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Thermal dimerization of [*n*]cumulenes (*n* = 5, 7, 9)

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The thermal dimerization of three [*n*]cumulenes (*n* = 5, 7, and 9) has been investigated, and a common reactivity pattern is observed that gives radialenes or expanded radialenes through regioselective cycloaddition reactions; all three products are characterized by X-ray crystallography.

Cycloaddition reactions of polyynes have been used create conjugated molecules that are otherwise difficult to obtain, and the regioselectivity of these reactions can often be controlled by the electronic nature of endcapping groups.[1–3] On the other hand, this same level of control has not yet been achieved for reactions for the sp-carbon chain of long [*n*]cumulenes (*n* ≥ 5).[4] There have been a handful of reports in which [5]cumulenes react with electron-poor olefins or alkynes, but the regiochemistry of cycloaddition reactions is difficult to predict.[5–8] Dimerization reactions under thermal, photochemical, or metal-catalysed conditions that give cyclic oligoynes or radialenes are also known.[9] The regiochemistry observed for these cycloaddition reactions has been typically attributed to either steric requirements or to the electronic structure of endcapping groups.[10–14] For example, the thermal dimerization of a [5]cumulene with bulky alkyl substituents, such **[5]tBu** (Scheme 1), results in dimerization at the central γ-bond to form symmetric [4]radialene **1a** (Scheme 1).[7] [5]Cumulenes functionalized with smaller groups (e.g., **[5]H** or **[5]Me**) show dimerization at the α-bonds, to give cyclynes **2**.[13,15,16] In the case of aryl substituents, the thermal reaction of **[5]Ph** forms **3** (Scheme 1), presumably via the [4]radialene **1b** and a subsequent [4 + 2] cycloaddition with **[5]Ph** followed by a [2 + 2] electrocyclization.[17] Finally, the dimerization of [5]cumulenes under Ni-catalysis has been reported by Iyoda and coworkers,[12] and the regiochemical outcome of these reactions centers on reaction at either the β- or γ-bond, dependent on the size and electronic makeup of the end groups. The reactivity of longer "odd" [*n*]cumulenes (i.e., *n* = 7

or 9) in cycloaddition reactions has not, to our knowledge, been reported to date.
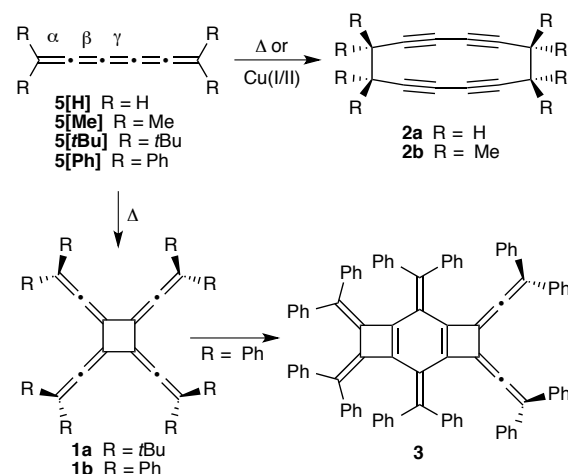
Scheme 1 Examples of thermal di- and trimerization reactions of [5]cumulenes.

We describe herein the dimerization of [*n*]cumulenes, including the first reported reactions of [7]- and [9]cumulenes. These transformations follow a similar reactivity pattern, and the products provide a unique series of expanded radialenes that have been characterized by X-ray crystallography.

Intrigued by the formation of **3** from **[5]Ph** as reported by Kawamura and coworkers, the thermal reaction of **[5]tBuPh**, recently synthesized in our laboratory,[18] was examined. After heating in toluene at reflux for 4 d (Scheme 2), the crude reaction mixture showed many products (by TLC analysis). The main product could be isolated by flash chromatography on silica gel, although NMR spectroscopy indicated the presence of several compounds. On the other hand, mass spectrometry showed a signal consistent with the mass expected for a dimer of **[5]tBuPh** (*m/z* 1657.3). Single crystals could be obtained by

