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# Synthesis and properties of long [*n*]cumulenes ($n \geq 5$)

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Molecules composed of a contiguous sequence of double bonds, the [*n*]cumulenes, share structural similarities to both of their conjugated relatives, the polyenes and polyynes. The synthesis and properties of [*n*]cumulenes are, however, quite different from those of either polyenes or polyynes. At an infinite length, [*n*]cumulenes would provide one structural form of the hypothetical sp-hybridized carbon allotrope carbyne, while shorter derivatives offer model compounds to help to predict the properties of carbyne. Finally, derivatization of the π-electron framework of [*n*]cumulenes provides a number of different synthetic transformations, with cycloaddition reactions being the most common. In this review, both historical and recent synthetic achievements toward long [*n*]cumulenes ($n \geq 5$) are discussed. This is followed by a description of our current understanding of the physical and electronic structure of [*n*]cumulenes based on UV/vis spectroscopy and X-ray crystallography. Finally, the reactivity of long [*n*]cumulenes is described.

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## 1. Introduction

For some years, we have concerned ourselves with the study of the one-dimensional carbon allotrope carbyne, which is constructed of only sp-hybridized carbon atoms (Fig. 1).[1–4] The existence of carbyne has been a topic of much, and sometimes controversial,[5,6] discussion over the years.[7–14] Its natural existence has been proposed in, for example, meteorites,[15,16] interstellar dust,[17] and shock-compressed graphite,[18] as well as terrestrial plant, fungal, and marine sources (in the case of polyynes).[19–21] Furthermore, carbyne has been reportedly formed in the laboratory by a variety of processes, *e.g.*, by solution-phase synthesis,[12,22,23] laser irradiation of graphite,[24] or gas-phase deposition methods.[25] Whether naturally occurring or produced

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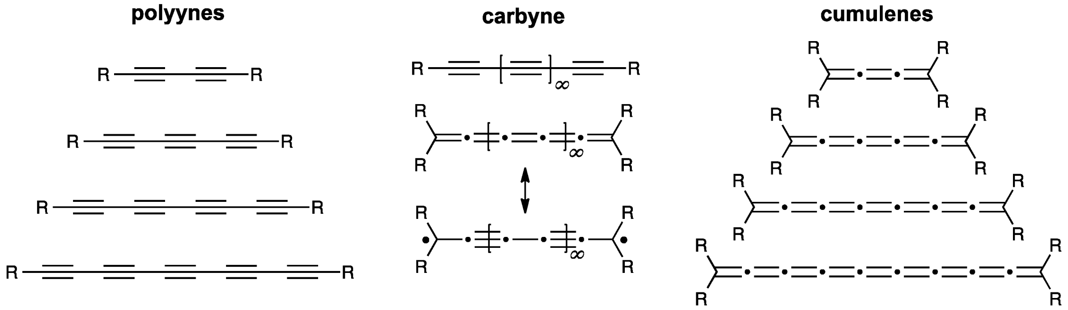


Fig. 1 Schematic depiction of carbyne and homologous series of polyynes and cumulenes as model compounds for carbyne.

in a laboratory, carbyne remains rather poorly characterized as a material, and the specific properties of carbyne are thus often difficult to define (at least in the opinion of the authors of this review). There are, nevertheless, quite a number of fascinating properties predicted for carbyne structures (or shorter polyyne/cumulene oligomers) from both theory and experiment, based on the unusual electrical and optical nature of sp-hybridized carbon.[26–32] This includes such applications as nanoelectronic or spintronic devices,[33] nonlinear optical materials,[34–37] molecular wires,[38–47] and others.[48–51] Recent theoretical calculations have also suggested that under tension, carbyne could be twice as stiff as the stiffest known materials, such as carbon nanotubes, graphene, and diamond.[33,52] Furthermore, even though carbyne might be extremely stiff against strain, it might also allow for deformation through bending without influencing the properties.[53]

In principle, two forms of carbyne might exist in a closed shell form (Fig. 1). One of these is the polyyne form which contains alternating triple and single bonds, giving a semiconductor at the carbyne limit, while the second possibility, the cumulene form, is composed of successive double bonds and should possess metallic behavior.[54,55] It has also been suggested that the cumulenic form might exist with diradical character that, with bond length alternation restored, could structurally resemble a polyyne.[56,57] Interestingly, Yakobson and coworkers predict a transition from cumulenic to acetylenic geometry as carbyne is stretched.[33] The reverse process has also been predicted, and studies suggest a transition from a polyyne structure to a cumulene form, for example, under UV photoexcitation[58] or charge transfer.[54] Theoretical calculations typically predict a higher stability for the polyyne form of carbyne.[33,59,60]

As should be noted from the brief literature survey presented above, the structure of carbyne is on the one hand fundamental to its properties, and on the other hand not well understood. Thus, investigation of carbyne might be best approached through the rational synthesis and study of molecules with defined structure (Fig. 1). For this reason, model compounds have been synthesized and studied as a function of length to predict properties of carbyne. To date, most synthetic work has been directed toward polyynes,[4,61–67] and the longest isolable polyyne so far contains 44 contiguous carbon atoms in a chain of 22 acetylene units.[4] Even at this length, however, polyynes have not yet achieved a carbyne-like ''status''. That is to say that UV/vis data show that saturation of the optical band gap has not yet been achieved, and extrapolation from this data predicts saturation at the point of *ca.* 48 acetylene units in order to form a carbyne-like compound, *i.e.*, where elongation through additional acetylene units has no effect. The results from UV/vis analysis are also supported by other studies, such as crystallographic analysis of bond length alternation.[68]

In comparison to polyynes, the investigation of [*n*]cumulenes (where *n* is the number of cumulated double bonds in a chain constructed of $n + 1$ carbon atoms) as model compounds for carbyne has barely been discussed in the literature.[69] To date, the longest cumulenes to be synthesized and studied are [9]cumulenes, *i.e.*, molecules with nine consecutive double bonds in a chain of 10 carbons.[70–73] On the basis of structure, a [9]cumulene is only approximately equal to the length of a rather short polyyne (a tetrayne). Unlike polyynes of this length, however, [9]cumulenes show dramatic instability under ambient conditions. The instability of [*n*]cumulenes has no doubt slowed progress on their synthesis and study. In this review, we discuss the history and evolution of cumulene synthesis, including current successes and limitations. The properties of long [*n*]cumulenes will then be discussed, in particular studies that address structural and electronic properties as they serve as model compounds for carbyne. As the structural motifs found throughout this review are rather large and appear numerous times, Fig. 2 offers a legend that introduces many of these structures and the associated nomenclature.

## 2. Synthesis of [*n*]cumulenes

Since Kuhn's early work on cumulenes in the 1930s,[74] quite a number of synthetic approaches have been developed to provide [*n*]cumulenes of various lengths. For the shorter analogues with $n = 3$ to 5, a number of common methods exist, mainly because of the greater stability of these cumulenes when compared to longer [*n*]cumulenes ($n > 5$). Better stability of the cumulene product also fosters greater functional group tolerance, and many more shorter cumulenes have been synthesized with $n < 5$. The synthesis of longer cumulenes benefited greatly from the pioneering advances for assembly of acetylenic compounds made by the groups of Bohlmann,[61,75]

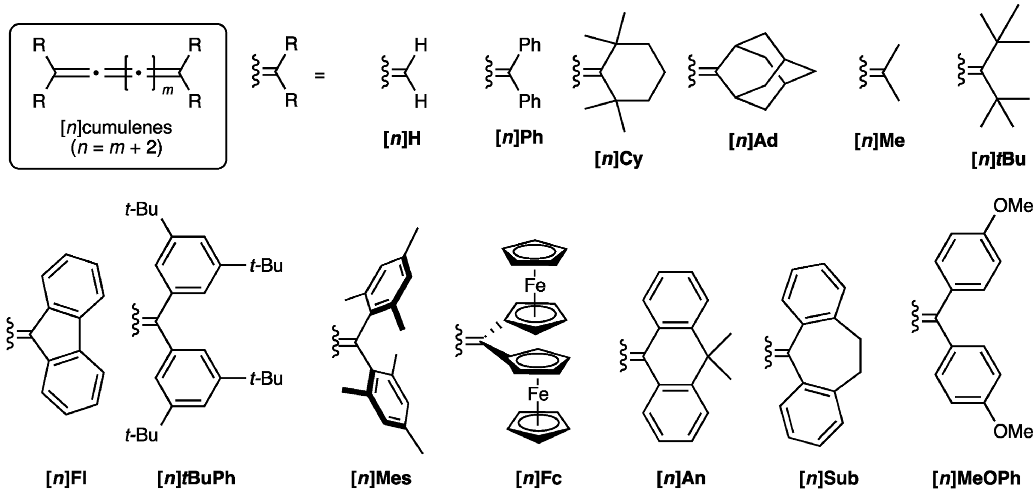


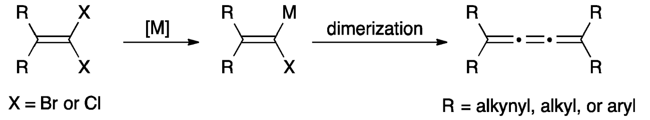
Fig. 2 Schematic depiction of major structural classes of [*n*]cumulenes discussed in this review, where *n* is the number of cumulated double bonds in a chain constructed of *n* + 1 carbon atoms.

Walton,[62,63,76] and Jones,[64,77] as well as others.[78–80] From this era, acetylene compounds, and more precisely oligoyne diols,[75,81] emerged as most convenient synthetic precursors for [*n*]cumulenes.

The following overview gives a summary of synthetic methods for cumulenes and is presented based on ascending molecular length, starting from [3]cumulenes and concluding with the longest [*n*]cumulenes known to date, the [9]cumulenes.[82] The goal of this synthetic section is twofold. First, the most common, or standard, synthetic pathways are presented, since these are most likely to be encountered in the current and future studies of cumulenes. Second, a number of alternative synthetic approaches are also described. These methods are often less general, but they offer insight into problems encountered with standard methods and provide a glimpse of the synthetic innovation that is often required for the synthesis of this challenging class of compounds. It is quickly recognized that most syntheses provide symmetrical substituted [*n*]cumulenes (four identical endgroups) with only a few exceptions. It is also noteworthy that the synthesis of tetraalkyl substituted [*n*]cumulenes is typically more difficult when compared to tetraaryl[*n*]cumulene, primarily due to stability of the products. Finally, the assembly of even-numbered [*n*]cumulenes (*n* = 4 and 6) is more complicated than that of odd-numbered [*n*]cumulenes (*n* = 5, 7, 9) due to synthetic accessibility of the precursors. Metallacumulenes are not included in this synthetic summary,[83–87] although cumulenes used as ligands for metal coordination will be discussed briefly in the reactivity section. For more comprehensive descriptions of the syntheses of shorter [*n*]cumulenes, the reader is directed to reviews, for example, by Chauvin,[88] Cadiot,[89] Bruneau,[90] and Ogasawara.[82]

