

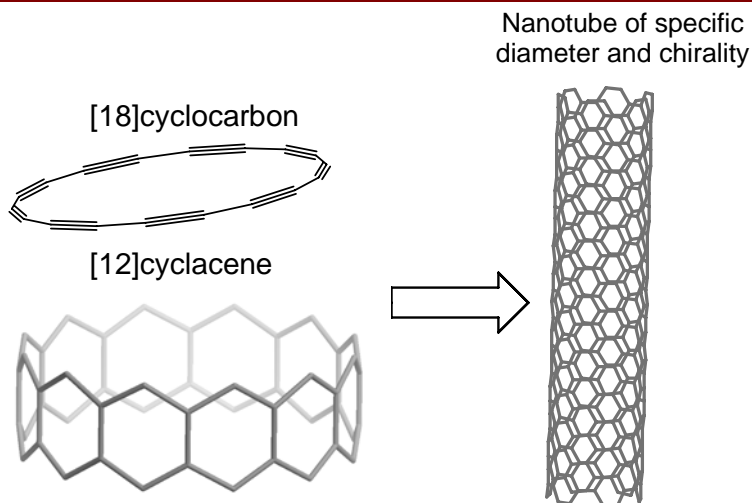
# Conjugated Molecular Belts

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## ABSTRACT



This review discusses the major efforts to synthesize a variety of conjugated molecular belts. A few of these synthetic efforts have led to completely unsaturated compounds, whereas in many cases the belt is only partially aromatized. In those cases, the challenges preventing a successful synthesis of the fully unsaturated belt are discussed from both an organic chemistry and theoretical chemistry perspective. The potential application in the synthesis of single-walled carbon nanotubes is discussed.

Methods for making single-walled carbon nanotubes involve very high temperatures and are not suitable for producing large quantities. The syntheses are essentially uncontrolled and proceed through very small carbon fragments with no well-defined starting point. As a result, the reactions produce a distribution of carbon species which are typically very difficult to separate. This mixture consists of a wide variety of nanotubes with vastly different physical properties. The ability to synthesize carbon nanotubes with specific diameter and chirality will allow access to compounds that previously were not readily available in pure form. Furthermore, this will allow a nanotube with specific properties to be tailored to a particular application. Inevitably, this will lead to more widespread use of single-walled carbon nanotubes.

This paper explores methods for using conjugated molecular belts as precursors in carbon nanotube syntheses. Conjugated molecular belts are particularly well-suited for this purpose as they are highly strained

curved aromatic structures<sup>1</sup> and have the same overall cyclic shape. Unlike the current methods for nanotube syntheses, the seed here is a well-defined organic compound so it should be possible to obtain nanotubes with a specific diameter and chirality from this. Despite widespread interest and significant effort, very few examples of a fully conjugated molecular belt have actually been successfully isolated<sup>2</sup>. There are, however, many examples of molecular belts that have not been synthesized in their fully unsaturated form.

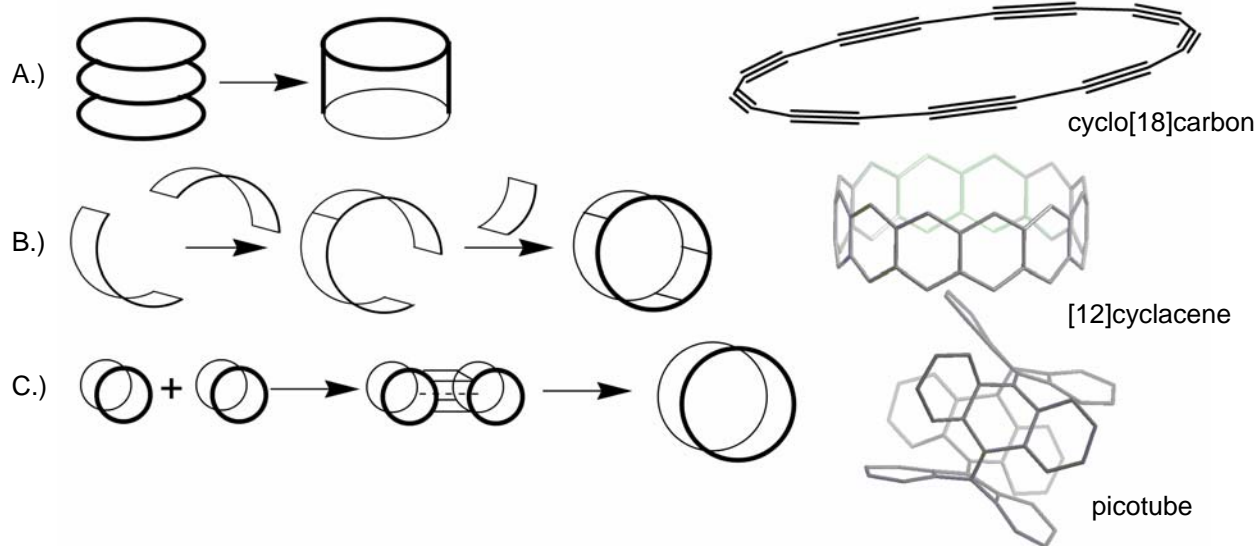
Efforts to synthesize and characterize fully conjugated belts has led to a variety of novel methods for introducing curvature and strain into aromatic compounds. Herges has summarized three general strategies for making a conjugated molecular belt or tube (see Figure 1)<sup>3</sup>. One of these is a layer-by-layer approach in which rings are stacked together on top of each other to form the