layering a CH$_2$Cl$_2$ solution with hexanes, and X-ray crystallography of the colorless crystals (vide infra) revealed the formation of the cross-conjugated,[19] four-fold symmetric [4]radialene **4a**. Further optimization of this reaction was explored, but, quite surprisingly, all attempts to repeat the formation of **4a** have been unsuccessful. It thus seemed clear that the increased steric bulk of the di-*tert*-butyl phenyl groups of **[5]tBuPh** were a problem in comparison to the phenyl groups in **[5]Ph**. Thus, the use of a less sterically shielded [5]cumulene was explored, **[5]Tol**, a member of a new series of [*n*]cumulenes endcapped by *ortho*-tolyl substituents (Scheme 2).[20] All attempts to date toward converting **[5]Tol** to radialene **4b** have been frustratingly unsuccessful (Scheme 2), and we have not been able to expand on the preliminary formation of **4a**.
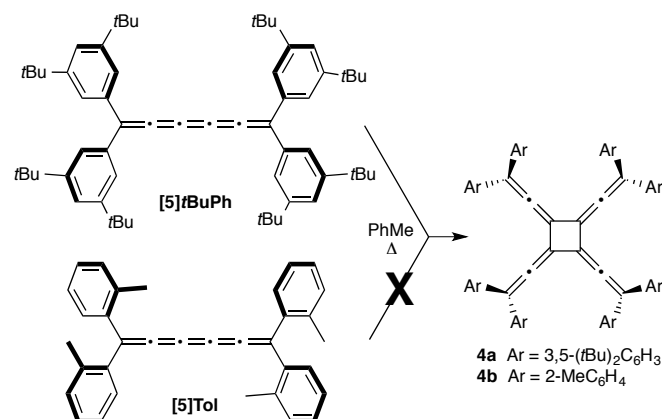

Scheme 2 Thermal dimerization reactions of **[5]tBuPh** and **[5]Tol**.

Although the investigations using [5]cumulenes were not generally successful, subsequent work with **[7]Tol** gave an interesting result.[20] When handling **[7]Tol** in solution at rt, it was obvious by TLC analysis that a second compound was being formed. ^{1}H and ^{13}C NMR spectroscopy offered only inconclusive evidence that the "by-product" contained a plethora of sp- and sp^2-hybridized carbon atoms, in addition to the presence of the methyl groups. Attempted purification of **[7]Tol** via crystallization at rt gave red crystals, and X-ray crystallographic analysis confirmed the formation of the dimeric, expanded radialene **5** (Scheme 3). Unlike the reactions with **[5]tBuPh**, however, dimerization of **[7]Tol** was quite reproducible. In a solution of CH$_2$Cl$_2$, the yield of **5** increased with longer reaction time, but the overall conversion was limited by the stability of **[7]Tol**, which decomposes in solution over a period of hours to give a light brown, insoluble precipitate. In the best case, the yield of **5** was 24%. Drawing from the seminal work by Iyoda and coworkers,[12] [Ni(CO)$_2$Cl$_2$] was explored as a catalyst toward improving the yield of **5**, but these attempts were not successful. Finally, it is worth noting that the dimerization reaction could be prevented if solutions of **[7]Tol** were maintained at low temperature (–20 °C).

The synthesis of **[9]Tol** provided an equally interesting outcome.[20] It was quickly noted that the stability of **[9]Tol** was

reduced compared to **[5]Tol** and **[7]Tol**, and purple solutions of **[9]Tol** in CH$_2$Cl$_2$ discolored within minutes at rt. Thus, a solution of **[9]Tol** in CH$_2$Cl$_2$ was layered with MeOH and stored at –20 °C. After several days grey needles were formed, and X-ray structural analysis indicated that the dimerization of **[9]Tol** had occurred to give expanded radialene **6** (Scheme 3). Similar to the dimerization of **[7]Tol** to **5**, the formation of expanded radialene **6** was also reproducible, giving yields of 5–10%.
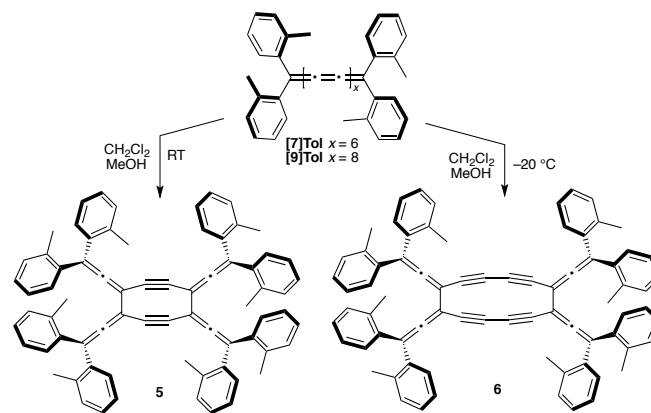
Scheme 3 Dimerization of **[7]**- and **[9]Tol** to expanded radialenes **5** and **6**, respectively.