### 2.1 Synthesis of [3]cumulenes

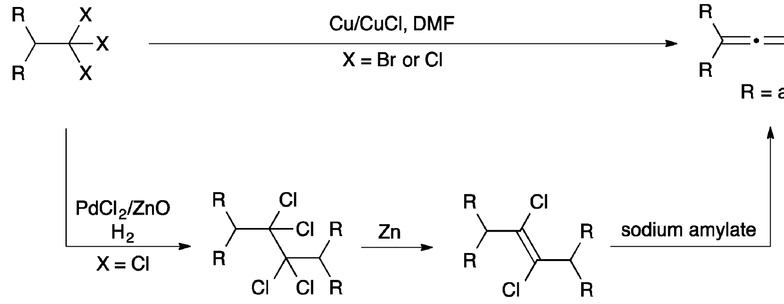
The synthesis of [3]cumulenes has recently been reviewed,[88] and only selected examples are discussed here. One of the most common routes to [3]cumulenes is the metal catalyzed dimerization of carbenes/carbenoids (Scheme 1), as summarized in a review by Stang.[91] These can be accomplished using the Cu(I) catalyst for aryl or alkynyl substituents as described by Diederich,[92,93] as well as Kunieda and Takizawa.[94] On the other hand, Iyoda[95,96] used a Ni(II) catalyst to form [3]cumulenes. Tetraalkyl[3]-cumulenes can be made directly from a lithium carbenoid as reported independently by, for example, Köbrich,[97] Komatsu,[98] and Oda.[99] Stang, on the other hand, successfully formed a variety of alkyl substituted [3]cumulene *via* the carbenoid route using ethynylvinyl triflates as precursors.[100,101]



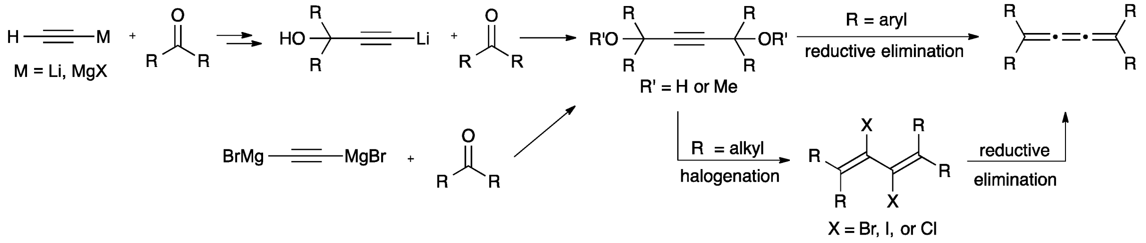
Scheme 1 Synthesis of [3]cumulenes based on the carbene/carbenoid route (M = metal).

An alternative method to generate carbenoids for the synthesis of [3]cumulenes is based on elimination of trihaloalkanes (Scheme 2). Direct elimination using a Cu/Cu(I) catalyst system gave [3]cumulene products in moderate yields (*ca.* 40–60%).[94] Brand and coworkers,[102,103] on the other hand, describe a route that proceeds through a dichloroalkene intermediate formed through reduction of the trihaloalkane, and this overall protocol gives higher yields (>85%) than the direct elimination although it requires three distinct synthetic steps.

The most common synthetic route to [3]cumulenes is based on the reduction of an acetylenic diol or diether derivative (Scheme 3). The precursor is usually a Li- or Mg-acetylide,[57,70,71,74,104–106] which is used in an addition reaction with a ketone that defines the endgroups. In cases where the free alcohols may not be compatible with subsequent synthetic steps, it can be blocked by the formation of, for example, methyl ethers through trapping with MeI.[70] From either the diol or diether, aryl substituted [3]cumulenes can be formed directly *via* reduction with $SnCl_2$,[70,106] although $P_2I_4$[74] or HI and $I_2$[105] have also been used. Tetraalkyl[3]cumulenes are usually



Scheme 2 Synthesis of [3]cumulenes based on reductive elimination of trihaloalkanes.



Scheme 3 Synthesis of [3]cumulenes based on acetylenic diol derivatives.

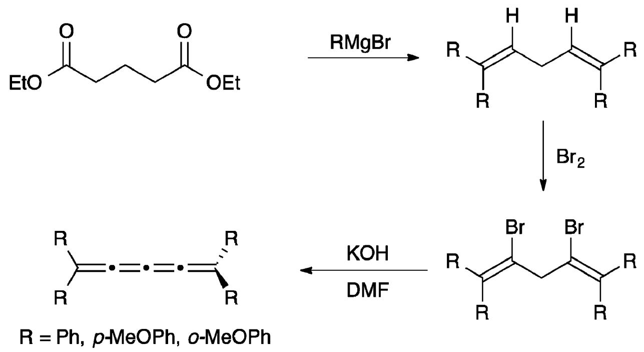
formed *via* halogenation, followed by reductive elimination (Scheme 3).[71,107,108]

## 2.2 Synthesis of [4]cumulenes

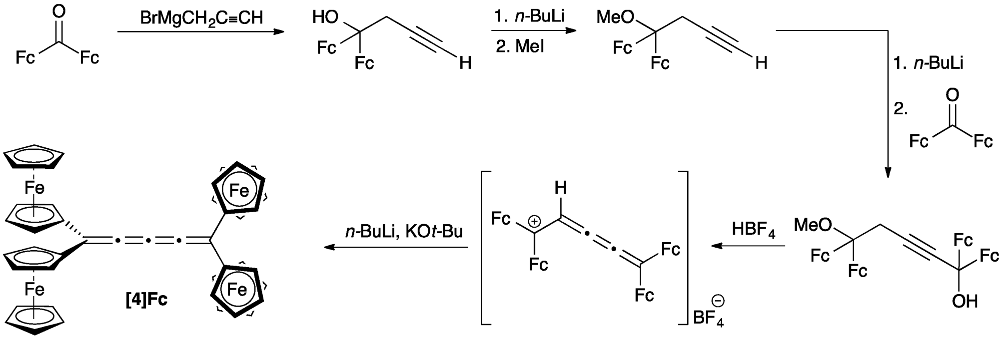
Bildstein and coworkers have reported the formation of **[4]Fc** based on an adaptation of the diol approach described above for [3]cumulenes (Scheme 4).[106,109] A homopropargylic ether is formed, lithiated, and then added to diferrocenylketone to complete the carbon skeleton. Treatment with acid ($HBF_4$) results in the stabilized (and isolable) [3]cumulene intermediate, which can then be converted to **[4]Fc** through base induced elimination. Bildstein's approach is conceptually similar to that reported earlier by Nakagawa and coworkers,[110] in which two different endgroups have been introduced in order to explore optical activity and racemization of [4]cumulenes.

Another possibility of the formation of tetraaryl[4]cumulenes has first been described by Kuhn[111] and then Karich and Jochims[112] and relies on the intermediate formation of dibromo-1,4-pentadienes from the appropriate unsubstituted dienes (Scheme 5). The diene is then converted to the [4]cumulene in good yield through base-induced elimination.

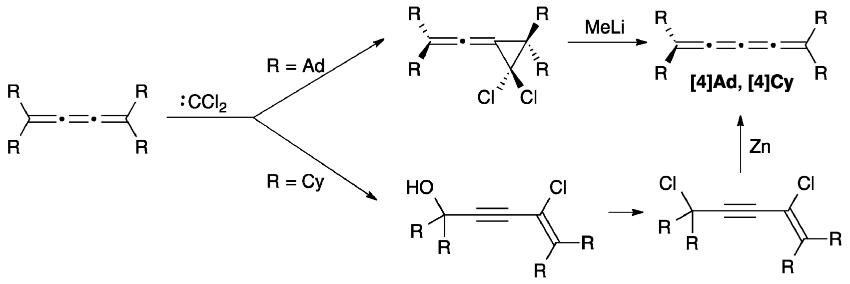
[3]Cumulenes can be converted to [4]cumulenes *via* addition of dichlorocarbene to a [3]cumulene, followed by rearrangement or reductive elimination, depending on the structure of



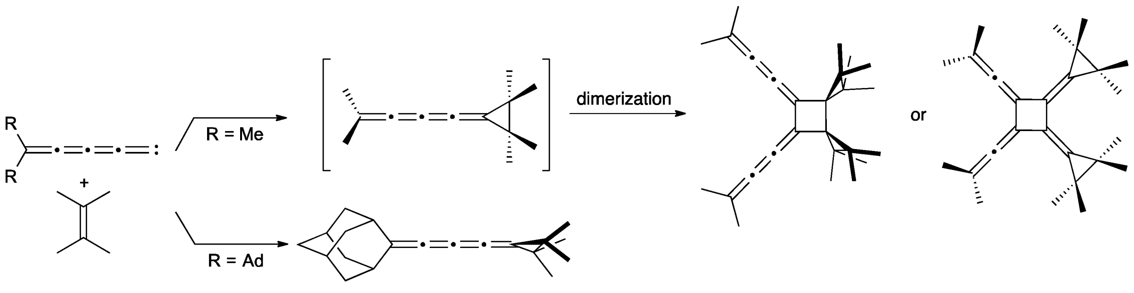
Scheme 5 Synthesis of [4]cumulenes from diesters.



Scheme 4 Synthesis of **[4]Fc** based on a diol derivative.



Scheme 6 Synthesis of [4]cumulenes from [3]cumulenes.



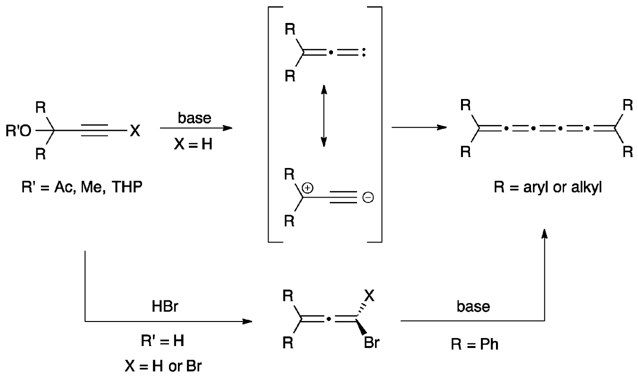
Scheme 7 Synthesis of a [4]cumulene *via* carbene trapping with an olefin.

the precursor (Scheme 6). Jochims and coworkers highlight the potential effectiveness of this route through formation of **[4]Ad**, where MeLi gives a quantitative yield in the reduction step. Their route also provides rare examples of mixed dialkyl/diaryl endcapped [4]cumulenes.[112] Irngartinger and Götzmann have developed a slightly modified version of this general protocol to synthesize **[4]Cy**, using Zn in the final reductive elimination step (Scheme 6).[113]

[4]Cumulenes can be obtained *via* carbene trapping as demonstrated by le Noble and coworkers (Scheme 7).[114,115] The dialkylpentatetraenylidene intermediate is formed and reacts *in situ* with tetramethylethylene to give the [4]cumulene, which quickly converts to a radialene through dimerization (in the case of R = Me). The analogous reaction with 2-adamantylpentatetraenylidene, on the other hand, forms the stable [4]cumulene.