<sup>1</sup> Faust, R. *Angew. Chem. Int. Ed.* **1998**, *37*, 2825.

<sup>2</sup> Scott, L.T. *Angew. Chem. Int. Ed.* **2003**, *42*, 4133.

<sup>3</sup> Kammermeier, S.; Jones, P.G.; Herges, R. *Angew. Chem. Int. Ed.* **1996**, *35*, 2669.

**Figure 1.** General Strategies for Belt and Tube Synthesis and Related Molecules



molecular belt. This is one possible mechanism for carbon nanotube formation using either arc discharge or chemical vapor deposition methods. The ribbon approach involves connecting convex molecules in a specific way to make a belt. Various functional groups are used to induce the curvature necessary and are then later removed to unmask the fully unsaturated form. This is the strategy employed in Stoddart's Diels-Alder attempt to synthesize [n]cyclacene<sup>4</sup> and in Diederich's attempt to synthesize cyclo[n]carbon<sup>5,6,7</sup>. Finally, there is the ring-expansion approach in which a small belt combines with another small belt and by releasing strain a larger belt is formed. This approach is used by Herges in his photochemical synthesis of the picotube<sup>3</sup>.

**Layer-by-Layer.** Diederich has successfully synthesized (see figure 1A) three different cyclo[n]carbon precursors of various sizes ( $n=18, 24,$  and  $30$ )<sup>5</sup>. Other cyclo[n]carbon precursors ( $n=12, 16,$  and  $20$ ) have also been synthesized<sup>8</sup>. However, attempts to isolate and characterize any cyclo[n]carbon have all failed even at very low temperatures ( $\sim 15\text{K}$ )<sup>5</sup>. Every attempt to isolate cyclo[n]carbon led to decomposition and formation of polymer<sup>9</sup>. This is probably attributed to being highly strained and very reactive. For cyclo[18]carbon, the bond angle is  $\sim 160^\circ$  significantly less than the typical  $180^\circ$ .

However, other cycloalkynes with bond angles less than  $160^\circ$  have been isolated<sup>10</sup>.

Using laser desorption Fourier mass spectroscopy, cyclo[n]carbon was detected as a transient species from the carbon oxide precursor<sup>11</sup>. For the negative ion, only the respective cyclo[n]carbon is detected. For the positive ion, however, higher fullerenes such as  $\text{C}_{60}$  and  $\text{C}_{70}$  are seen as well. The exact mechanism for fullerene formation in the gas phase is still unknown. This research has led to other highly strained acetylene containing compounds which are being explored as potential precursors to either carbon nanotubes or fullerenes<sup>1,12</sup>.

**Ribbon.** Many years before the discovery of carbon nanotubes in 1991, Vögtle proposed [n]cyclacene (see figure 1B) as a major synthetic target for conjugated molecular belts<sup>13</sup>. In many ways, this is an ideal carbon nanotube precursor because it is the repeating unit found in a zigzag carbon nanotube. Stoddart published the first attempt at synthesizing [12]cyclacene in 1987<sup>14</sup>. As shown in scheme 1, this involves successive Diels-Alder reactions between convex dienes and dienophiles in such a way that a belt is formed. After the Diels-Alder reactions, the compound is aromatized through successive dehydration steps. Upon dehydration, rearrangement occurs to yield **1**. Despite many attempts to synthesize the desired cyclacene **2**, to date it has never been made.

<sup>4</sup> Ashton, P.R.; Brown, G.R.; Isaacs, N.S.; Giuffrida, D.; Kohnke, F.H.; Mathias, J.P.; Slawin, A.M.Z.; Smith, D.R.; Stoddart, J.F.; Williams, D.J. *J. Am. Chem. Soc.* **1992**, *114*, 6330.

