

# Synthetic approaches to aromatic belts: building up strain in macrocyclic polyarenes

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This *tutorial review* discusses synthetic strategies towards aromatic belts, defined here as double-stranded conjugated macrocycles, such as  $[n]$ cyclacenes,  $[n]$ cyclophenacenes, Schlüter belt, and Vögtle belt. Their appeal stems, firstly, from the unique nature of their conjugation, having p orbitals oriented *radially* rather than perpendicular to the plane of the macrocycle. Secondly, as aromatic belts are model compounds of carbon nanotubes of different chiralities, a synthetic strategy towards the buildup of structural strain in these compounds could finally open a route towards rational chemical synthesis of carbon nanotubes. The elusiveness of these compounds has stimulated fascinating and ingenious synthetic strategies over the last decades. The various strategies are classified here by their approach to the buildup of structural strain, which is the main obstacle in the preparation of these curved polyarenes.

## 1. The quest for aromatic belts: introduction

Aromatic belts (Fig. 1) have been challenging the chemical community for several decades.<sup>1</sup> They belong to a unique class of conjugated macrocycles that are interesting because of their radially oriented p orbitals. However, it is not only the aesthetic appeal and remarkable elusiveness of aromatic belts that has captivated the imagination of synthetic chemists. Rather, it is the possibility that their preparation could open the way to a rational chemical synthesis of carbon

nanotubes.<sup>2,3</sup> This fundamental objective is next in line after the first rational synthesis of [60]fullerene in 2002.<sup>4</sup> Almost twenty years after nanotubes have been discovered,<sup>5</sup> they are still being extracted from soot, rather than prepared with desired chirality in a designed synthesis. Mastering the buildup of structural strain in aromatic belts might suggest a rational synthetic plan towards carbon nanotubes, which, in turn, could open up new opportunities towards the study and application of these unique carbon compounds.

Theoretical chemists have been the first to set their sights on aromatic belts. Heilbronner studied the orbital structure in the hypothetical  $[n]$ cyclacenes (e.g., **1**) in 1954,<sup>6</sup> and theoretical investigations of aromatic belts continue to this day.<sup>7,8</sup> These calculations aim at understanding the role of conjugation and aromaticity in systems with radially oriented p orbitals. In

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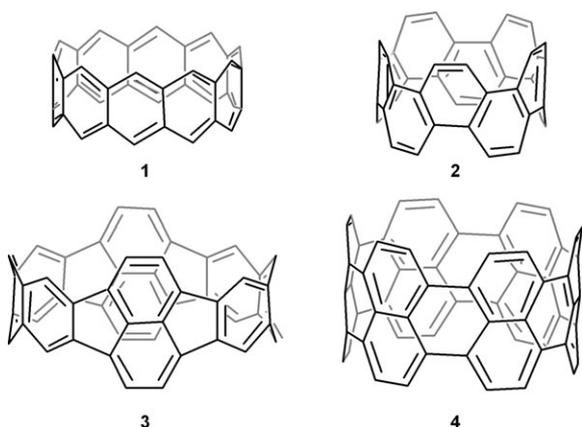
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Roy Shenhar (born 1971 in Israel) received his BSc in Chemistry and Computer Science in 1995 and his PhD in 2002 from the Hebrew University of Jerusalem. His graduate work (with Mordecai Rabinovitz and Itamar Willner) concentrated on aggregation and photophysical phenomena in highly charged polycyclic aromatic hydrocarbons. After 3 years as a Fulbright post-doctoral fellow with Vincent Rotello at the University of Massachusetts-Amherst and another year as a Zeff fellow with Nir Tessler at the Technion, he started his independent lab at the Institute of Chemistry of the Hebrew University. His research centers on the development of polymer-based self-assembly methods for nanotechnological applications, which includes the creation of novel supramolecular polymers.



**Fig. 1** Examples of aromatic belts: [10]cyclacene (**1**), [10]cyclophenacene (**2**), Schlüter belt (**3**) and Vögtle belt (**4**).

addition, the interplay of strain and aromaticity in these compounds is expected to shed light on special properties of fullerenes and carbon nanotubes.

The electronic properties of aromatic belts are also of interest to material scientists.<sup>9</sup> Their predicted photo- and electroluminescence properties are expected to lead to devices that are tunable and exhibit special photophysical properties. Furthermore, the tubular shape and the expected difference in reactivity between the concave and convex sides of these belts might be used in different applications such as cation hosts or in affinity chromatography of fullerenes.<sup>10</sup>

The quest towards double-stranded, conjugated macrocycles (Fig. 1) has been accelerating recently, as the nature of the obstacles has become clearer and new creative solutions have been brought forward. The synthetic targets range from [n]cyclacenes (*e.g.*, **1**) and [n]cyclophenacenes (*e.g.*, **2**), which represent the thinnest slices of zigzag and armchair nanotubes,



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respectively, to equator regions of fullerenes (*e.g.*, **3**) and other sections of carbon nanotubes (*e.g.*, **4**). Fascinating breakthroughs have been made in the last five years towards novel derivatives of aromatic belts, and while none of the compounds in Fig. 1 has been prepared yet, this goal seems closer than ever.

This review is limited to *double*-stranded macrocycles, and does not cover the numerous approaches and successes towards the closely related *single*-stranded conjugated ‘nano-hoops’, such as the [n]cycloparaphenylene and [n]cycloparaphenylenethynylene series.<sup>1,2,11</sup>

## 2. The main obstacles: reactivity and strain

### 2.1 High predicted reactivity of [n]cyclacenes

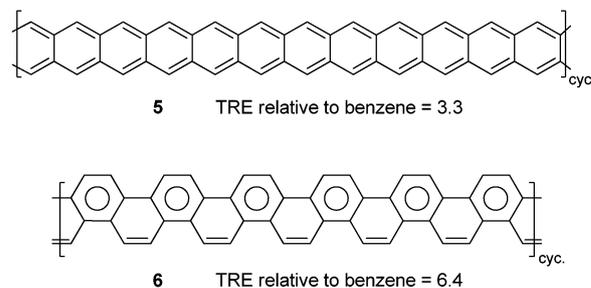
Early synthetic attempts towards [n]cyclacenes (Section 3) were hindered both by their highly strained structures (Section 2.2) and high expected reactivity, stemming from the small singlet–triplet energy gaps.<sup>7</sup> Other aromaticity indices, such as topological resonance energy (TRE) relative to benzene,<sup>12</sup> support the hypothesis that [n]cyclacenes are less stable than [n]cyclophenacenes (Fig. 2).<sup>13</sup> Analysis of Clar structures<sup>14</sup> shows that no isolated sextets can be identified in [n]cyclacene,<sup>13</sup> while  $n/2$  aromatic sextets are present in the Clar structure of [n]cyclophenacene (Fig. 2), thus underlining the higher stability of the latter.

### 2.2 Building up strain—classification of approaches

The first and foremost challenge in the synthesis of aromatic belts is bending the arene skeleton. All synthetic strategies that have been applied so far can be divided into two classes: (i) those that take up the challenge of building up the enormous structural strain, which is inherent to aromatic belts, during the synthetic pathway (Sections 3 and 4), and (ii) those that devise ways of avoiding it, by preparing clever derivatives of double-stranded, conjugated macrocycles (Sections 5 and 6).

Two general strategies can be further identified in the first approach. The first strategy focuses on constructing a double-stranded, yet partially saturated macrocycle, and attempting to further aromatize it completely (Section 3). The second strategy centers on preparing a single-stranded, conjugated macrocycle, and trying to ‘stitch up’ the fjord regions (Section 4). At the time of writing this review, neither strategy has been successful.

The second principal approach avoids the necessity of building up strain during the reaction. So far, two elegant



**Fig. 2** Clar structures with TRE values for [12]cyclacene (**5**) and [12]cyclophenacene (**6**).

solutions have been realized. The first solution concentrates on incorporating a naturally convex, and yet conjugated, structural element into the belt—such as a boat-like cyclo-octatetraene—to give an unusual and unstrained aromatic belt (Section 5). The second strategy exploits the structural strain already present in a strained precursor, *e.g.*, [60]fullerene, followed by selective destruction of the conjugation at the poles, leaving an isolated aromatic belt along the equator (Section 6).