## 2.3 Synthesis of [5]cumulenes

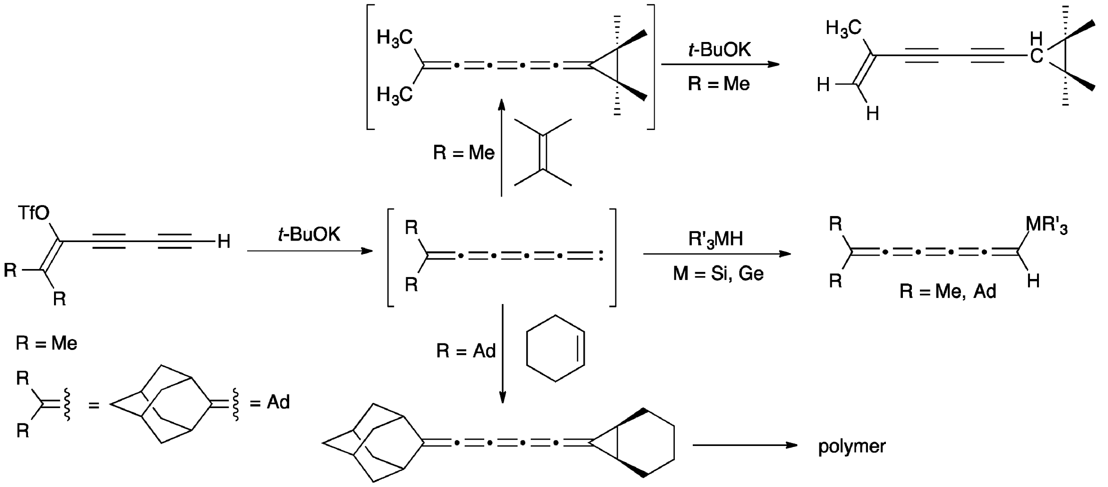
Of the higher [$n$]cumulenes ($n \geq 5$), [5]cumulenes are by far the most studied and there are thus a number of efficient routes that have been developed for their synthesis.[82] In analogy to the syntheses described for [3]cumulenes, dimerization reactions of carbenes have been used to give [5]cumulenes (Scheme 8).[57,106,116–120] Starting with a terminal acetylene and a leaving group in the propargylic position, reaction with base produces a carbene intermediate, which leads to the [5]cumulene *via* dimerization. An alternative carbenoid route to [5]cumulenes has been described by Kollmar and Fischer,[121] in which the vinylidene carbenoid is generated directly from a haloallene (Scheme 8). It is interesting to note that the influence of endgroups in this reaction is likely enhanced *versus* the analogous reaction to give [3]cumulenes, considering the mesomeric stabilization of this intermediate carbene (Scheme 8).



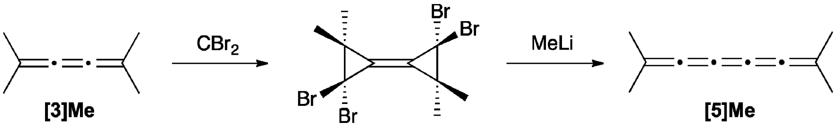
Scheme 8 Synthesis of [5]cumulenes based on carbenes/carbenoids.

Unsymmetrical [5]cumulenes can be synthesized through trapping of vinylidene carbenes, as reported by Stang and coworkers (Scheme 9).[101,122,123] More specifically, elimination of a diyne vinyl triflate forms the intermediate carbene, which can be trapped by either addition to electron rich alkenes (*i.e.*, tetramethylethylene and cyclohexene) or M–H bond insertion using $R_3MH$ (M = Si, Ge). In some cases, the resulting [5]cumulene is not stable and isomerizes or polymerizes during the reaction.

[5]Cumulenes can be formed based on the reaction of a [3]cumulene with dibromocarbene as described by Skattebol (Scheme 10).[124] The addition of dibromocarbene to tetramethyl[3]cumulene gave the bicyclopropylidene product, and the subsequent rearrangement reaction, induced with MeLi, gives the unstable **[5]Me** product.



Scheme 9 Synthesis of unsymmetrical substituted [5]cumulenes based on carbenoids.

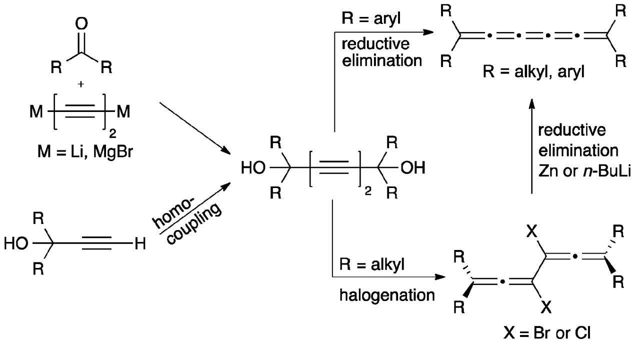


**[3]Me** **[5]Me**

Scheme 10 Synthesis of **[5]Me** from **[3]Me**.

Assembly of [5]cumulenes based on acetylenic diol precursors is quite common (Scheme 11), in part because the necessary precursor, a diyne diol, can be efficiently formed *via* a number of routes. Often mimicking strategies described for [3]cumulenes, acetylenic diols are thus readily assembled through, for example, the addition of a Li- or Mg-acetylide to a ketone. Alternatively, oxidative homocoupling of propargyl alcohol derivatives is usually quite efficient.

With the diyne diol in hand, conversion directly to an aryl substituted [5]cumulene is accomplished *via* reduction with $P_2I_4$,[74] $CrCl_2$,[125] or $SnCl_2$.[70,126,127] In the majority of the recent studies, $SnCl_2$ is the reductant of choice and usually gives good yields. In the case of alkyl substitution, conversion of the diyne diol to the corresponding dihalide with $PI_3$,[71] $PBr_3$,[71,127] HBr,[127] or HCl[127] is required, which is then followed by reductive elimination using Zn or *n*-BuLi.



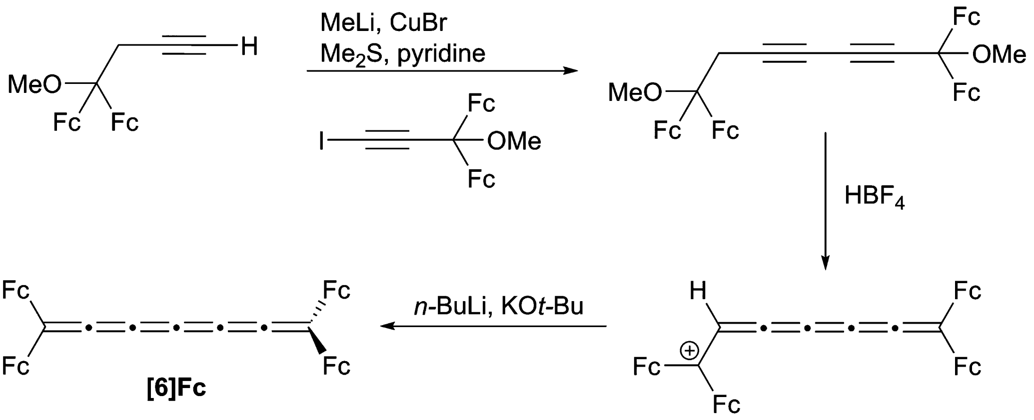
Scheme 11 Synthesis of [5]cumulenes based on acetylenic diol derivatives.

### 2.4 Synthesis of [6]cumulenes

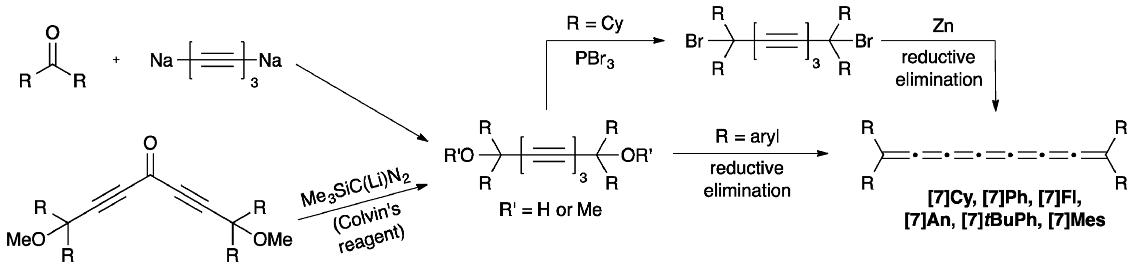
To date, only one synthesis has been reported for a [6]cumulene, namely **[6]Fc** (Scheme 12). Bildstein and coworkers[128] have shown that a diyne diether can be readily assembled *via* an acetylenic cross-coupling reaction, and the [6]cumulene is then realized through an elimination process similar to the synthesis of the **[4]Fc**. It is worth mentioning that after the first elimination step, an unusual, air-stable cumulenium salt is obtained, and the stability is explained by the presence of four ferrocene donor groups and the unsaturated cumulene chain. Unfortunately, the resulting air-sensitive **[6]Fc** product could not be isolated, but UV/vis spectroscopy confirms the formation of the cumulene framework.

### 2.5 Synthesis of [7]cumulenes

To our knowledge, only seven tetraaryl[7]cumulenes and one tetraalkyl[7]cumulene have been reported to date.[70,71,129–131] All [7]cumulenes have been assembled from the corresponding triyne diol precursor (Scheme 13), which is typically formed as described above for [3]- and [5]cumulene syntheses. An alternative approach to the requisite diol has recently been reported, using a carbenoid Fritsch–Buttenberg–Wiechell (FBW) rearrangement[1–3] in combination with Colvin's reagent[132–134] to form the triyne framework.[70] Following the trends established by [3]- and [5]cumulene syntheses, formation of the tetraalkyl[7]cumulene requires conversion of the diol to the dibromide, followed by reductive elimination with Zn. In contrast, the tetraaryl[7]cumulenes can be formed directly by reduction with either $P_2I_4$ or $SnCl_2$. In most cases, the [7]cumulenes tend to decompose quickly, either in solution



Scheme 12 Synthesis of **[6]Fc**.



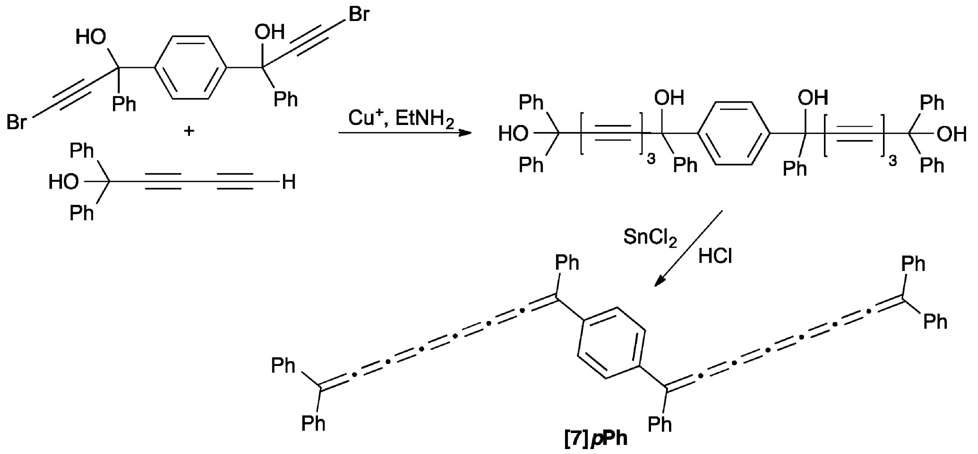
Scheme 13 Synthesis of [7]cumulenes based on acetylenic diol derivatives.

or in the solid state. In the most recent report on cumulene synthesis, however, Januszewski *et al.* show that **[7]*t*BuPh** and **[7]Mes** are sufficiently stabilized using sterically demanding aryl endcapping groups to provide crystalline products.[70]

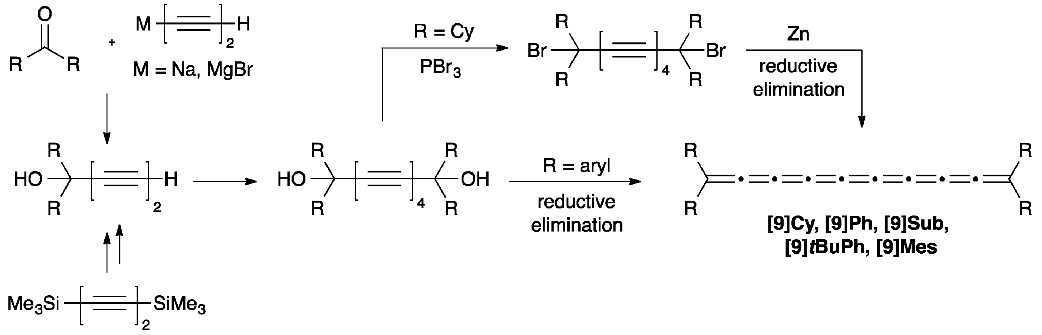
Perhaps the most structurally interesting [7]cumulene reported to date, **[7]*p*Ph**, was synthesized by Cadiot and coworkers through a variation of the diol approach as outlined in Scheme 14.[131] In this case, the acetylenic diol precursor was assembled using a Cu-catalyzed heterocoupling between a terminal diacetylene and a bromoacetylene derivative. While the final product could not be isolated, UV/vis spectroscopy confirmed formation, with a lowest energy absorption at 700 nm that is red-shifted *versus* that of all other [7]cumulenes (*vide infra*).