<sup>5</sup> Diederich, F.; Rubin, Y.; Chapman, O.L.; Goroff, N.S. *Helv. Chim. Acta* **1994**, *77*, 1441.

<sup>6</sup> Siemsen, P.; Livingston, R.C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 2632.

<sup>7</sup> Diederich, F. *Chem. Commun.* **2001**, 219.

<sup>8</sup> Tobe, Y.; Matsumoto, H.; Naemura, K.; Achiba, Y.; Wakabayashi, T. *Angew. Chem. Int. Ed.* **1996**, *35*, 1800

<sup>9</sup> Diederich, F.; Rubin, Y. *Angew. Chem. Int. Ed.* **1992**, *31*, 1101.

<sup>10</sup> Wang, X.; Wang, R.; Mak, T.C.W.; Wong, H.N.C. *J. Am. Chem. Soc.* **1990**, *112*, 7790

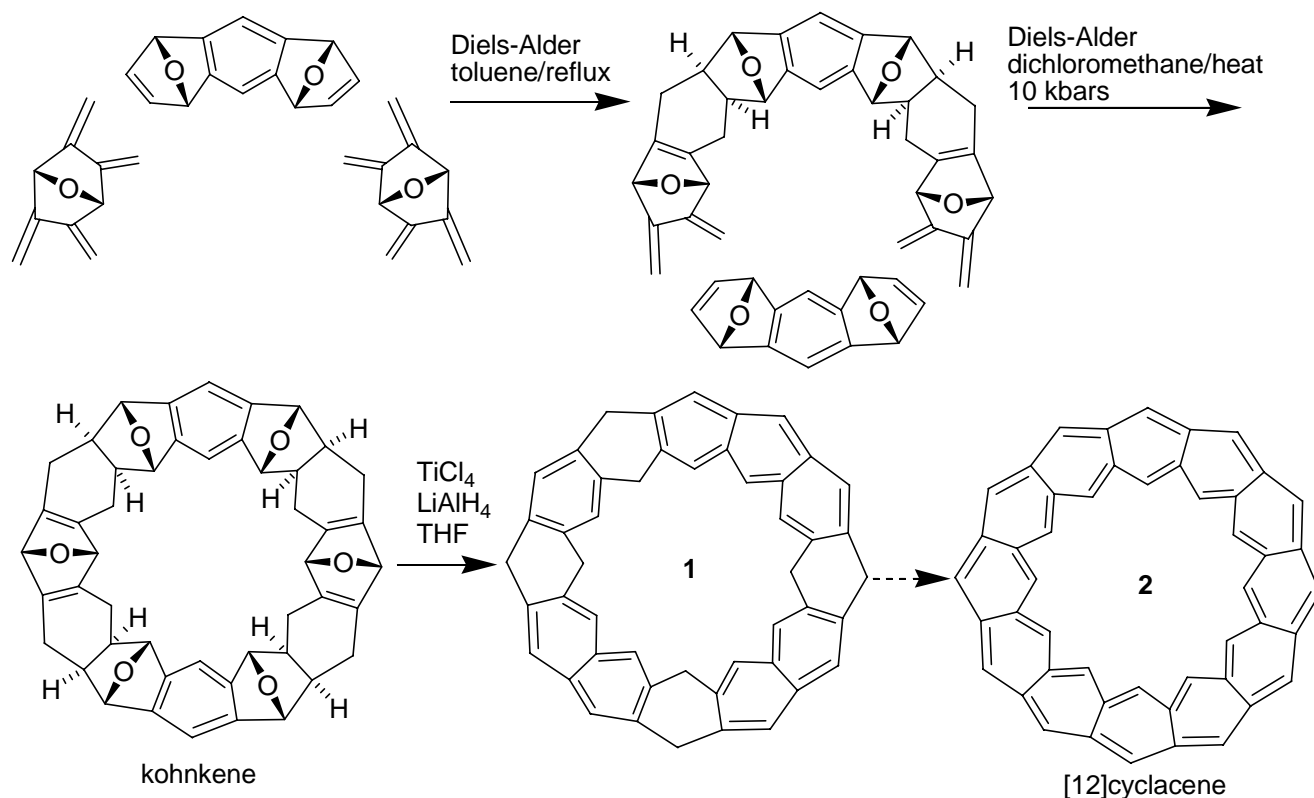
<sup>11</sup> McElvany, S.W.; Ross, M.M.; Goroff, N.S.; Diederich, F. *Science* **1993**, *259*, 1594.