The present review recounts the synthetic efforts towards aromatic belts along this four-fold classification, in an approximately chronological order.

### 3. First strategy: aromatization of a double-stranded belt

The first conceptual approach to aromatic belts started at the design and synthesis of a double-stranded, partially saturated macrocycle, and continued with the attempt to aromatize it completely.

#### 3.1 From double-stranded macrocycles towards cyclacenes

Stoddart and coworkers have explored the following approach towards [*n*]cyclacenes. They prepared double-stranded and saturated belts using bifunctional monomers in a repetitive Diels–Alder oligomerization (Scheme 1).<sup>15</sup> They dubbed their general method ‘substrate-directed synthesis’, or, more playfully, ‘molecular LEGO<sup>®</sup>’, underlining the useful stereoselectivity of the Diels–Alder methodology. The monomers, a bisdiene (such as **7**) and a bisdienophile (such as **8**), contained oxygen bridges for two reasons: (1) to enforce curvature and rigidity in the monomers, and thus to facilitate the formation of a belt with a set size; (2) to achieve complete aromatization of the belt in further steps by removal of these bridges, which is known to be facile in planar compounds.

The first double-stranded macrocycle prepared in the Stoddart group in 1987 was kohnkene (**10**),<sup>16</sup> a hexaepoxyoctacosahydro-derivative of [12]cyclacene (**6**). The Diels–Alder reaction was performed for 12 h in refluxing toluene, and produced two intermediates: the 1 : 1 and 2 : 1 adducts of **7** and **8**. Kohnkene could be prepared from either of them, but the reaction of the 2 : 1 adduct (**9**) with bisdienophile **8** (Scheme 1), catalyzed by high pressures in the liquid phase, resulted in higher yields (20%).

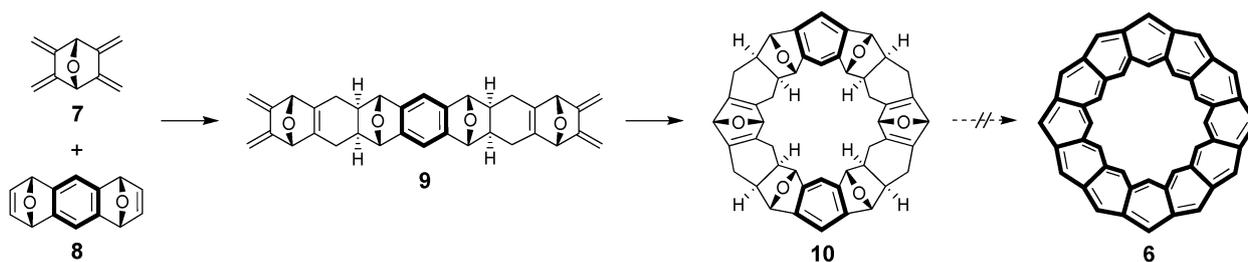
Attempts at aromatizing kohnkene have only been partially successful (Scheme 2).<sup>17</sup> At the first step, two oxygen bridges could be removed from **10** by deoxygenation with TiCl<sub>4</sub>/LiAlH<sub>4</sub>, affording **11**. Later, the four remaining ‘water’

molecules were removed from the skeleton (each ‘water’ molecule consisted of the oxygen bridge and the two adjacent hydrogens), resulting in **13**. The expected dehydration product was **12**, with two anthracenic and two benzenic aromatic fragments, but apparently one anthracene moiety underwent rearrangement to afford **13**, which consists of only one anthracenic, two naphthalenic, and one benzenic fragments. The rearrangement served to decrease the macro-ring strain energy in the belt, demonstrating for the first time the main obstacle associated with this general strategy: overcoming the buildup of strain energy that is inherent in aromatizing a double-stranded macrocycle. Attempts have been made to aromatize **13**,<sup>18</sup> using different dehydrogenating reagents such as Pd/C, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil) under different reaction conditions. However, they were all unsuccessful.

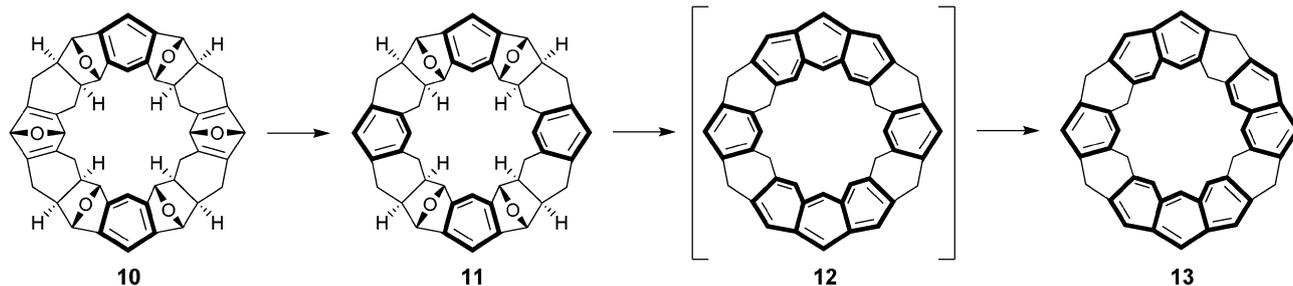
Variations of the monomers allowed for the preparation of other double-stranded macrocycles. For example, a larger belt that can be viewed as a derivative of [14]cyclacene, or a belt with methylenes replacing the oxygen bridges.<sup>19</sup> However, the ‘angular’ belt (**15**, Scheme 3), prepared from the angular monomer **14**, was the most promising for aromatization.<sup>20</sup> The angular monomer **14** features [a,c]-fused six-membered rings, which were known to increase stability in polyacenes,<sup>15</sup> rather than the previously discussed [a,d]-fused rings in monomer **8** (Scheme 1). Thus, the preparation of **17** was meant to avoid an obstacle in [*n*]cyclacene synthesis, namely their theoretically predicted high reactivity. In addition, **17** was expected to be more aromatic than **6**, based on Hückel rules.<sup>15</sup> [12]Cyclacene **6** can be viewed as consisting of two [24]annulenes joined by 12 σ-bonds, while **17** is made of two annulenes, similarly connected, but with a Hückel number of π electrons in each (22 and 26). However, aromatization of the ‘angular’ belt **15** did not proceed past **16**, the product of double deoxygenation with TiCl<sub>4</sub>/LiAlH<sub>4</sub>, analogous to that of **10**. Further attempts to dehydrate **16** to give belt **17** have also failed.

#### 3.2 Attempted synthesis of [8]cyclacene using flexible monomers

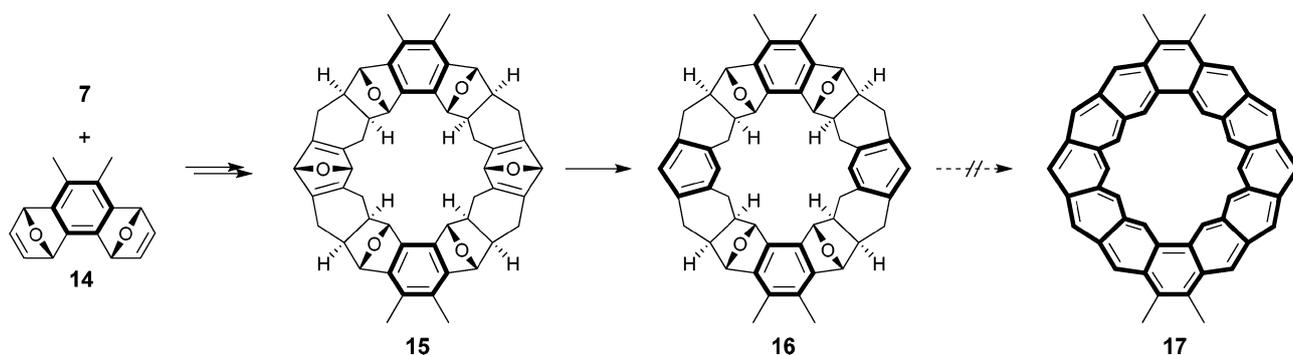
In 1996, Cory proposed a different synthetic strategy for macrocyclic belts, in an attempt to furnish [8]cyclacene.<sup>21</sup> Cory’s strategy was also based on bifunctional monomers in a double Diels–Alder macrocyclization, but unlike Stoddart’s rigid monomers, featuring a curvature that leads to a belt of predetermined size, a flexible monomer was employed. The flexibility allowed for a more ‘natural’ size for the belt, with



Scheme 1 Synthesis of kohnkene (**10**), a precursor of [12]cyclacene (**6**).