### 2.6 Synthesis of [9]cumulenes

As a result of instability of the final product, very few [9]cumulenes have been successfully assembled, and there are only five examples to be found in the literature, including four tetraaryl- (**[9]Ph**, **[9]Sub**, **[9]*t*BuPh**, **[9]Mes**)[70,72,73] and one tetraalkyl[9]cumulene (**[9]Cy**).[71] The synthetic pathway to [9]cumulenes is, predictably, analogous to that of [5]cumulenes, except that diynes provide the precursors for the dimerization, rather than terminal



Scheme 14 Synthesis of the bis[7]cumulene **[7]*p*Ph**.



Scheme 15 Synthesis of [9]cumulenes based on acetylenic diol derivatives.

alkynes (Scheme 15). As per usual, tetraaryl derivatives are formed directly from the diol *via* reduction using $P_2I_4$ or $SnCl_2$, while the tetraalkyl[9]cumulene **[9]Cy** must be synthesized from the dibromide, *via* reduction with Zn. Isolated yields have not been reported for any of the [9]cumulenes due to the inability to isolate the unstable product.

## 3. UV/vis spectroscopy

UV/vis spectroscopy has been the most common characterization method for long [*n*]cumulenes and in early studies it was the essential tool to confirm formation of [7]- and [9]-cumulenes.[135] Using homologous series of [*n*]cumulenes, UV/vis spectroscopy allows analysis of electronic trends, *i.e.*, optical band gap, as a function of cumulene length and substitution. Similar to that demonstrated for polyynes,[136] UV/vis spectroscopic analysis *versus* molecular length might also allow extrapolation to an infinite chain length, which would offer a prediction of the band gap of the cumulenic version of carbyne. To date, however, this has not been possible due to the limited number of model compounds that are currently available.

In principle, three major factors govern trends typically observed in the UV/vis spectra of [*n*]cumulenes, including (1) structure of the [*n*]cumulene (odd- *versus* even-numbered [*n*]cumulenes), (2) molecular length, and (3) the nature of the terminal substitution, *i.e.*, endgroup effects (aryl *versus* alkyl giving mesomeric *versus* inductive effects, respectively).

### 3.1 Comparison of odd- *versus* even-numbered [*n*]cumulenes

The influence of odd- *versus* even-numbered [*n*]cumulenes is delineated schematically in Fig. 3, and this also demonstrates the potential mesomeric or inductive contribution from the endgroups. For even-numbered cumulenes, there are two π-systems that are degenerate and spatially orthogonal (Fig. 3a). In the case of aryl endcapping groups, each orthogonal π-system can conjugate with substituents at one end of the cumulenic framework, but not both. The situation is distinctly different for odd-numbered cumulenes (Fig. 3b), where the two π-systems of the sp-carbon framework are no longer degenerate. In this case, one π-system spans the length of the cumulene skeleton and can conjugate with both sets of endgroups (Fig. 3b, in red). The other π-system (in blue) does not communicate directly with the endgroups (*i.e.*, *via* resonance) and is thus considerably shortened, although hyperconjugation with terminal groups is easily envisioned. It is worth noting that the influence of odd- *versus* even-numbered [*n*]cumulene structure should also be observed in the bond length alternation (BLA) of cumulenes. As shown by the mesomeric structures in Fig. 3b, increased BLA is expected for odd [*n*]cumulenes and should be further enhanced by groups able to conjugate to the cumulene core.

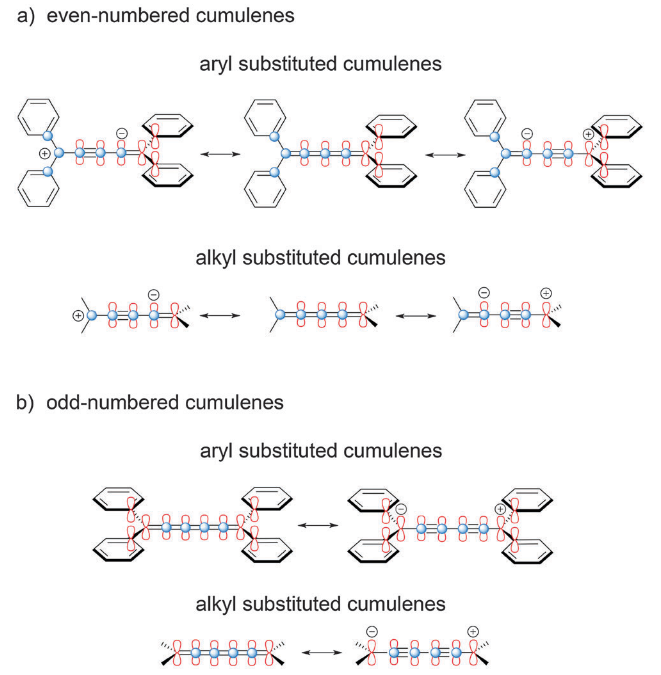


Fig. 3 Electronic effects based on odd- and even-numbered [*n*]cumulenes, as demonstrated schematically with canonical structures for [4]- and [5]cumulenes.

### 3.2 Comparison of [*n*]cumulenes as a function of length *n*

The UV/vis spectroscopic data of a series of tetraaryl- and tetraalkyl[*n*]cumulenes (**[*n*]*t*BuPh** and **[*n*]Cy**, respectively) are given in Fig. 4, and these two examples include the most complete analyses reported to date with $n = 3, 5, 7$, and 9 for both sets of molecules. A distinct signal pattern is immediately observed, showing two regions of absorption bands for both tetraaryl- and tetraalkyl[*n*]cumulenes, with the most intense

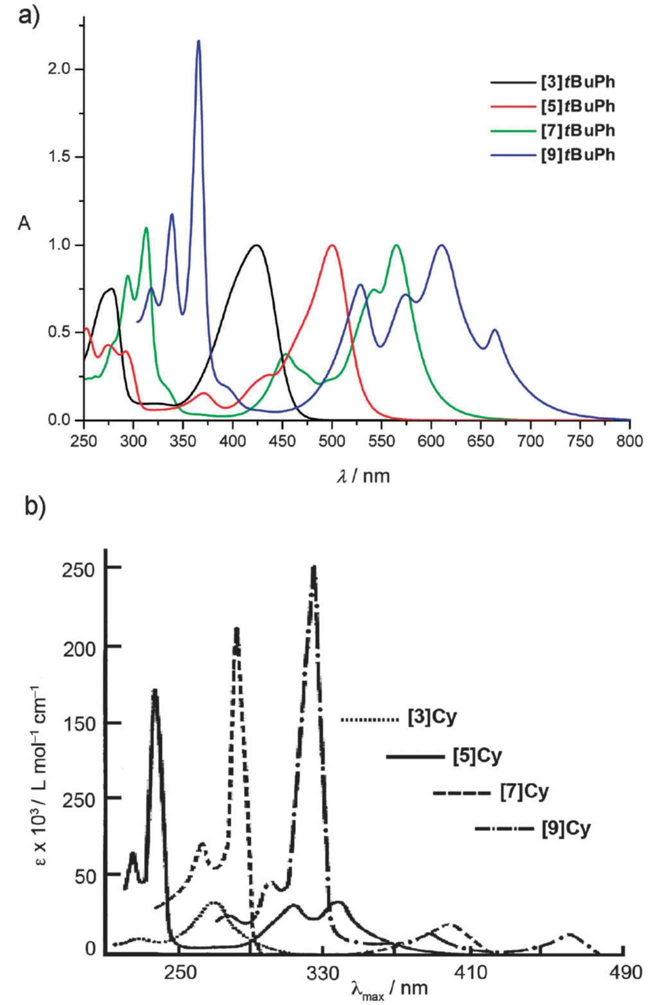


Fig. 4 UV/vis spectra of [*n*]cumulenes. (a) **[*n*]*t*BuPh** measured in $Et_2O$; spectra normalized to the most intense low energy absorption and (b) **[*n*]Cy** measured in $Et_2O$ (adapted with permission from ref. 135. Copyright 1964 John Wiley & Sons).

absorptions mostly found at higher energy in the UV region (<400 nm). The observation that the fine structure of the absorption in the UV region often increases as a function of molecular length is noteworthy. The second set of absorptions is found in the visible region for tetraaryl[*n*]cumulenes from 420–670 nm, and at much higher energy for the tetraalkyl[*n*]cumulenes due to the absence of conjugation with the alkyl endgroups and the cumulene core (see Fig. 3).

The most obvious consequence of π-electron conjugation is observed in $\lambda_{max}$ values as a function of cumulene length chain, as demonstrated by values of the four [*n*]cumulene series listed in Table 1. As expected, $\lambda_{max}$ values of tetraarylcumulenes are found at much lower energy than those of the tetraalkylcumulenes, *e.g.*, 663 nm *versus* 465 nm, respectively, for **[9]Ph** and **[9]Cy**. A monotonic red-shift in $\lambda_{max}$ is clearly visible as the cumulene length is increased within each series, indicating a decreasing HOMO → LUMO energy gap. It would be expected that at some cumulene length this effect reaches saturation, and $\lambda_{max}$ would reach a minimum and constant value. This limiting value would then represent an estimate of energy gap ($E_g$) of the material "cumulenic" carbyne. Several methods have been used for polyynes to describe the relationship between $E_g$, $\lambda_{max}$, and *n*, such as an empirical power-law[137,138] ($E_g = 1/\lambda_{max} \sim n^{-x}$) or the exponential function proposed by Meier and coworkers.[139] Unfortunately, attempts to apply these protocols to the cumulenes reported in Table 1 provide inconclusive estimates for $E_g$, and longer cumulenes ($n > 9$) are needed to complete this analysis. Thus, no experimental estimate for the cumulenic form of carbyne is currently available.

Table 1 UV/vis spectroscopic data ($\lambda_{max}$ in nm) for **[*n*]Ph**, **[*n*]*t*BuPh**, **[*n*]Mes**, and **[*n*]Cy** as a function of molecule length *n*

| [*n*]cumulene | **[*n*]Ph**[a] | **[*n*]*t*BuPh**[b] | **[*n*]Mes**[b] | **[*n*]Cy**[b] |
|---|---|---|---|---|
| 3 | 420 | 424 | — | 272 |
| 4 | 422[c] | — | — | 342[c] |
| 5 | 489 | 500 | 460 | 339 |
| 7 | 557 | 564 | 560 | 401 |
| 9 | 663[b] | 664 | 666 | 465 |
| Ref. | 72, 74, 103, 111, 129, 140 | 70 | 70 | 71, 113 |

[a] Benzene. [b] $Et_2O$. [c] Cyclohexane.