<sup>12</sup> Boese, R.; Matzger, A.J.; Vollhardt, K.P.C. *J. Am. Chem. Soc.* **1997**, *119*, 2052.

<sup>13</sup> Vögtle, F. *Topics Curr. Chem.* **1983**, *115*, 157.

<sup>14</sup> Kohnke, F.H.; Slawin, A.M.Z.; Stoddart, J.F.; Williams, D.J. *Angew. Chem.* **1987**, 99.

**Scheme 1.** Stoddart's [12]cyclacene synthesis



The electronic and structural relationship of [n]cyclacenes to infinite polyacenes and to two weakly interacting polyacetylenes has been studied extensively using theoretical calculations<sup>15</sup>. These show that the bond lengths in both cyclacenes and linear polyacenes are very similar and are not affected significantly by molecular strain. Houk and colleagues, using B3LYP and UB3LYP density functional methods, have shown that [n]cyclacene should have a triplet ground state making them very reactive<sup>16</sup>. This is compared to the triplet ground state of linear octacene, which also has not been isolated.

Schlüter has incorporated peri-condensed naphthalene units with two adjacent five-membered rings into linear polyacenes<sup>17</sup>. This breaks the conjugation and leads to considerable stabilization. This technique has been extended to making molecular belts (see scheme 2)<sup>18</sup>. A similar approach to Stoddart is used in that convex dienes and dienophiles undergo a Diels-Alder reaction to make the molecular belt (see compound 3) followed by

aromatization reactions. Unexpectedly upon dehydration compound 4 is formed instead of the fully aromatized compound 5. AM1 calculated macrocyclic strain energies were determined for the four dehydration intermediates between compounds 3 and 5. The first two dehydration reactions which lead to compound 4 are exothermic and increase the macrocyclic strain energy only slightly. However, the next step two dehydration steps were shown to be energetically unfavored. It is expected that compound 5 will be relatively stable and could possibly be made if a different synthetic route is employed.

**Ring Expansion.** Herge's picotube synthesis uses another strategy for molecular belt formation (see figure 1C). The route to the picotube 7 utilizes the photochemical dimerization of anthracene and a photochemical metathesis reaction. After the photodimerization of 9-bromoanthracene across the 9 and 10 (see scheme 3) positions and a double dehydrodehalogenation reaction, tetrahydrodianthracene (TDDA) 6<sup>19</sup> is obtained. The next step in the synthesis of the picotube is to irradiate

<sup>15</sup> Choi, H.S.; Kim, K.S. *Angew. Chem. Int. Ed.* **1999**, 38, 2256.

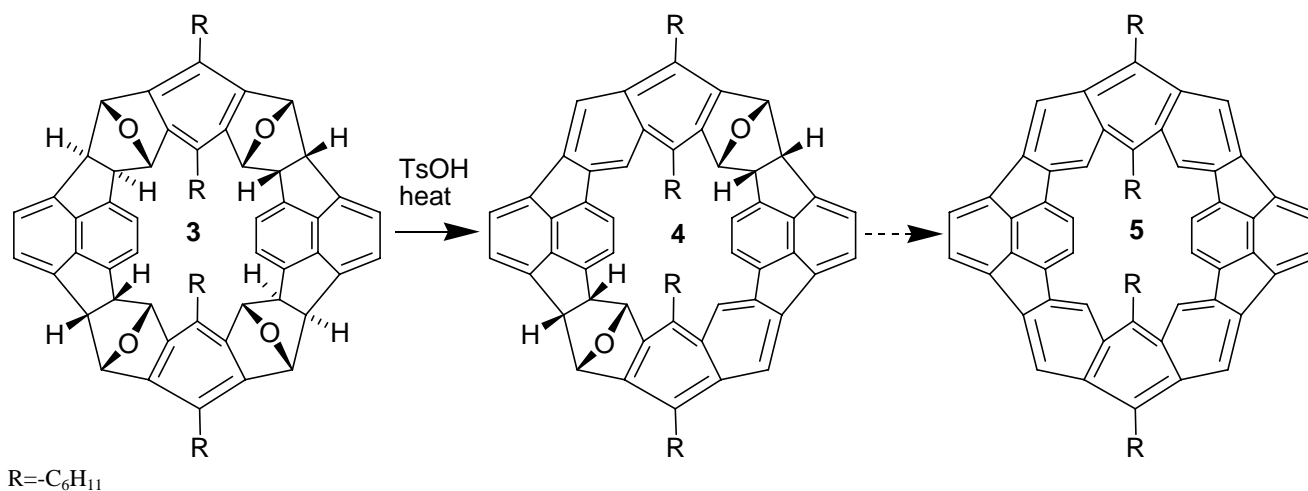
<sup>16</sup> Houk, K.N.; Lee, P.S.; Nendel, M. *J. Org. Chem.* **2001**, 66, 5517.