Scheme 2 Partial aromatizations of kohnkene (**10**).

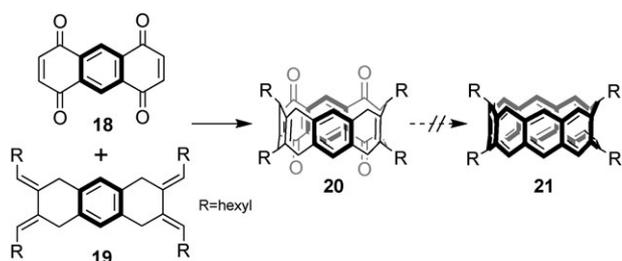


Scheme 3 Synthesis and partial aromatization of an 'angular' kohnkene (**15**), aiming at aromatic belt **17**.

the lower strain making it, theoretically, more susceptible to aromatization.<sup>22</sup>

The reactants were a rigid bisdienophile, diquinone **18**, and a flexible bisdiene, **19** (Scheme 4).<sup>21</sup> Diels–Alder cycloaddition was found to favor macrocyclization over polymerization when separate solutions of **18** and **19** were slowly added simultaneously to refluxing dioxane, producing **20** in 69% yield.

Three attempts to aromatize **20** were reported, all with partial success (Scheme 5).<sup>23</sup> Firstly, dehydrogenation of **20** with DDQ in benzene afforded **22** in 95% yield. Thus, the aromatic nucleus was increased by a single ring, from benzene to naphthalene. Another aromatization scheme began with epoxidation of **20** with *m*-chloroperoxybenzoic acid (MCPBA, 90% yield), followed by dehydration using *p*-toluenesulfonic acid (PTSA) in refluxing benzene. However, the formation of an anthracene unit (**24**) was avoided. Instead, the interesting bisdiene **23** was created (60% yield), where the unsaturation was extended to the same level as in **24**, but without increasing the strain energy. Finally, oxidation of **20** with pyridinium chlorochromate (PCC) on Celite<sup>®</sup> in refluxing benzene resulted in the anthroquinone-containing cyclophane **25** (35% yield).

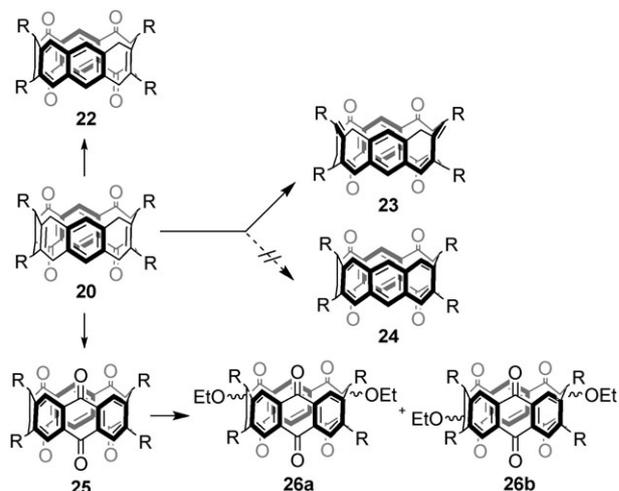


Scheme 4 Synthesis of macrocycle **20**, aiming at [8]cyclacene (**21**).

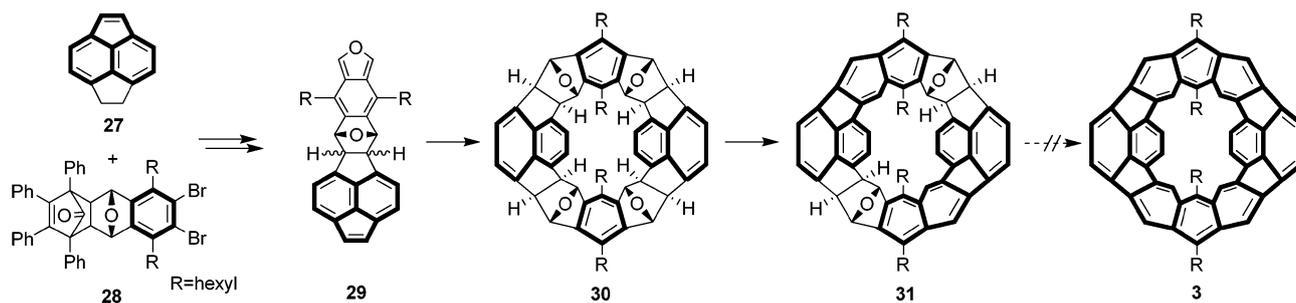
Further oxidation of **25** with oxygen in alcoholic potassium hydroxide failed to aromatize the remaining saturated rings, leading to a side reaction of ethoxylation by the solvent (**26**).

### 3.3 Towards a wider belt: the belt region of [84]fullerene ( $D_2$ )

Following the difficulties described above, chemists started suspecting that cyclacenes might be impossible to prepare because of their high reactivity, stemming from their low singlet–triplet energy gap. Therefore, in 2003, Schlüter suggested another aromatic belt as a synthetic target: **3**, the belt region of [84]fullerene, the  $D_2$  symmetry isomer.<sup>24</sup> Schlüter's belt is expected to be less reactive than [*n*]cyclacenes and also less strained, because of the curvature-inducing five-membered rings incorporated in the skeleton. The Diels–Alder synthesis



Scheme 5 Partial aromatization and unexpected reactions of **20**.



**Scheme 6** Synthesis and partial aromatization of macrocycle **30**, aiming at a Schlüter belt (**3**).

(Scheme 6) employed a single bifunctional AB-type monomer (**29**), rather than using two monomers like Stoddart and Cory, thus avoiding stoichiometric issues.

Macrocycle **30** was prepared in a five-step reaction from dihydropyracylene **27** and the isobenzofuran derivative **28**.<sup>24</sup> The adduct of **27** and **28** was dehydrogenated with DDQ, and the products were subjected to furan additions, affording the AB-type monomer **29**. Compound **29** was subjected to a tetraphenyl-cyclopentadienone (tetracyclone) addition, and both *endo* and *exo* isomers of the adducts underwent successful cyclodimerization to give **30**. The cyclization could also be carried out in the bulk (at 200 °C under high-vacuum conditions), demonstrating for the first time a preference for cyclization over linear polymerization in the bulk phase in double-stranded Diels–Alder monomers.

The skeleton of **30** features four ‘water’ molecules, and two of them could be removed with PTSA, to afford rigid, elliptical **31** in 47% yield (Scheme 6).<sup>24</sup> **30** and **31** were treated with a comprehensive variety of protic and Lewis acids,<sup>25</sup> under various conditions, in an attempt to dehydrate the skeleton or, at least, to create a library of precursors that could be aromatized in some other fashion, for example by treatment with heat or a base. Some acidic treatments led to substitutions on the skeleton, *e.g.* nitration (with nitric acid), while others converted the oxygen bridges to lactones (with  $\text{Ac}_2\text{O}/\text{ZnCl}_2$ ) or to ‘toluenes’ (with *p*TsOH in toluene), to name a few interesting transformations. In some cases, the compounds remained unchanged. A striking example for the latter case is the ineffective boiling of **31** in concentrated  $\text{H}_2\text{SO}_4$  at 150 °C, for 24 h.<sup>25</sup> For comparison, planar model compounds could be dehydrated easily with various reagents, often at much milder conditions. This demonstrates, once again, the headstrong resistance of strained macrocycles to aromatization. At long reaction times with methanesulfonic acid in nitrobenzene, **31** was consumed and a black insoluble material precipitated.<sup>25</sup> As tempting as it is to conjecture that the desired **3** formed and underwent further cross-linking, neither nuclear magnetic resonance (NMR), X-ray diffraction (XRD) or mass spectrometry (MS) lend any definite evidence to support this hypothesis.