The nature of the four endgroups appended to the cumulene framework is expected to play an import role in $\lambda_{max}$ values (*i.e.*, alkyl *versus* aryl). Within a series of cumulenes, however, experimental data show that the influence of the endgroups decreases rapidly as a function of cumulene length. For example, $\lambda_{max}$ values of the tetraaryl[5]cumulenes **[5]Ph**, **[5]*t*BuPh**, and **[5]Mes** (489, 500, and 460 nm, respectively), vary rather significantly (Table 1). The $\lambda_{max}$ values of the longer analogues **[7]Ph**/**[7]*t*BuPh**/**[7]Mes** and **[9]Ph**/**[9]*t*BuPh**/**[9]Mes** are, however, nearly identical, with values of about 560 nm and 665 nm, respectively.

### 3.3 Comparison of [5]cumulenes as a function of endcapping group

In Table 2, $\lambda_{max}$ values are given for a selection of [5]cumulenes, and the comparison of these values offers insight into the specific influence of the endgroup. The biggest shift to lower energy is observed for cumulenes in which the pendent aryl rings are forced to be coplanar to the cumulene framework, namely **[5]An** ($\lambda_{max}$ = 555 nm) and **[5]Fl** ($\lambda_{max}$ = 542 nm). Thus planarity of aryl endgroups appears to be a dominant factor. This supposition is also supported by $\lambda_{max}$ value measured for **[5]Mes** (465 nm), for which steric hindrance from the 2- and 6-methyl groups inhibits coplanarity of the aryl groups with the cumulene core, a fact supported by X-ray crystallographic analysis (*vide infra*).

Substituted [5]cumulenes **[5]MeOPh** and **[5]*t*BuPh** show red-shifted $\lambda_{max}$ values relative to **[5]Ph** with $\lambda_{max}$ = 517 and 510 nm, respectively. These features are readily explained by mesomeric and inductive effects of the MeO- and *t*Bu endgroups, respectively, which donate electron density into the electron deficient sp-carbon framework.

Finally, the greatest blue shift in $\lambda_{max}$ is found for tetraalkyl cumulene **[5]*t*Bu** ($\lambda_{max}$ = 337 nm in $Et_2O$), which is at *ca.* 150 nm

Table 2 UV/vis spectroscopic data ($\lambda_{max}$ in nm) of [5]cumulenes with different endgroups

| | **[5]An** | **[5]Fl** | **[5]MeOPh** | **[5]*t*BuPh** | **[5]Ph** | **[5]Mes** | **[5]Cy** | **[5]*t*Bu** | **[5]Me** |
|---|---|---|---|---|---|---|---|---|---|
| | 555[a] | 542[a]<br>540[a]<br>543[b]<br>547[c] | 517[a] | 510[a]<br>500[d] | 488[a]<br>489[b]<br>485[e]<br>493[c] | 465[a]<br>460[d] | 339[d] | 337[d]<br>336[f,g] | 320[h] |
| Ref. | 130 | 74, 140, 120 | 120 | 70 | 119, 120, 127, 140 | 70 | 71 | 57, 141 | 142 |

[a] $CHCl_3$. [b] Benzene. [c] Pyridine. [d] $Et_2O$. [e] THF. [f] Isooctane. [g] Ref. 57 reports the lowest energy absorption value as 417 nm, but with negligibly low $\varepsilon$ value of 870 L $mol^{-1}$ $cm^{-1}$, thus the next higher energy value of 336 nm was taken here for comparison. [h] EtOH.

higher energy *versus* **[5]Ph**. There is, obviously, no mesomeric contribution from the alkyl endgroups to the conjugated structure of **[5]*t*Bu**, but hyperconjugation with the four *t*-butyl groups appears to be present based on the comparison to **[5]Me** ($\lambda_{max}$ = 320 nm).

### 3.4 Comparison of [*n*]cumulenes to polyenes and polyynes

It is interesting to compare the UV/vis spectroscopic behavior of [*n*]cumulenes *versus* other conjugated oligomers of analogous size and substitution patterns, such as polyenes and polyynes (Table 3 and Fig. 5). The main goal of this analysis is to offer an empirical evaluation of electronic delocalization for the three compound classes; thus, comparisons of $\lambda_{max}$ values are made between molecules that share the same number of π-electrons in the longest conjugated segment. It is noted that for the phenyl endcapped series, however, a "fair" comparison is not possible due to the different valency requirements of the terminal atoms of each chain, *i.e.*, termination with sp- *versus* $sp^2$-carbon. It is also important to emphasize again the different π-electron system(s) present in each molecule, as described earlier in Fig. 3. Namely polyenes have only a single π-system, while polyynes possess two degenerate, orthogonal π-systems (Fig. 5). Finally, [*n*]cumulenes have two non-degenerate π-systems, *i.e.*, one that extends the length of the molecule and conjugates to the endgroups (in red, Fig. 5) and a shorter π-system that is orthogonal and cannot conjugated to the endgroups (in blue, Fig. 5). The electron count for each molecule shown in Table 3 includes only electrons found in the longest conjugated π-system in each case.

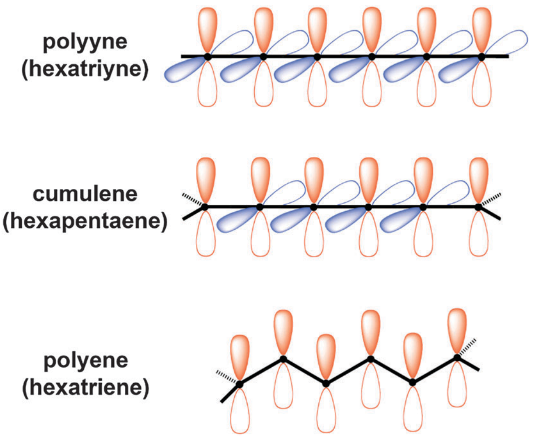
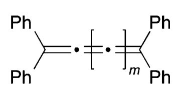


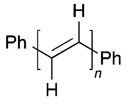
Fig. 5 Schematic depiction of π-orbitals of structures with six π-electrons in the longest conjugated segment shown in red: a polyyne, cumulene, and polyene. The orthogonal and degenerate six π-electron segment of the hexatriyne and the orthogonal four π-electron segment of the [5]cumulene are shown in blue.

The most interesting point to be gleaned from these comparisons is that for all series of molecules with equivalent π-electron counts, cumulenes show the lowest energy absorption, followed by polyenes and then polyynes (except for the pentayne $\mathbf{Ph_{(\equiv)}[5]}$). The nature of the endcapping group also

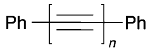
Table 3 Comparison of UV/vis spectroscopic data ($\lambda_{max}$ in nm) of cumulene, polyenes, and polyynes containing phenyl or alkyl endgroups (based on the number of π-electrons in the longest conjugated segment)



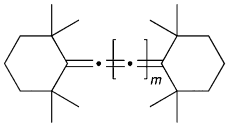
**[*n*]Ph**
*n* = *m* + 2



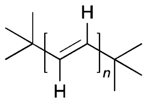
**Ph₍₌₎[*n*]**



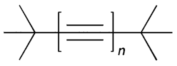
**Ph₍≡₎[*n*]**



**[*n*]Cy**
*n* = *m* + 2



**tBu₍₌₎[*n*]**



**tBu₍≡₎[*n*]**

| π-Electrons | [*n*]Ph | $\mathbf{Ph_{(=)}[\mathit{n}]}$[a] | $\mathbf{Ph_{(\equiv)}[\mathit{n}]}$[a] | [*n*]Cy[b] | $\mathbf{tBu_{(=)}[\mathit{n}]}$[c] | $\mathbf{tBu_{(\equiv)}[\mathit{n}]}$[d] |
|---|---|---|---|---|---|---|
| 4[e] | 420 | 352 | 331 | 272 | 237 | —[f] |
| 6[g] | 489 | 377 | 363 | 339 | 276 | 213 |
| 8[h] | 557 | 404 | 402 | 401 | 311 | 240 |
| 10[i] | 663[a] | 424 | 437 | 465 | 343 | 266 |
| Ref. | 74, 103, 129, 72, 140 | 143, 144 | 144 | 71 | 145 | 68 |

[a] Benzene. [b] $Et_2O$. [c] *n*-Pentane. [d] Hexanes. [e] A [3]cumulene, diene, and diyne. [f] No measureable UV-absorption in solution (*i.e.*, sample absorption lies under solvent absorption). [g] A [5]cumulene, triene, and triyne. [h] A [7]cumulene, tetraene, and tetrayne. [i] A [9]cumulene, pentaene, and pentayne.

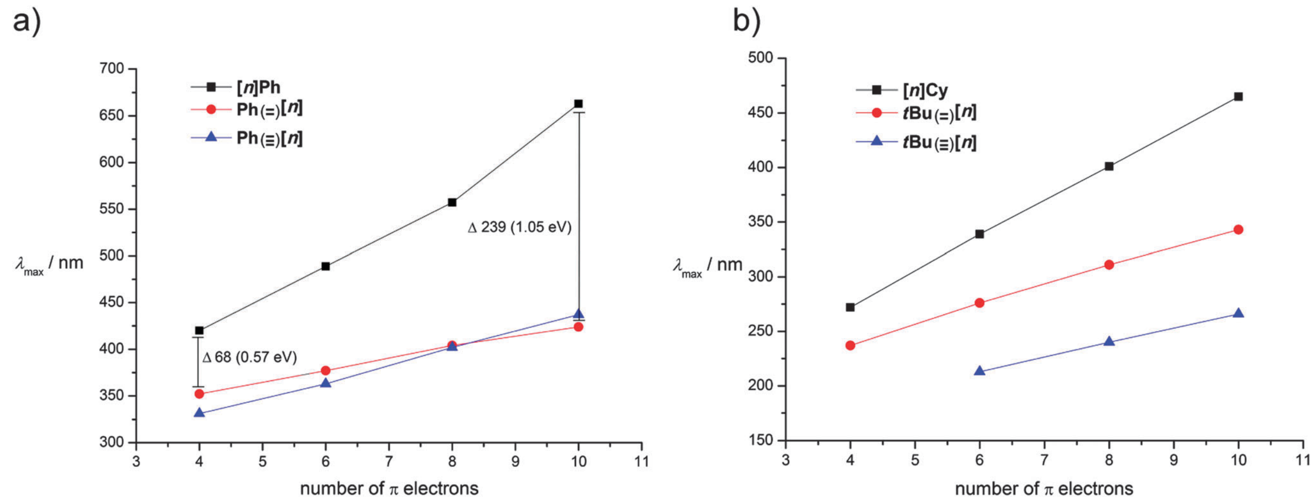


Fig. 6 Plot of lowest energy absorption $\lambda_{max}$ *versus* number of π-electrons for (a) phenyl- and (b) alkyl substituted cumulenes, polyenes, and polyynes. Values taken from Table 3.

does play a role. In the presence of a conjugating endgroup, $\lambda_{max}$ for polyynes and polyynes (**Ph$_{(=)}$[*n*]** and **Ph$_{(\equiv)}$[*n*]**) are nearly the same (Fig. 6a), while this is not the case with alkyl endcapping groups (Fig. 6b).

Interestingly, $\lambda_{max}$ values for phenyl substituted [*n*]cumulenes move to a lower energy in a much more dramatic fashion than those of either polyenes or polyynes (Fig. 6a). This demonstrates a significantly stronger increase of the conjugation with increase of chain length in the case of cumulenes than in polyenes or polyynes, a trend that is also supported by bond length alternation (BLA) data presented in the next section. For alkyl substituted [*n*]cumulenes, the same general trend is also observed but to a lesser extent than in phenyl substituted cumulenes.