<sup>17</sup> Schlicke, B.; Schirmer, H.; Schlüter, A.D. *Adv. Mater.* **1995**, 7, 544.

<sup>18</sup> Neudorff, W.D.; Lentz, D.; Anibarro, M.; Schlüter, A.D. *Chem. Eur. J.* **2003**, 9, 2745.

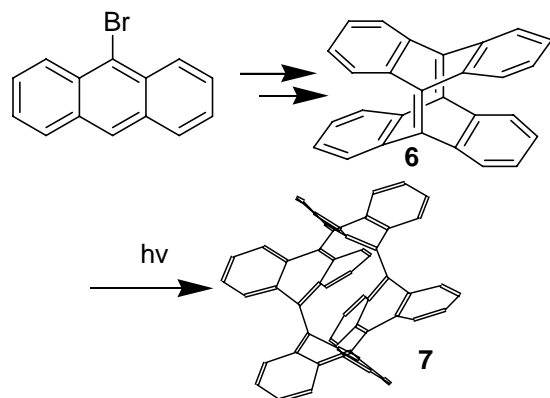
<sup>19</sup> Viavattene, R.L.; Greene, F.D.; Cheung, L.D.; Majeste, R.; Trefonas, L.M. *J. Am. Chem. Soc.* **1974**, 96, 4342.

**Scheme 2.** Schlüter's C<sub>84</sub> belt fragment Synthesis



TDDA in a dilute benzene solution to form **7** by a photochemically induced metathesis. The chemistry of the picotube has been studied<sup>3,20</sup>. Attempts to oxidatively cyclize the **8** remaining positions to form a very small (4,4)-nanotube fragment from the picotube by flash vacuum pyrolysis of **7** at 800°C were unsuccessful<sup>21</sup>. A rearrangement reaction predominates.

**Scheme 3.** Herge's Picotube Synthesis

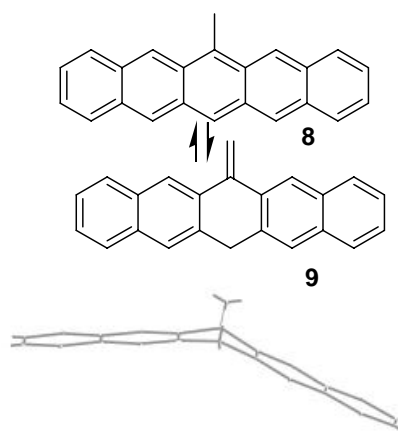


In both Stoddart's and Schlüter's attempt at synthesizing molecular belts, the synthesis fails at the aromatization step. Recently, the x-ray crystal structure of methylpentacene (see scheme 4) was obtained<sup>22</sup>. This structure is bent significantly from planarity. By taking advantage of the tautomerization between the two forms

of methylpentacene **8** and **9** it might be possible to synthesize molecular belts without having to worry about the aromatization step in the end. The compound will only have to tautomerize to achieve the aromatic form.

In the future it might be possible to use molecular belts similar to either **2**, **5**, or **7** as seeds for nanotube growth. To demonstrate this principle, Smalley has recently reported a technique for continuing carbon nanotube growth from previously prepared open carbon nanotubes<sup>23</sup>. He has shown that the nanotube's chirality was maintained in the continuation. The ability to incorporate molecular belts into this technique would be a huge leap in progress for carbon nanotube synthesis.

**Scheme 4.** 6-Methylpentacene and X-ray Structure



<sup>20</sup>Trietel, N.; Deichmann, M.; Sternfeld, T.; Sheradsky, T.; Herges, R.; Rabinovitz, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 1172.

<sup>21</sup>Diechmann, M.; Nather, C.; Herges, R. *Org. Lett.* **2003**, *5*, 1269.

<sup>22</sup>Horoszewski, D.; Steigerwald, M.; Nuckolls, C. unpublished results

<sup>23</sup>Wang, Y.; Kim, M.J.; Shan, H.; Kittrell, C.; Fan, H.; Ericson, L.M.; Hwang, W.F.; Arepalli, S.; Hauge, R.H.; Smalley, R.E. *Nano Letters* **2005**, *5*, 997.