Pyrolysis of various macrocyclic precursors has also been unsuccessful in aromatizing the compounds.<sup>26</sup> Pyrolysis at 330 °C of the tetraacetate derivative of **31** did produce a mass spectrometry peak at  $m/z$  932, the position expected for **3**, and also at  $m/z$  934 and 936; however, the authors’ density functional theory (DFT) and Gaussian-3 theory (G3)

calculations suggest that these could be either rearranged isomers or products of hydrogenation. Both 1,5-hydrogen shifts and hydrogenations at the 9,10-positions on the anthracene moieties are theoretically predicted to offer substantial relief to the macrocycle strain.

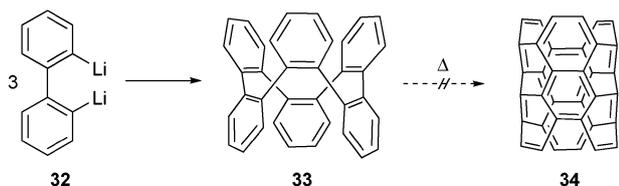
Semiempirical AM1 calculations performed by the Schlüter group demonstrated that removing the first two ‘water’ molecules from **30** to afford **31** raises the macrocyclic strain energy (MSE) only slightly, by 4.0 and 0.5 kcal mol<sup>-1</sup> for the first and second oxygen bridges, respectively.<sup>23</sup> However, further aromatization of elliptical **31** entails a major leap in MSE: 70 kcal mol<sup>-1</sup> for another single dehydration of **31**, and another 37 kcal mol<sup>-1</sup> to reach the desired **3**. Calculations of heats of reaction at the same level of theory support this conclusion: the entire strain energy that is inherent to aromatic belt **3** is to be created in one or two steps at the very end of the synthetic route. This discouraging conclusion applies to the other approaches described in this section as well: since partially saturated macrocyclic precursors, such as **10**, **16**, **20** and **31**, can adopt unstrained conformations, performing a complete aromatization requires the buildup of huge strain energy in the very last stages of the synthetic route, rendering it highly difficult.

## 4. Second strategy: stitching up fjord regions in conjugated macrocycles

The second strategy reviewed here aims at constructing single-stranded, conjugated loops, and then closing up the fjord regions by dehydrogenative cyclization. Although some of the conjugated macrocycles were synthesized long before the 1990s (Section 4.1), they were not immediately defined as precursors to benzenoid belts. In the meantime, the cyclacenes lost their appeal as synthetic targets (Section 3). Therefore, further research was aimed only at belts with angularly fused benzene rings: [*n*]cyclophenacenes or Vögtle belts.

### 4.1 Benzoannelated all-*cis*-[*n*]annulenes

Starting from 1957, Wittig has prepared a series of benzoannulenes by reacting 2,2′-dilithiobiphenyl (**32**) with various metal salts (Scheme 7).<sup>27,28</sup> One of these macrocycles is all-*cis*-hexabenz[12]annulene (**33**),<sup>28</sup> which can be viewed as a precursor to a triple-stranded belt with a periphery of six benzene rings, or a section of a (3,3)armchair carbon nanotube (**34**). However, thermolysis of **33** afforded only products



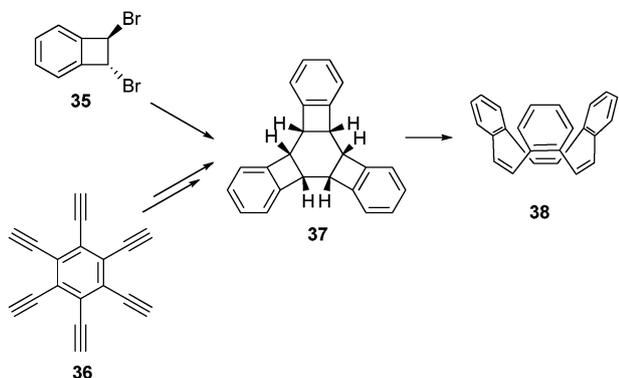
**Scheme 7** Synthesis of hexabenz[12]annulene (**33**), a possible precursor to (3,3)armchair carbon nanotube (**34**).

derived from C–C bond cleavage, with no evidence of dehydrogenative cyclization.<sup>27</sup>

In the late 1980s, Vollhardt and Iyoda have independently reported the thermolytic preparation of all-*cis*-tribenzo[12]-annulene (**38**) by a [2 + 2 + 2] cycloreversion of hydrocarbon **37** (Scheme 8).<sup>29,30</sup> **37** was synthesized in the Iyoda group by a nickel-catalyzed cyclotrimerization of **35** in 42% yield, including an isomer of **37** with two *anti* hydrogens on the central hexagon.<sup>30</sup> In the Vollhardt group, **37** was prepared by cobalt-catalyzed 3-fold cyclization of hexaethynylbenzene (**36**), followed by protidesilylation (in 30% yield).<sup>27</sup> Both groups have demonstrated the thermal isomerization of **37** to give **38**: Iyoda in 90% yield after 16 h in refluxing *o*-dichlorobenzene, and Vollhardt in 95% yield after several days of reflux in deuterated benzene.

The benzoannulenes were defined as potential precursors to [*n*]cyclophenacenes in 2000, in a seminal work by the Iyoda group.<sup>31</sup> A new and general method for the preparation of **38** was reported, and applied to its wider derivatives, **42**, **43** and **44** (Scheme 9).<sup>31,32</sup> Iyoda's general synthetic strategy is based on an intramolecular pinacol coupling of a linear poly *cis*-stilbene dialdehyde (**39**, *n* = 1–4), followed by a modified Corey–Winter dehydroxylation protocol.

To convert the benzoannulenes into cyclophenacenes, the fjord regions in the molecule need to be closed up, and for this they need to be brought together. The extent of rigidity of the cyclization precursor could, therefore, influence the reaction outcome in two ways. On the one hand, a certain extent of flexibility is desired to enable the right conformation for cyclization. On the other hand, a macrocycle that is already fixed in a somewhat rigid, tubular configuration, would already contain most of the strain energy of the desired product and will thus require less strain energy to be built



**Scheme 8** Two synthetic approaches to the all-*cis*-tribenzo[12]-annulene (**38**).

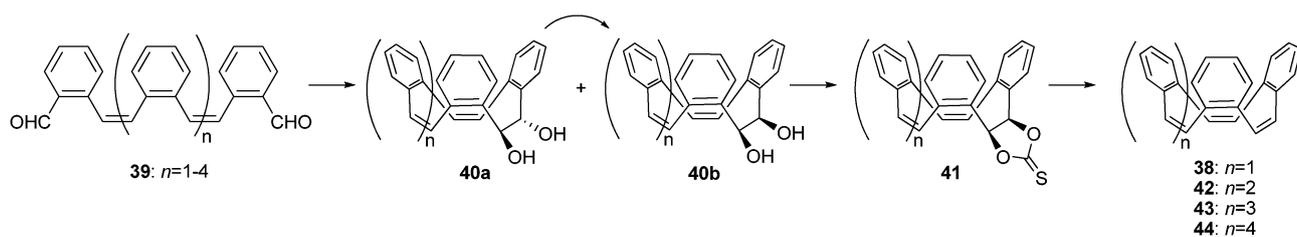
up during the cyclization reaction. In this context, Iyoda reported an interesting trend in the structural rigidity of the benzoannulenes as their diameter is increased.<sup>31</sup> The NMR spectrum of compound **38** exhibited no dependence on temperature, probably due to its rigidity. Compound **42** is more flexible, and an energy barrier of 12.7 kcal mol<sup>−1</sup> was measured with variable temperature NMR for the transition between two C<sub>2v</sub> conformations of the molecule. Compound **43** is even more flexible, and only an average C<sub>5v</sub> conformation was observed in NMR. However, the largest **44** is more rigid again,<sup>32</sup> probably because of the stabilization of the species at C<sub>3</sub> symmetry by CH–π interactions between the benzene moieties. Only one brief and promising attempt to perform dehydrogenative cyclization of benzoannulenes has been reported by Kuwatani and Iyoda in 2002.<sup>33</sup> While efforts to cyclodehydrogenate **42** and **43** chemically or photochemically have failed, a peak that can be attributed to the desired [8]cyclophenacene cation was observed in the mass-spectrum of the laser-desorption of **42**. This was the first evidence that cyclodehydrogenative aromatization is a possible route towards the desired [*n*]cyclophenacenes. However, no further reports have followed this initial finding.