## 4. Structural analysis by X-ray crystallography

X-ray crystallographic analysis is relatively uncommon for [*n*]cumulenes ($n \geq 5$) due to instability under ambient conditions and limited synthetic accessibility. This method, however, offers profound insight into both the physical and electronic structure of cumulenes, especially *via* the analysis of bond length alternation (BLA) as a function of molecular length (BLA, defined as the bond length difference between the two central-most double bonds of the cumulene chain). As discussed above, UV/vis spectroscopy shows nicely that there is a relationship between the optical HOMO–LUMO gap and the length of the cumulene chain. In principle, this change in the HOMO–LUMO gap should coincide with structural changes of the cumulene framework. More specifically, BLA should diminish for longer cumulenes and eventually reach a constant value. Several theoretical calculations for cumulenes have suggested that BLA cumulenes should approach a value of nearly zero,[55,146,147] although at the time of these reports experimental validation of these predictions was not possible. In this section, selected X-ray crystallographic data are discussed in terms of structural trends, followed by a summary of BLA analysis based on an overview of the experimental results available to date for cumulenes.

In Fig. 7, bond lengths for **[*n*]*t*BuPh** ($n$ = 3, 5, 7)[70] and **[*n*]Cy** ($n$ = 3, 4, 5)[113,148] are summarized. First and foremost, it is clear that the cumulated double bonds are not equal in length in these molecules. Rather, there is an alternating sequence of longer and shorter bonds that is reminiscent of a polyyne structure, especially in [3]cumulenes. This trend is more pronounced in the tetraarylcumulenes,[70] due to conjugation of the phenyl rings to the cumulene chain. The terminal cumulenic double bond (α) is consistently the longest and the observed values are only slightly longer than that found for a standard double bond. Conversely, the next double bond (β) is usually the shortest of the cumulene chain (except for **[7]*t*BuPh** and **[7]Mes**), with values slightly longer than a typical triple bond. Thus, bond length alternation is observed in all cumulenes studied to date.

In general, strongest bond length alternation can be expected from odd-numbered cumulenes in which a resonance contribution from the terminal groups is present, as discussed above for Fig. 3b. Conversely, reduced BLA is predicted for even-numbered tetraalkylcumulenes, as a result of the two orthogonal π-systems and restricted conjugation to the endgroups. A third situation also exists, however, in which restricted bond rotation would limit π-conjugation of terminal aryl rings to the cumulene core. In this case, the magnitude of the twist angles of the aryl endgroups should play a role in the observed BLA values. This is exactly the case for the **[*n*]Mes** series shown in Fig. 8,[70] in which all four aryl groups are twisted significantly out of the plane of the cumulene skeleton, in the range of 45–52°.[149] In comparison, only one aryl endgroup at each terminus of the **[*n*]*t*BuPh** cumulenes is appreciably twisted (44–55°), while the remaining two aryl groups are more coplanar (twist angles from 14–21°). Looking at bond lengths for the two

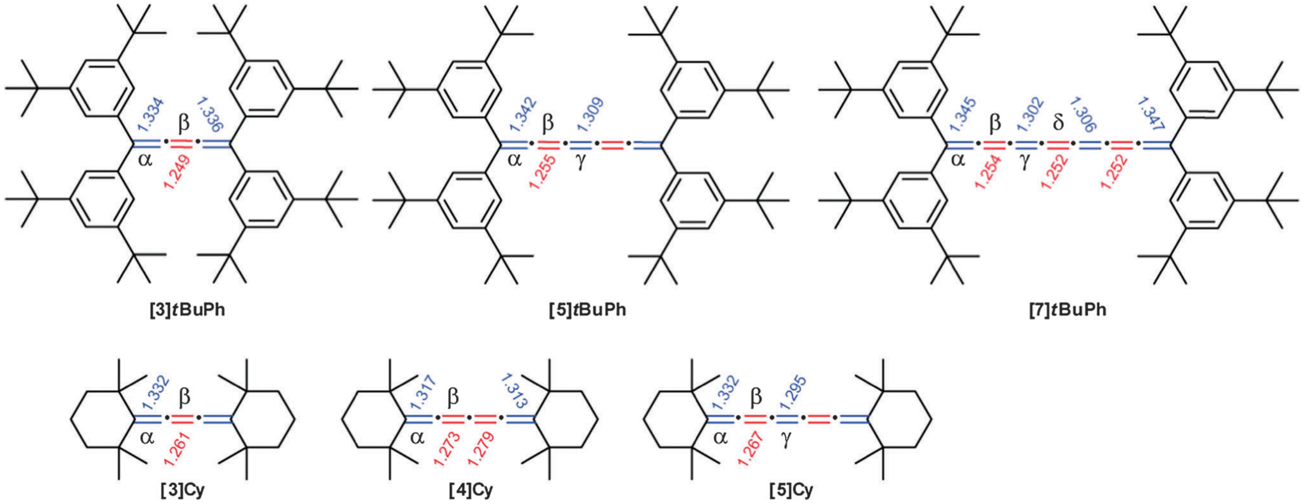


Fig. 7 Chemical structures of **[*n*]*t*BuPh** and **[*n*]Cy** cumulenes including bond lengths in Å as determined by X-ray crystallography.

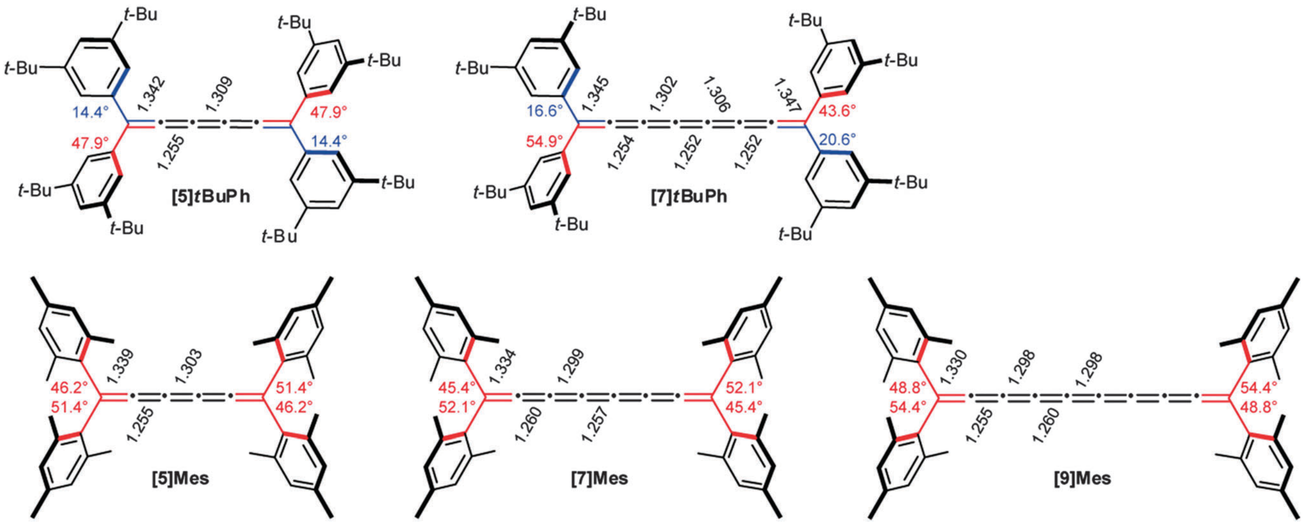
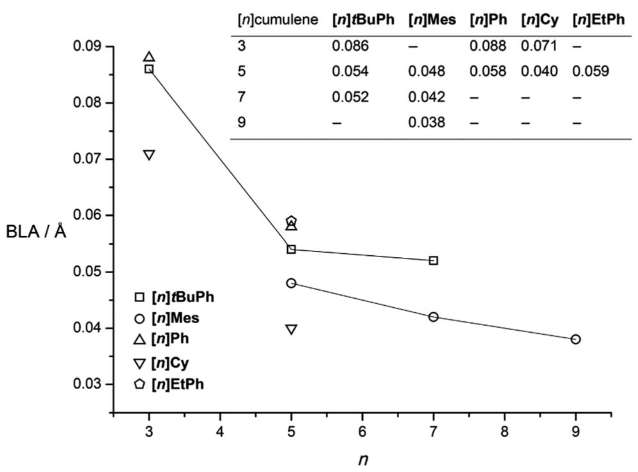


Fig. 8 Twist angles of the aromatic ring relative to cumulenic framework of **[5]-** and **[7]*t*BuPh** (top) and **[5]-**, **[7]-**, and **[9]Mes** (bottom) as determined by X-ray crystallography.

series, the above hypothesis is confirmed, and the increased conjugation in the **[*n*]*t*BuPh** cumulenes results in reduced BLA for **[*n*]Mes** (see also Fig. 9).

The analysis of data for **[*n*]*t*BuPh** cumulenes shows a steady decrease in BLA with increasing molecular length, ranging from 0.086 Å (**[3]*t*BuPh**) to 0.052 Å (**[7]*t*BuPh**, Fig. 9).[70] The mesityl end-capped cumulenes show an analogous reduction in BLA *versus* length, from 0.048 Å (**[5]Mes**) to 0.038 Å (**[9]Mes**).[70] In comparison to **[*n*]*t*BuPh**, however, BLA values for the **[*n*]Mes** derivatives are lower as discussed above. The X-ray data of other aryl substituted cumulenes are also included, and BLA values for **[3]Ph**,[150] **[5]Ph**,[151] and **[5]EtPh**[152] are also consistent with trends for the series **[*n*]Mes** and **[*n*]*t*BuPh.** In contrast to aryl substituted cumulenes, data for alkyl substituted cumulenes, **[3]Cy** and **[5]Cy** show the lowest BLA values known so far for cumulenes.[113,148]

A plot of BLA values for **[*n*]Mes** and **[*n*]*t*BuPh** against the number of cumulated double bonds *n* suggests an asymptotic



| [*n*]cumulene | [*n*]*t*BuPh | [*n*]Mes | [*n*]Ph | [*n*]Cy | [*n*]EtPh |
|---|---|---|---|---|---|
| 3 | 0.086 | – | 0.088 | 0.071 | – |
| 5 | 0.054 | 0.048 | 0.058 | 0.040 | 0.059 |
| 7 | 0.052 | 0.042 | – | – | – |
| 9 | – | 0.038 | – | – | – |

Fig. 9 BLA values (insert) *versus* [*n*]cumulenic chain length, *n* (lines are only a guide for the eye).

limit of 0.03–0.05 Å (Fig. 9). This prediction is somewhat higher than that from computational studies for the ''parent'' series of [*n*]cumulenes (**[*n*]H**). While computational results can differ depending on the method of analysis, the computational trend is clear that BLA $\leq$ 0.01 Å by the length of **[9]H**.[146,147] The difference between experiment and theory likely arises from endgroup effects, but this hypothesis awaits confirmation.