With the X-ray crystallographic data of **4a**, **5**, and **6** in hand, general structural characteristics were examined, in comparison to other analogous macrocycles (Fig. 1). The exocyclic allene units of **5** and **6** are, in general, slightly bent from linearity, showing angles of ca. 173–177°. This is, more or less, consistent with values for **7**[12] and **8**,[21] which fall between 174–178°. In the case of **4a**, the bending of the allene results in dispersive interactions between the *tert*-butyl group and the neighboring aromatic ring, with the shortest C–H•••π distance of 2.95 Å (Fig. 1).[22]

For symmetrical [4]radialenes **4a**, **7**, and **9**,[23] the vinylidene/allenylidene angles (133–137°) deviate little from the expected values of 135°. In unsymmetric radialene **8**, on the other hand, steric bulk of the *tert*-butyl groups seems to play a role, and the two allene units are slightly expanded away from the vinyl groups, giving reduced bond angles on the allene "side" (129.0°). Finally, the presence of the vinylidene phenyl rings in the plane of the octaphenyl[4]radialene **9** produces a puckered structure (34.7°) that is similar to cyclobutane (ca. 32–35°, see reference 24).

The structure of expanded radialene **5** (Fig. 3) is most similar to that of **10**, reported by Diederich and coworkers.[25] Compound **5** also shares structural similarities with cyclooctadiyne **11**,[26] as wells as annulenes **12**[27,28] and **13**.[29] The acetylene units of **5** are significantly bent with angles of 156.8° and 156.9°, which is in the same range as values determined for molecules **10**–**12** (155.3–159.3°). It is interesting to consider the transannular distances between the acetylene carbons in **5**, from the standpoint of homoconjugation. The closest distance in **5**, C4–C5', is 2.64 Å, which is in good agreement with other known cyclooctadiynes
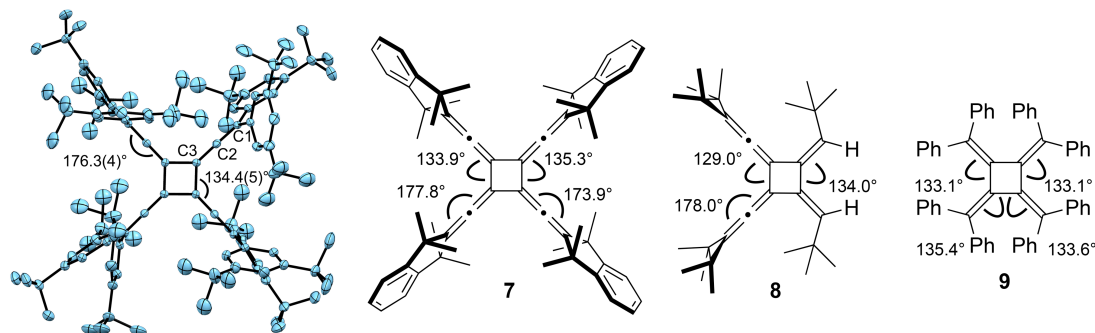
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Fig. 1 ORTEP drawing of radialene **4a** (ellipsoids at 30% probability level; hydrogen atoms not shown), in comparison to **7**–**9**.
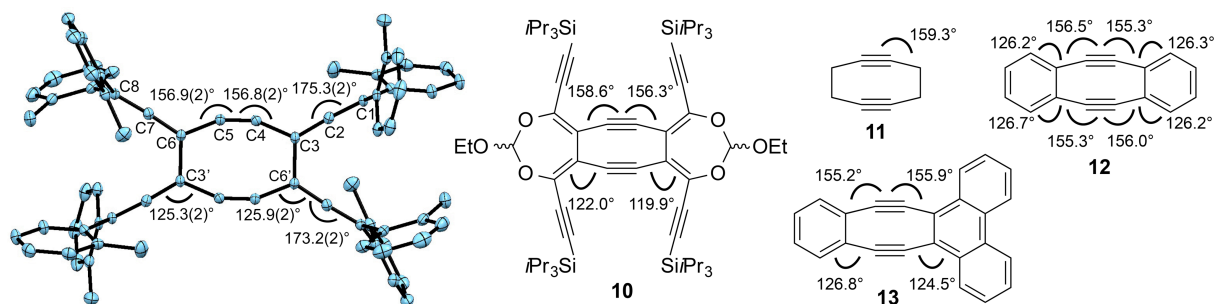