#### 4.2 Approaches based on flash vacuum pyrolysis (FVP)

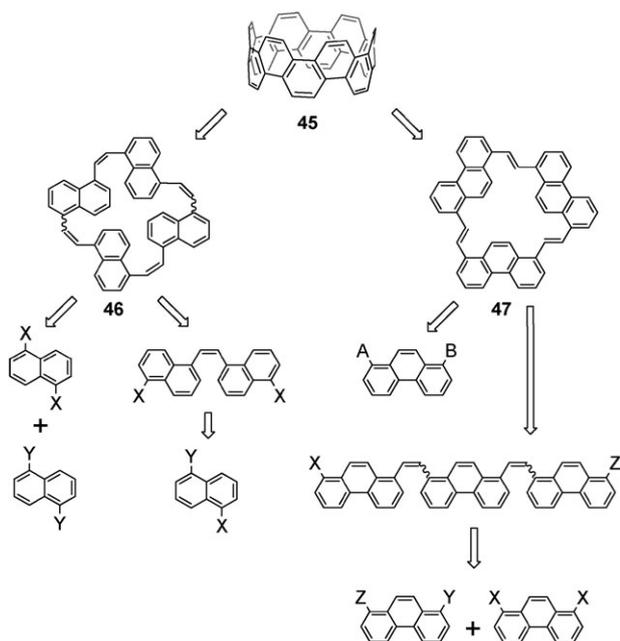
The FVP method is especially effective in creating strained polyarenes from unstrained precursors.<sup>34</sup> In this method, the precursor is rapidly heated to high temperatures (500–1100 °C) in the gas phase. Scott and coworkers, who have been using FVP to construct various geodesic molecules,<sup>34</sup> including the first rational synthesis of [60]fullerene in 2002,<sup>4</sup> have set out to prepare [12]cyclophenacene (**45**). Two possible precursors were identified (Scheme 10), one based on naphthalene units (**46**) and one on phenanthrene units (**47**).<sup>13</sup> For each precursor, two general approaches were envisioned: a single-step “shotgun” assembly from either naphthalenic or phenanthrenic monomers, or a step-by-step synthesis, culminating in macrocyclization.

Despite extensive synthetic efforts,<sup>13,35</sup> neither **46** or **47** could be prepared. The desired macrocycles eluded a vast number of synthetic methods and variations, including some indirect approaches, ranging from valence isomerization/dehydrogenation (VID) chemistry (see Section 4.3) to olefin metathesis. Two principal problems arose: first, the precursors used exhibited significant differences in reactivity compared to the model literature compounds, despite seemingly insignificant differences in the substitution pattern; second, most of these precursors were extremely insoluble. The only macrocyclic precursor that could be prepared involved *t*-butyl substituents, but these groups were expected to be labile under FVP conditions, leading to undesired side reactions. The butyl groups could not be removed without unwanted rearrangement of the skeleton, so FVP was not attempted.

The FVP method was applied by the Herges group in an attempt to pyrolytically close the walls of an interesting tubular hydrocarbon, termed “picotube” (**49**).<sup>36</sup> In the synthesis of **49**, Herges and coworkers pursued an approach based on a ring-expanding metathesis reaction, analogous to creating a large bubble by combining two small ones.<sup>37</sup> Tetradehydroanthracene (TDDA, **48**) was chosen as the



**Scheme 9** A general synthesis of benzoannulenes (**38**, **42–44**).



**Scheme 10** A retrosynthetic analysis of [12]cyclophenacene (**45**).

starting material,<sup>38</sup> both for its well-suited structure, and for its inherent strain energy, useful as a driving force for the metathesis ring expansion. Compound **48** underwent dimerization upon photolysis in a suspension in benzene, probably through a solid-phase mechanism, in 32% yield (Scheme 11).<sup>37</sup>

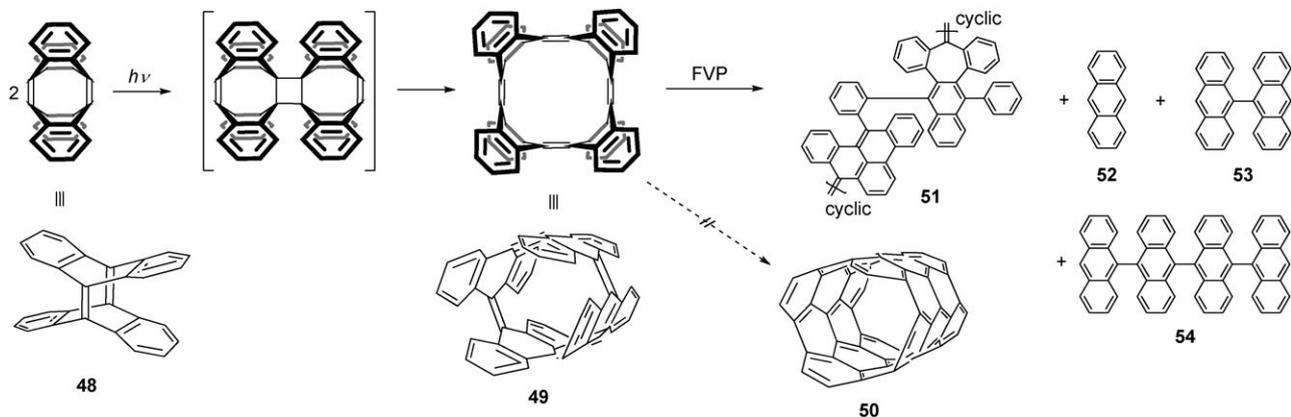
Multiple cyclodehydrogenations of the picotube would afford a short section of a (4,4)armchair nanotube (**50**). According to AM1 semiempirical calculations, eliminations of

hydrogen molecules from the picotube should be endothermic.<sup>37</sup> However, while the first four cyclodehydrogenation steps are only slightly endothermic (1.4–8.5 kcal mol<sup>-1</sup>), the reaction barriers for the last four eliminations are much higher, ranging from 38 to 60 kcal mol<sup>-1</sup>.

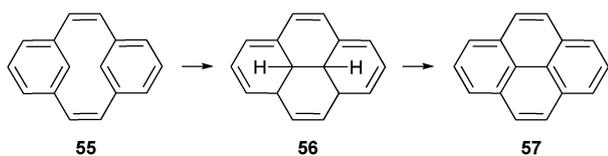
Although FVP is capable of building up strain energy of such magnitudes,<sup>34</sup> Herges and coworkers reported the failure of an attempt to close the walls of the picotube pyrolytically at 800 °C (Scheme 11).<sup>36</sup> Instead of cyclodehydrogenation, the pyrolysis reaction led to a mixture of products, in most of which the quinoid bonds and the neighboring single bonds were cleaved (**52**, **53**, **54**). An unexpected rearrangement also took place, affording an odd conjugated belt (**51**) that includes a seven-membered ring, probably formed in a radical mechanism. DFT calculations (B3LYP/6-31G\*) revealed that the rearrangement product **51** is 52 kcal mol<sup>-1</sup> more stable than **49**, stressing the significant inherent strain of the picotube. Other synthetic methods also fell short in closing the fjord regions in **48**.<sup>36</sup> Herges reported the failure of oxidative procedures, such as Scholl or Kovacic conditions or irradiation in the presence of iodine. In addition, reduction with alkali metals, known to lead to cyclodehydrogenation in some cases,<sup>39</sup> was attempted in the Rabinovitz group but did not lead to reductive ring closure.<sup>40</sup> Potassium reduction seemed to have cleaved the picotube, and lithium could only reduce **49** to a tetraanion without structural changes.

