with donor groups (apart from **57_n**), that partly point inside the cavities.

6. Summary and Outlook

As carbon nanotubes are of growing interest and importance, cyclacenes representing their smallest subunits have gained new interest. Several calculations and a number of synthetic efforts to prepare [6]_ncyclacenes suggest that they are not very stable at ambient conditions. On the look for stable cyclacenes we have shown three options. Angularly annelated cyclacenes, such as cyclo[n]phenacenes, have theoretically been predicted to be stable species, and the synthesis of a C₆₀-embedded cyclo[10]phenacene by Nakamura and co-workers¹⁵ has brought experimental evidence. Second, we have shown theoretically and experimentally that new types of cyclacenes incorporating eight-membered, unsaturated rings in their belt are stable species. With the syntheses of [6.8]₃cyclacene and metal stabilized [4.8]₃cyclacenes two new types of cyclacenes have been made synthetically accessible. An expansion of the [4.8]_n- and [6.8]_ncyclacene scaffold in the direction of the principal molecular axis leads to new types of carbon nanotubes whose molecular patterns comprise four-, six- and eight-membered rings. They represent yet unknown types of carbon nanotubes and are promising targets to investigate. Third, heteroatoms, such as S or NH, can provide an electron pair and thereby substitute for CC-double bonds and open up a new field of stable cyclacenes. Our calculations have shown examples of such thia- and azacyclacenes. We hope that this Account may encourage the search for and syntheses of new and stable cyclacenes.

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BIOGRAPHICAL INFORMATION

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FOOTNOTES

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