Fig. 2 ORTEP drawing of expanded radialene **5** (ellipsoids at 30% probability level; hydrogen atoms and cocrystallized solvent molecules not shown), in comparison to **10**–**13**.
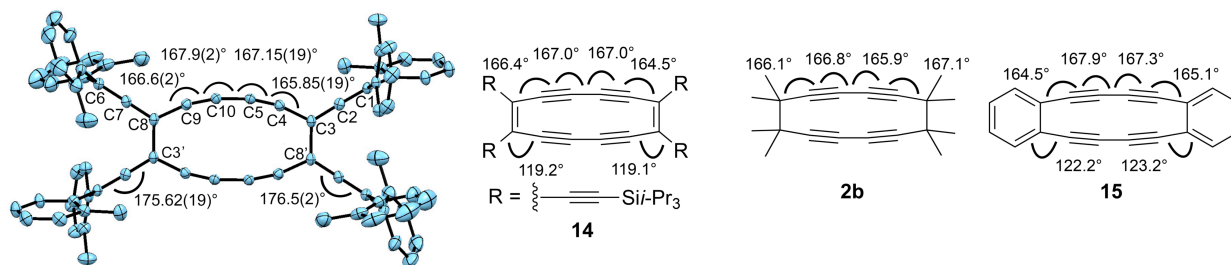

Fig. 3 ORTEP drawing of expanded radialene **6** (ellipsoids at 30% probability level; hydrogen atoms not shown), in comparison to **2b**, **14**, and **15**.

10 (2.59 Å), **11** (2.60 Å), **12** (2.62 Å), and **13** (2.57 and 2.60 Å). In all cases, this distance is less than the van der Waals radii, and, according to Gleiter and coworkers, a transannular distance of 3 Å or less is necessary for through-space interactions to occur.[30] It is, however, hard to determine if through-space conjugation plays a significant role.[31]

A comparison of the structure of **6** to that of the antiaromatic annulene **14**,[32] dodecatetrayne **2b**,[10,33] and benzoannulenes such as **15**[34] shows that all four molecules share a very similar geometry. Namely, the C–C≡C bonds fall within a narrow range of 164.5–167.9°.

A couple of comments regarding the ^{13}C NMR shifts of the sp-hybridized allene carbon of compounds **5** and **6** are noteworthy, since the resonances fall in a unique range[35] (the ^{13}C NMR spectrum of **4b** was, unfortunately, not available). In compounds **5** and **6**, the allene carbons resonate at 207.9 and 209.7 ppm, respectively, consistent with other 1,1-diarylallenes (210–200 ppm).[36] Tetraalkylallenes, on the other hand, generally show allene resonances in the range of 200–165 ppm.[37] The more ring strain present by the terminating rings, the farther upfield the signal shifts, as evident by a comparison of resonances in **7** (cyclopentyl endgroup) and **8** (cyclopropyl endgroup) at 189.8 and 178.7 ppm, respectively. Thus, ring strain might be reflected in the chemical shift of the allene carbon of **5** and **6**, although the effect is small.

Finally, it is perhaps expected that molecules such as **5** and **6** feature low energy absorptions due to their conjugated, carbon-rich framework. Like other radialenes and expanded radialenes without donor and/or acceptor groups, however, expanded radialenes **5** and **6** absorb in the high-energy region of the UV/Vis spectrum, with lowest energy absorption maxima (λ_{max}) at 275 and 359 nm, respectively.[19] This is at much higher energy compared to, for example, dehydroannulenes such as **14** (λ_{max} = 660 nm),[32] where linear-conjugation extends throughout the macrocycle.

In summary, we report the formation of three new radialenes (**4a**, **5**, and **6**) from the dimerization of [*n*]cumulenes (*n* = 5, 7, and 9). The formation of **5** and **6** from **[7]Tol** and **[9]Tol**, respectively, offers the first examples of expanded radialenes with allenylidene groups at the vertices. All three products are characterized by X-ray crystallography, and the most interesting structural feature is the significant strain in the acetylene unit (C3–C4–C5) in **5**, which is bent 23.2° from linearity. The dimerization reactions of all three derivatives, **[5]tBuPh**, **[7]Tol**, and **[9]Tol**, follow a similar pattern, and we are currently exploring if these reactions follow a concerted (i.e., pericyclic) or radical pathway.

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