### 4.3 Vögtle belts

Aromatic belts with a repeating pyrene (or rylene) motif, such as **4**, were defined by Vögtle as interesting synthetic targets as early as in 1983.<sup>41</sup> He aimed at applying cyclophane chemistry, together with the valence isomerization/dehydrogenation



**Scheme 11** Synthesis of picotube **49**, and attempt to close its walls pyrolytically to prepare aromatic belt **50**.



**Scheme 12** The valence isomerization/dehydrogenation reaction.

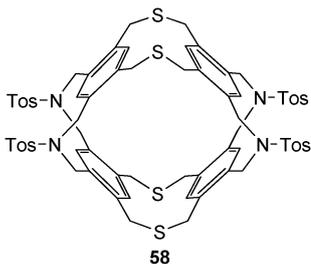
(VID) methodology, to achieve these interesting  $[n]$ cyclophenacene congeners. The VID reaction, first reported by Mitchell and Boekelheide in 1970, is capable of creating a pyrene (**57**) from a [2.2]metacyclophane-1,9-diene (**55**, Scheme 12).<sup>42</sup>

Vögtle planned on starting from a double-stranded macrocyclic cyclophane such as **58** (Fig. 3), continuing with ring contraction, and finally performing a VID reaction to create the desired Vögtle belt.<sup>43</sup> However, **58** was the largest macrocyclic precursor that could be isolated by Vögtle and coworkers, but not large enough as a precursor to a stable aromatic belt.

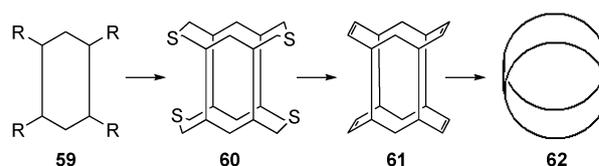
Bodwell and coworkers used the VID method as a basis for a new chemistry of pyrenophanes. It turned out that the high aromatic stabilization energy (ASE) of pyrene,  $74 \pm 1 \text{ kcal mol}^{-1}$ , can counterbalance the increase in strain energy that accompanies the bending of the pyrene unit.<sup>44</sup> Therefore, this powerful method for bending pyrenes could be used to synthesize Vögtle belts.<sup>45</sup> Lately, Bodwell proposed a general strategy towards aromatic belts with a repeating pyrene motif (Scheme 13): connecting two arenes ('molecular boards') with sulfur bridges, converting the bridges into double bonds, and performing a double VID reaction to close the bay region and form the belt.<sup>44</sup>

Molecular board **65** (Scheme 14) was suggested first as a precursor to a Vögtle belt.<sup>44</sup> However, a fourfold ring contraction could not be performed in **63** or **64** using various synthetic methods. Next, the trimmed molecular board **71** was prepared as a precursor for a new type of aromatic belt (Scheme 15).<sup>44</sup> The carbon skeleton (**69**) was assembled using Sonogashira couplings, followed by hydrogenation, bromination and a Pd-catalyzed double direct arylation, to give **71** in 35% overall yield. But while severe solubility problems could be overcome in the synthesis of **71**, they spoiled the further connection of boards **73** and **74**, the tetrabromide and tetra thiol derivatives of **71**, respectively. No progress in this direction has been reported since.

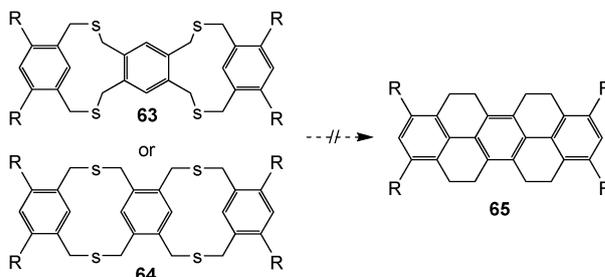
Recently, an important new pyrenophane was synthesized in the Bodwell group (Fig. 4, **75**).<sup>46</sup> This molecule contains a large segment of an aromatic belt, that can be viewed as one half of a Vögtle belt, tethered with an alkane ring. The arene



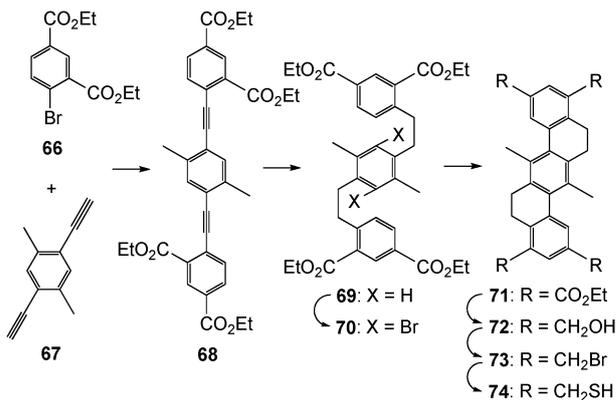
**Fig. 3** Cyclophane **58**, a potential precursor to a Vögtle belt.



**Scheme 13** A general strategy towards Vögtle belts.



**Scheme 14** Attempted synthesis of molecular board **65**.

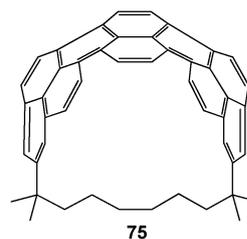


**Scheme 15** Synthesis of molecular boards **71-74**.

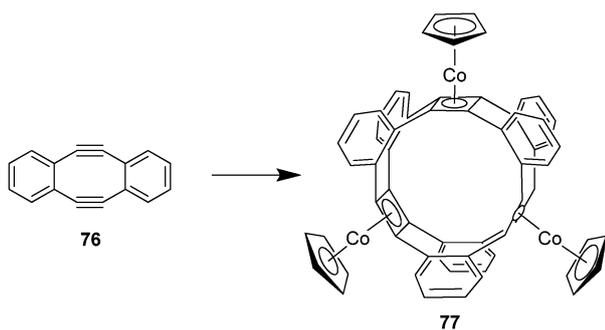
strip is bent onto itself with a  $167^\circ$  angle, close to a complete  $180^\circ$ , thus demonstrating convincingly that the VID method is capable of creating the necessary strain in polyarene segments. This highly strained polyarene maintains the hope that the long awaited synthesis of a Vögtle belt is in sight, and only awaits the right precursor.

## 5. Unstrained non-benzenoid cyclacenes

Gleiter's strategy bypassed altogether the necessity of building up strain during the reaction, by incorporating into the belt naturally convex, yet still conjugated, structural elements. Stoddart had used convex building blocks before (**7** and **8**, Scheme 1) to construct his macrocycles, but the bending motif



**Fig. 4** Bent pyrenophane **75**.



Scheme 16 Synthesis of [4.8]<sub>3</sub>cyclocene (77).

was an etheric bridge that had to be removed to achieve aromatization, thus straining the structure again. Gleiter suggested cyclooctatetraene rings, with their naturally adopted boat-like conformation, as building blocks for a new family of unusual cyclocenes.<sup>47</sup>

Compound 77 was the first conjugated, double-stranded macrocycle consisting of annelated rings that was prepared within this framework.<sup>47</sup> The belt was composed of alternating four- and eight-membered conjugated rings (a [4.8]<sub>3</sub>cyclocene according to Gleiter's generalized nomenclature),<sup>47</sup> with the cyclobutadiene units stabilized by metal ions. Compound 77 was prepared in a one-pot reaction by irradiation of the highly strained cyclodiyne 76 in the presence of [CpCoL<sub>2</sub>] in decalin for three days, with 14% yield (Scheme 16).