## 5. Reactivity of longer [*n*]cumulenes ($n \geq 5$)

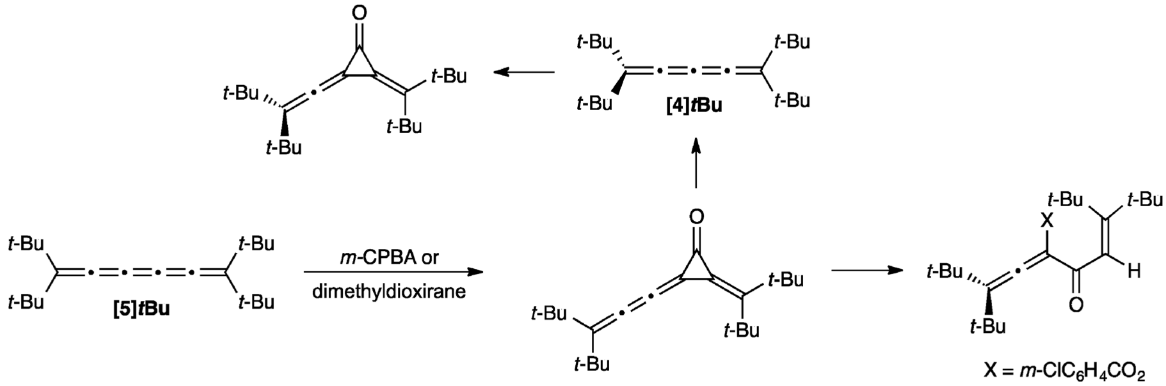
The reactivity of [*n*]cumulenes with $n$ = 2 and 3 has been reviewed by Diederich,[153] Chauvin,[88] and Ma.[154] Due to the increasing instability in longer [*n*]cumulenes ($n \geq 5$), the reactions of these molecules have been rare and are limited almost exclusively to reactions of [5]cumulenes.

### 5.1 Miscellaneous reactions

Simple reactions of [5]cumulenes have been reported such as hydrogenations[118,142] and partial hydrogenations[155,156] of the cumulene core using $H_2$/Rh/alumina and Al/Hg or the Lindlar catalyst, for example. The oxidation of a [5]cumulene *via* epoxidation has been described by Crandall and coworkers (Scheme 16).[157] For example, the reaction of **[5]*t*Bu** with *m*-CPBA gives a cyclopropanone intermediate, which goes on to give an allenic ester as the product. Epoxidation with dimethyldioxirane gives the cyclopropanone as a stable product, which can then be used to form **[4]*t*Bu** through either thermal or photochemical loss of carbon monoxide. The [4]cumulene **[4]*t*Bu** has also been subjected to oxidation with *m*-CPBA, and this reaction also gives the cyclopropanone product.

Theoretical predictions regarding the reactivity of cumulenes have been recently reported, particularly concerning oxygen sensitivity with respect to the carbon allotrope carbyne.[158,159] Using density functional theory calculations, Moseler and coworkers report that reaction of $O_2$ with the cumulene chain can cause cleavage, followed by repeated shortening of the chain through additional oxidation and loss of $CO_2$.[160]

A variety of metal complexes can be formed through the reaction of an electrophilic metal with the π-rich skeleton of a [5]cumulene (Fig. 10).[161] Complexes of **[5]Ph** with rhodium prefer bonding to the β-bond when triphenylphoshine is used as a ligand.[162] The analogous system with i-$Pr_3P$ ligands shows rhodium bonded to the γ-bond at low temperature (the kinetic product), while complete conversion to thermodynamic product with Rh-complexation at the β-bond is achieved upon warming.[163,164] Complexation of $(Ph_3P)_2Pt$ to **[5]Ph** reveals similar behaviour, namely an equilibrium between the kinetic complex at the γ-bond and the thermodynamic complex at the β-bond.[162] The reaction of **[5]*t*Bu** with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ gives a mixture of the mono- and dinuclear iron complexes,[165] while Iyoda and coworkers have shown that under the appropriate conditions using non-sterically demanding endgroups, the reaction of either **[5]H** or **[5]*t*Bu** with $Fe_3(CO)_{12}$ can be forced all the way to the tetranuclear iron complex.[166,167] Finally, Suzuki and coworkers have shown that [5]cumulenes can be trapped with the low-valent zirconocene–bisphosphine



Scheme 16 Oxidation products of **[5]*t*Bu**.

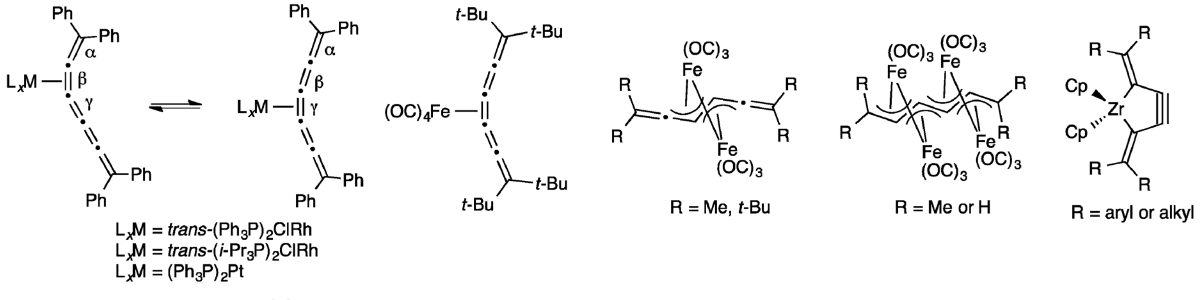


Fig. 10 Selected metal complexes of [5]cumulenes.

complex [$Cp_2Zr(PMe_3)_2$] to give the very strained zirconacyclopent-3-yne products.[168–170]

Finally, one example of the reactivity of a [6]cumulene has been reported.[128] In this study, Bildstein and coworkers describe the hydrolysis of **[6]Fc** to give a heptatetraenone.

### 5.2 Cycloadditions with alkenes and alkynes

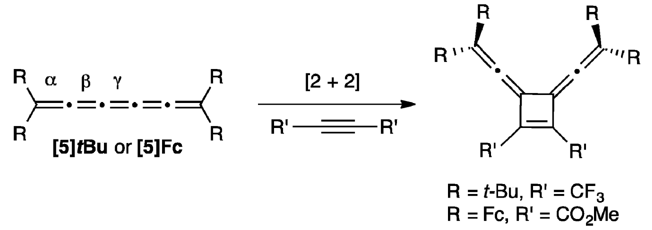
The most commonly investigated reactions for [5]cumulenes are cycloadditions, including cumulene oligomerization and either the addition of alkenes or alkynes. The presence of several double bonds in a cumulene framework offers several reaction sites, and products thus vary in symmetry and conjugation depending on the regiochemistry of the addition. For example, Scheme 17 describes the addition of alkenes to [5]cumulenes. On the one hand, it has been reported that tetrafluoroethylene (TFE) attacks the central γ-bond of **[5]*t*Bu** to give a symmetric cyclobutane derivative.[57,117] On the other hand, Bildstein and coworkers have shown that cycloaddition reaction of **[5]Fc** with either tetracyanoethylene (TCNE) or $C_{60}$ (at a 6,6-ring junction) occurs at the β-bond, which affords the unsymmetrical cyclobutane derivatives.[116] It is noteworthy that all three known examples in Scheme 17 utilize electron deficient alkenes, but nevertheless two different reactivity patterns are clearly operative, *i.e.*, at the β- or γ-bond. Bildstein suggests that addition to the β-bond is the thermodynamic reaction pathway, while the alternative, addition to the γ-bond to give the symmetrical adduct, is described as the kinetic reaction pathway,[171] similar to the situation described for metal complexes in Section 5.1.

Hartzler, on the other hand, suggests that the [2+2] addition probably occurs by way of a thermally accessible diradical of the cumulene, and thus cycloaddition reactions at the central double bond might be expected, especially if the terminal carbon atoms are sterically hindered by substituents such as *t*-butyl (Fig. 11). This is consistent with the experimental results, which showed that addition of the highly reactive reagent tetrafluoroethylene occurs at the γ-bond.

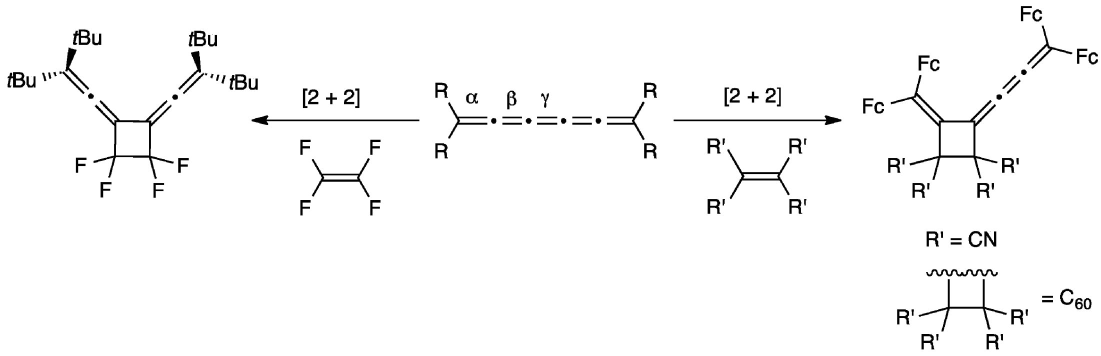
Two examples of alkyne addition to [5]cumulenes have been reported, and both reactions use highly activated acetylenes to give a symmetrical [2+2] cyclobutene adduct *via* reaction at the central γ-bond (Scheme 18).[57,116] The nature of the cumulene varied significantly in these two reactions, from R = *t*-Bu to R = Fc, but both authors suggest that the addition to the γ-bond is observed because of steric hindrance resulting from endgroups.

### 5.3 Di- and trimerizations

The reaction of [5]cumulenes often results in a formal cycloaddition between two cumulene molecules. Most commonly, such reactions proceed either thermally or *via* a Ni-catalyzed reaction (Scheme 19). Thermal dimerization is often observed for cumulenes with bulky alkyl substituents, giving a symmetrical



Scheme 18 Addition of alkynes to [5]cumulenes.



Scheme 17 Cycloaddition of alkenes to a [5]cumulene ($C_{60}$ = buckminsterfullerene).

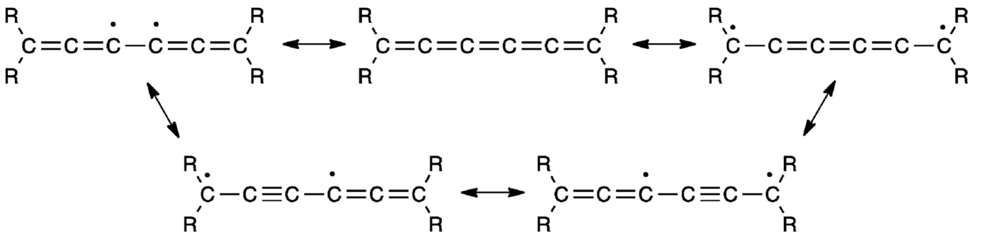
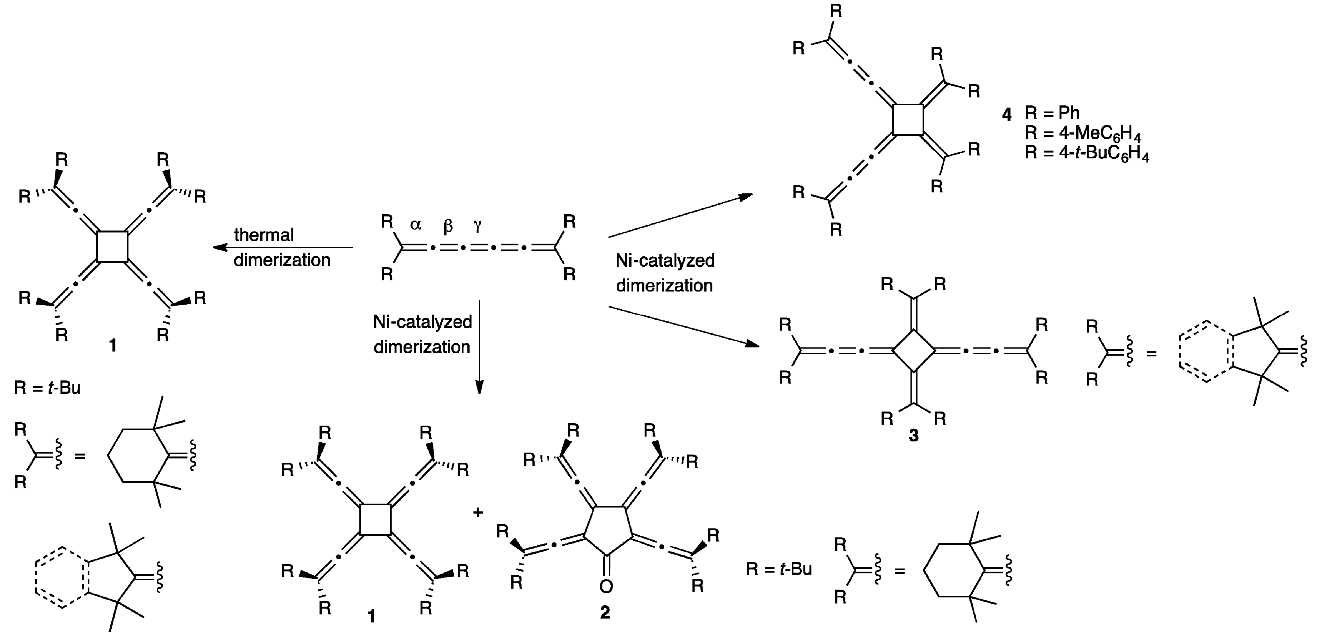


Fig. 11 Diradical mesomeric structures as suggested by Hartzler for reactions of a [5]cumulene.[57]



Scheme 19 Dimerization reactions of [5]cumulenes.