The next breakthrough was the synthesis of a purely hydrocarbon [6.8]<sub>3</sub>cyclocene (82), consisting of alternating six- and eight-membered rings.<sup>48</sup> The boat-shaped eight-membered rings helped circumventing both obstacles of cyclocene synthesis: the bending problem and the predicted high reactivity of cyclocenes that arises from their small singlet–triplet energy gap. Compound 82 was prepared in eight steps from the commercially available 4,6-dimethyl-iso-phthalaldehyde 78 (Scheme 17). Trimer 80 was assembled through an intermolecular Wittig cyclization, according to Wennerström's procedure<sup>49</sup> (4% yield from 78). After converting the *E,Z,Z* isomer into an all-*Z* isomer by irradiation, and following *N*-bromosuccinimide (NBS) bromination and oxidation with 2-iodoxybenzoic acid (13% yield from 80), 81 was finally transformed into the unusual cyclocene 82 through a McMurry coupling in 8% yield.

The researchers underlined the reduced conjugation in 82, estimating the degree of conjugation to be about 31% for the cyclocene torus, based on the angles between the double bonds of the eight-membered rings and the adjacent aromatic rings. The [6.8]<sub>3</sub>cyclocene (82) is the smallest and most strained

member of the [6.8]<sub>*n*</sub>cyclocene family, and it represents an unusual type of carbon nanotube. First steps have already been made towards [6.8]<sub>4</sub>cyclocene.<sup>50</sup> Macrocyclic 86 was prepared as a precursor to [24]*meta*-cyclophanetetraene 87 (Scheme 18).<sup>50</sup> Compound 86 was synthesized by Sonogashira couplings, followed by an intermolecular McMurry homo-coupling (10% yield from 83). Once 86 is prepared, another McMurry coupling is expected to close it up to give [6.8]<sub>4</sub>cyclocene, similarly to the 82 synthesis (Scheme 17).

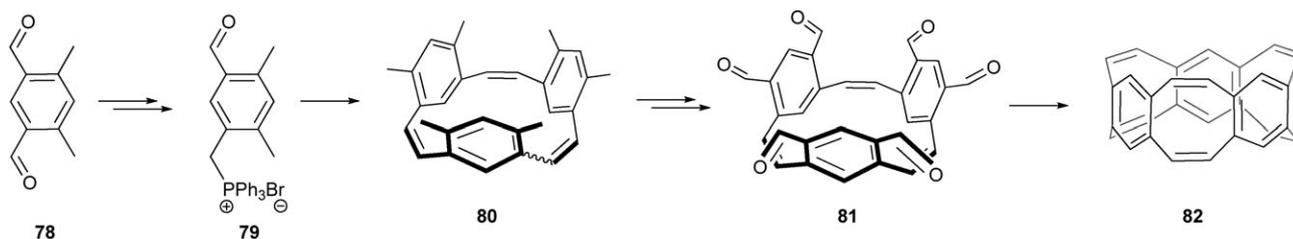
## 6. Fullerene-derived [10]cyclophenacene

Another way of avoiding the necessity of building up strain during the synthesis is to begin with highly strained precursors. Nakamura has applied this idea by starting with [60]fullerene (88), a curved surface composed of sp<sup>2</sup> carbons. After multiple site-selective additions to the north and south poles of the fullerene, a double-stranded, conjugated belt was isolated around the equator, corresponding to [10]cyclophenacene (92).

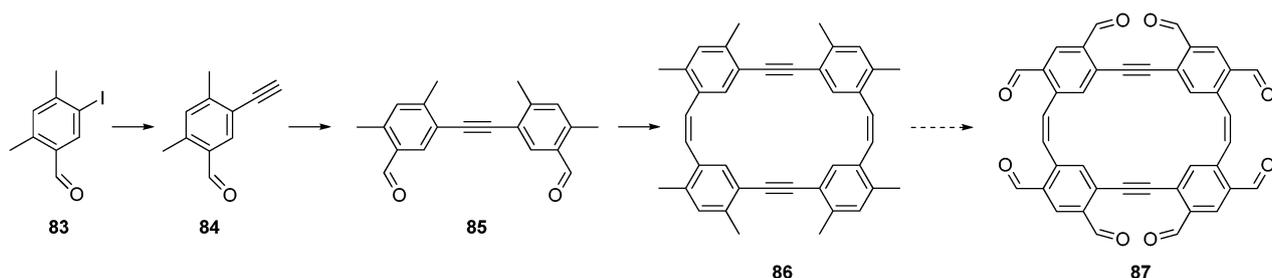
The first synthesis performed in the Nakamura group was based on two separate penta-additions (Scheme 19).<sup>51</sup> Five methyl groups were installed at one pole with an organocopper reagent, isolating a cyclopentadiene moiety (89). The acidic hydrogen had to be protected from deprotonation by the copper reagent with a cyano group, and then a second penta-addition of phenyl groups was performed at the other pole of the fullerene. After removal of the cyano group, the overall yield was 7%, resulting in the first ever cyclophenacene derivative (92). Nucleus independent chemical shift (NICS) calculations for the six-membered rings in the cyclophenacene moiety support the idea that 92, as well as the parent [10]cyclophenacene, are aromatic, with values of –11.46 to –11.99 for the former and –8.6 for the latter.<sup>51</sup>

Later on Nakamura and coworkers further improved on the synthesis, by shortening it to a single step of regioselective ten-fold addition.<sup>52</sup> By reacting 88 with the organocopper reagent in the presence of an appropriately excessive amount of pyridine, the desired [10]cyclophenacene derivative 93 was obtained, along with other products of deca- and penta-addition (Scheme 20), in 92% overall yield. Substitution of the pyridine enabled some tweaking of the relative yields of the products, thus revealing the two mechanistic pathways for the multiple addition reactions. However, pure pyridine was ultimately the best for the production of 93 (35% yield).

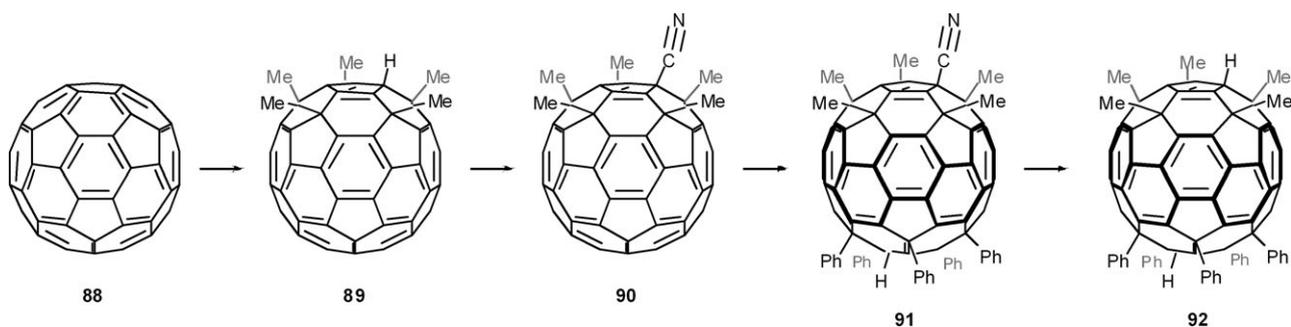
Nakamura also pioneered the study and application of the material properties of the cyclophenacene derivatives. The photophysical properties of compounds with radially oriented p orbitals were investigated, and carefully designed derivatives