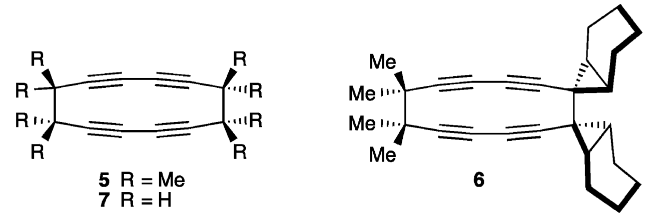


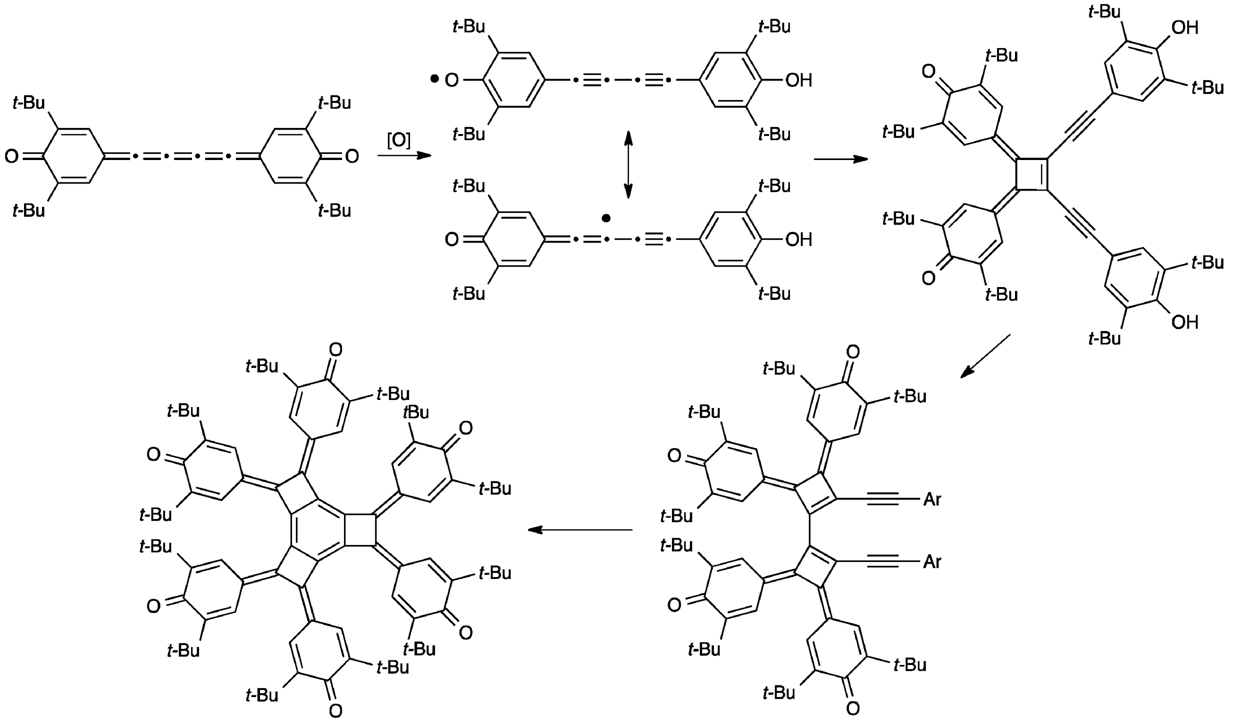
Fig. 12 Dimerization reactions of [5]cumulenes.

vinylidene substituted [4]radialene **1**, *i.e.*, a cyclobutane ring that possesses four equally substituted exocyclic allene units.[172,173] This was first demonstrated by Hartzler and coworkers for **[5]*t*Bu**, *i.e.*, when **[5]*t*Bu** melts, the resulting liquid resolidifies with the formation of the radialene product.[57] In a later report by Iyoda, it was suggested that the dimerization reaction occurs at the central, γ-double bond, due to the crisscross nature of the structure (transition state) that would be required for a thermal [2+2] reaction.[127] It is interesting to ponder why the thermal reactions of tetraaryl[5]cumulenes do not seem to follow a similar pathway in the solid state, *i.e.*, dimerization to give a radialene. It might be due to molecular structure and stronger BLA (*vide supra*), or perhaps steric factors based on the endgroups. Alternatively, it is also conceivable that favorable intermolecular stacking interactions of the aryl endgroups might prevent a crisscross orientation that would be necessary for a thermal [2+2] reaction.

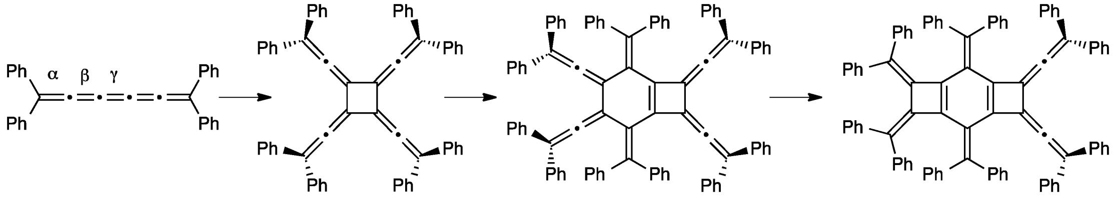
Aside from solid state reactions, radialenes **1** are also formed from alkyl substituted cumulenes in solution under Ni-catalysis, and these reactions also give [5]radialenones **2**.[127] With slightly less bulky alkyl endgroups, Ni-catalyzed head-to-tail dimerization at the β-bond results in the formation of [4]radialenes **3**, while tetraaryl[5]cumulenes afford the deep blue head-to-head dimers **4**. The authors suggest that the bulkiness of the terminal substituents in the [5]cumulenes controls the course of metal coordination, and leads to the selectivity observed in the oligomerization reactions.[127]

The final mode of dimerization reaction for [5]cumulenes has been documented independently by the studies of Stang[174] and Scott,[118] and later by Hopf and coworkers with the unsubstituted **[5]H**.[175] In these three cases, the lack of sterically encumbered endgroups permits reaction at the α-bonds, with concomitant rearrangement of the cumulene framework to give a butadiyne moiety (Fig. 12). Scott has reported that the Cu(I) catalyzed cyclodimerization of **[5]Me** leads to the symmetrical 12-membered ring **5**. Stang and coworkers have shown that no metal catalysis is necessary, and macrocycle **6** is isolated in a 31% yield as the only viable product. In the case of **6**, a radical has been is suggested, which avoids the necessity of a symmetry forbidden [6+6] thermal cycloaddition. Finally, Hopf and coworkers report the formation of macrocycle **7**, conceivably through dimerization of the parent system, **[5]H**, although the intermediate presence of **[5]H** has not been established.

Similar to dimerization, [5]cumulenes have also been shown to formally undergo trimerization reactions, although in each of the two reported cases, dimerization precedes the formation of the trimer. The first example from Kawase *et al.* is outlined in Scheme 20 and forms a novel tricyclobutabenzene derivative from a precursor in which a [5]cumulene links two quinone rings.[176] The authors suggest a mechanism in which the [5]cumulene is converted to a radical intermediate *via* oxidation. This intermediate then dimerizes to a cyclobutene-intermediate and subsequent addition of the third [5]cumulene unit gives a dicyclobutene intermediate. Finally, further oxidation and cyclization gives the tricyclobutabenzene product.



Scheme 20 Trimerization reaction of a [5]cumulene.



Scheme 21 Trimerization reaction of **[5]Ph**.

The second trimerization example describes the cyclotrimerization of **[5]Ph** to a tricyclodecadiene derivative as reported by Kawamura and coworkers (Scheme 21).[177] The authors suggest that the reaction initiates with a solution-state dimerization of **[5]Ph** to give the symmetrical [4]radialene. A third equivalent of **[5]Ph** adds to this intermediate and gives the Diels–Alder adduct, which is ultimately converted to the product *via* an electrocyclization reaction. The reaction yield is quite reasonable (up to *ca.* 70%), as long as the concentration of **[5]Ph** is $>13$ mmol $L^{-1}$. The product is rather stable, and subsequent Diels–Alder or electrocyclic reactions are not observed. This overall reaction is particularly unusual since it relies on the thermal dimerization of a tetraaryl[5]cumulene at the $\gamma$-bond, which is a reactivity pattern typically reserved for [5]cumulenes with sterically bulky alkyl groups.

## 6. Conclusions and perspectives

The synthesis and study of long [*n*]cumulenes ($n \geq 5$) is historically a rich area of organic chemistry that spans over 70 years. Much of what has been learned about these molecules has been reported in the early studies, while periodic advances have been recently described for both the synthesis and physical characteristics of long [*n*]cumulenes. There is a growing fundamental interest in long [*n*]cumulenes as model compounds for sp-carbon allotrope carbyne, and insight from the study of [*n*]cumulenes of defined length should allow researchers to compare and contrast the properties of the cumulenic and polyyne versions of carbyne. For example, the effect of structure and molecular length on the basic property of bond length alternation has recently been reported, and offers a platform for conducting further studies of physical structure and comparisons to theory. On the other hand, the unique π-electronic structure of cumulenes provides distinctive electronic and optical properties that suggest fascinating opportunities in molecular electronics and materials science. Key to exploiting this potential is the development of more stable cumulene structures, and synthetic methods to realize these targets.

The interest in long [*n*]cumulenes is not, however, restricted to material applications. There is, without a doubt, a wealth of possible synthetic transformations that might exploit the reactive π-system offered by a cumulene, particularly in the realm of cycloaddition reactions. To date, however, there is insufficient data to outline a predictive scheme of what products might be expected, based on, for example, reactions that might be of either kinetic or thermodynamic control. In the studies of cumulene dimerization reactions, Professor Peter Stang offers perhaps the best assessment of the reactivity of [5]cumulenes, ''What is not yet clear is what exactly controls the mode of cyclodimerizations and why seemingly similar cumulenes… result in such different cyclodimers.''[174] The answer to this and many other questions await the future efforts of organic chemists.

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