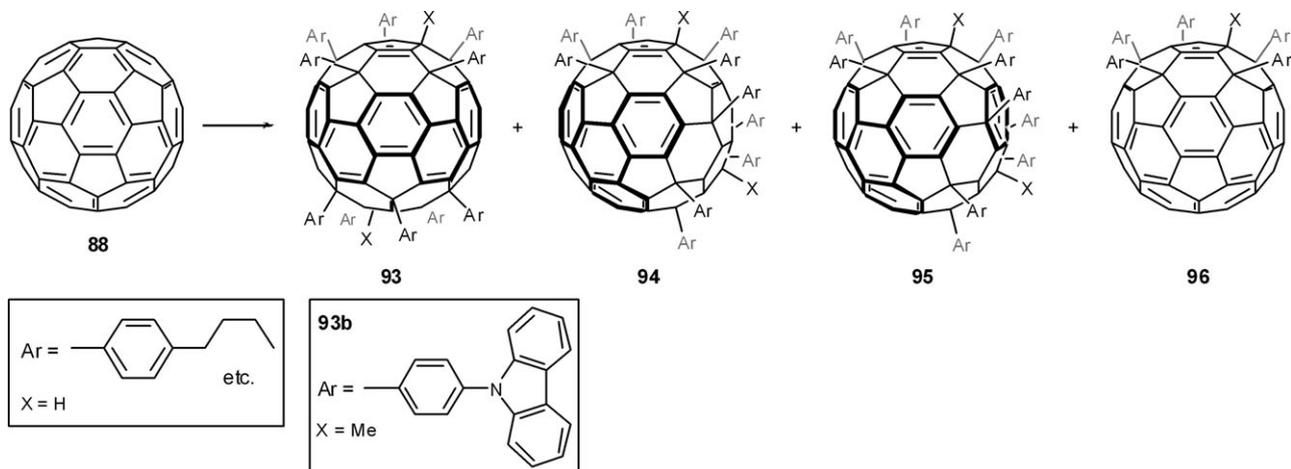
Scheme 17 Synthesis of [6.8]<sub>3</sub>cyclocene (82).



**Scheme 18** Synthesis of **86**, en route to **87**, a precursor for [6.8]<sub>4</sub>cyclocene.



**Scheme 19** Synthesis of a fullerene-derived [10]cyclophenacene (**92**).



**Scheme 20** Single-step synthesis of [10]cyclophenacene derivative **93** and other products of multiple additions (**94–96**). Dendritic derivative **93b** was the target of photophysical investigations.

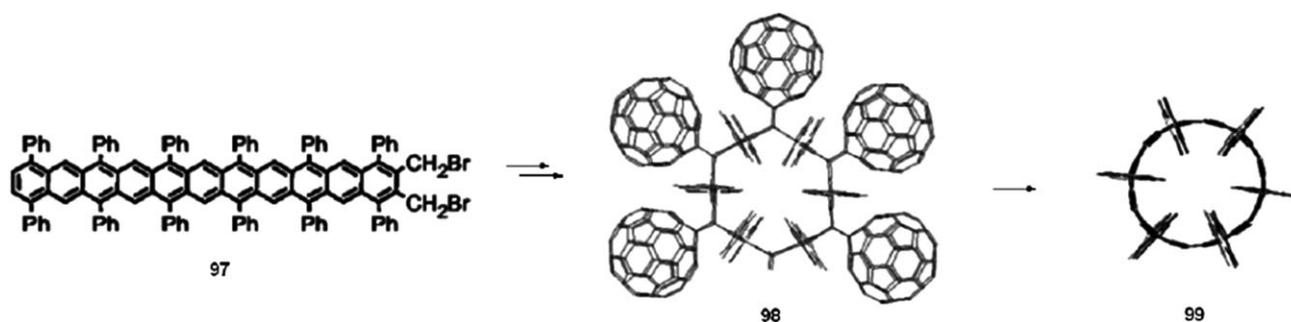
were shown to exhibit promising photoactive properties. For example, intramolecular energy transfer and electron transfer took place in a light emitting dendritic [10]cyclophenacene derivative (**93b**), where ten carbazolyphenyl groups were installed at the poles of a [60]fullerene.<sup>53</sup> In another recent work, it was demonstrated how a [10]cyclophenacene derivative, together with two other multifunctionalized organo[60]fullerenes, could be embedded in  $\pi$ -conjugated polymers to create an organic electroluminescent diode device that emits white light.<sup>54</sup>

## 7. Conclusions and outlook

The synthetic effort of a dozen different research groups towards double-stranded, conjugated macrocycles has been reviewed. So far, those who tried to take the bull by its horns

and devise a synthesis that builds up the strain that is inherent to aromatic belts have not met with success. Whether they tried aromatizing a partially-saturated belt or closing fjord regions in conjugated macrocycles, the barrier of structural strain could not be overcome, yet. A synthesis that delays the buildup of strain to the last step of the synthetic route (Section 3) seems to be less likely to succeed than a method that manages to spread the buildup of strain along the reaction pathway (Section 4). Various fascinating belt-shaped structures have been prepared, and methods have been suggested (such as FVP and VID) that could probably create the necessary strain in the future, once the right precursor is identified.

The success stories in the field currently belong to those who evaded the yoke of synthetic strain buildup. Gleiter prepared



**Scheme 21** A proposed synthesis of [12]cyclacene (**99**). Reprinted with permission from ref 55. Copyright 2006, American Institute of Physics.

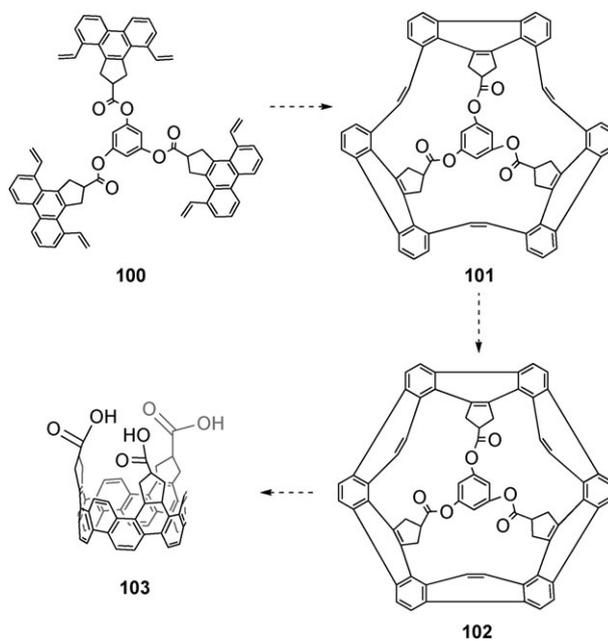
unstrained conjugated belts, by including a naturally-convex cyclooctatetraene element in the belt. This was the first preparation of a pure hydrocarbon, fully unsaturated double-stranded belt. Nakamura started at the strained [60]fullerene, and isolated the [12]cyclophenacene structure on its equator. This was the first cyclophenacene-type system to be prepared, and its photophysical properties were studied for the first time. In both cases, these dazzling compounds represented major milestones in the field. However, learning how to master the buildup of structural strain in polyarenes is one of the goals that motivate the field of aromatic belts, and evading it only solves half the problem.

As has been demonstrated, much of the progress in the field of aromatic belts has been made very recently. New players continue to come into the ring and novel strategies are being proposed. Two examples for such entries, that have not been implemented yet, are also presented here.

In 2006, Miller and coworkers suggested bending linear acenes by adding fullerenes selectively to one of their sides, and finally closing the belt using a coupling method (Scheme 21), to give a novel [12]cyclacene derivative (**99**).<sup>55</sup> The plan is based on the surprising discovery that several fullerenes can be added to an acene with high regioselectivity, probably directed by mutual stabilization of the buckyballs. This strategy has not been implemented yet. It seems that the known problems of strain and reactivity of [12]cyclacenes will challenge this approach as well, unless the fullerene substituents change the chemistry of the compounds dramatically.

Goroff and coworkers have outlined a novel synthetic route towards [12]cyclophenacene (Scheme 22), based on a benzene scaffold.<sup>56</sup> They are currently working on the preparation of **100**, a benzene precursor with three phenanthrene units. The phenanthrenes are to be connected at the next stage, and the fjord regions stitched up, resulting, hopefully, in a tube-shaped [12]cyclophenacene derivative **103**. The use of the scaffold to dictate a cylindrical shape is intended to help the three-fold macrocyclization of the phenanthrenes. However, in this strategy the buildup of strain is delayed to the last reaction, when the phenanthrenes are being bent, and this could be hard to perform.

To conclude, the field of aromatic belts is still growing, and the synthetic efforts will probably continue until at least one of the stand-alone belts depicted in Fig. 1 is prepared and bottled.



**Scheme 22** A proposed synthesis of [12]cyclophenacene (**103**).

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