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Reactions of [5]Cumulenes

Unexpected Formation of a [4]Radialene and Dendralenes by Addition of Tetracyanoethylene to a Tetraaryl[5]cumulene**

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Dedicated to Professor Kendall (Ken) Houk on the occasion of his 70th birthday

Abstract: *The use of cumulenes in synthetic transformations offers the possibility to form structurally interesting and potentially useful conjugated molecules. The cycloaddition reaction of a tetraaryl[5]cumulene with the electron-deficient olefin tetracyanoethylene affords unusual products, including functionalized dendralenes and alkylidene cyclobutanes, as well as a symmetric [4]radialene that shows unique solvatochromism, with λ_{max} values approaching the near-IR region. These carbon-rich products have been investigated spectroscopically and by X-ray crystallographic analysis (five structures). The cycloaddition reaction sequence has also been explored by mechanistic and theoretical studies. The obtained results clearly demonstrate the potential of [5]cumulenes to serve as precursors for unprecedented conjugated structures.*

The [n]cumulenes (n = number of cumulated double bonds in a chain of $n+1$ carbon atoms) constitute a class of compounds with interesting physical properties.[1] For example, the one-dimensional framework constructed of cumulated sp-hybridized carbon atoms can serve as building blocks for molecular wires or as linkers in unprecedented carbon nanostructures.[2] The chemistry and reactivity of lower [n]cumulenes, namely, $n=2$ (allenes)[3] and $n=3$ (butatrienes),[4,5] has been explored in recent years, but longer [n]cumulenes ($n \geq 5$) have received only sporadic attention over the past four decades.[1,6]

Cumulenes typically undergo thermal or photochemical cycloaddition reactions. To date, no general guidelines in regard to these reactions have been reported, but the general reactivity pattern is summarized in Scheme 1. [5]Cumulenes can undergo a thermal dimerization reaction at the central γ-bond to give radialenes **1** with either alkyl[7,8] or aryl[9] substituents. Furthermore, Iyoda and co-workers have shown that [5]cumulenes also undergo dimerization reactions at the β-bond under Ni^0 catalysis to afford the less-symmetrical radialenes **2** (R = aryl) or **3** (R = alkyl).[8,10] The reaction of [5]cumulenes with electron-deficient acetylenes seems to occur preferentially at the central γ-bond to give the [2+2] products **4**.[7,11] A similar reaction between tetrafluoroethene and tetra(*tert*-butyl)[5]cumulene gives **5**.[7]

These results suggest that reaction at the more electron-rich β-bond of the cumulene skeleton is not observed because of unfavorable steric interactions between the end groups. The reaction of tetraferrocenyl[5]cumulene with C_{60} and tetracyanoethylene (TCNE),[11] however, readily occurs at the β-bond to give **6**, which suggests that the reaction outcome is probably not governed solely by steric factors.

Cumulenes are a class of molecules based on sp-hybridized carbon atoms, and polyynes represent another. The [2+2] reaction of polyynes with TCNE has been established by Diederich and co-workers,[12,13] and others,[14] to be a very efficient "click reaction" that forms new chromophores with outstanding stability and unique optical properties. Unfortunately, the reported studies offer little guidance as to whether the regiochemistry of a cycloaddition reaction of a [5]cumulene with TCNE would be governed by steric or electronic factors. Thus, we performed density-functional (DFT) calculations to offer insight. These calculations show that the two central-most carbon atoms bear a slight negative charge, while the neighboring carbon atoms are slightly positively charged (see the Supporting Information for details). This charge distribution may guide the highly electrophilic TCNE towards the γ-bond. Furthermore, the bulky aryl groups at the terminus are expected to hinder the approach of the TCNE to the β-bond. Considering the reaction of TCNE and **7** shown in Scheme 2 and examining the frontier molecular orbitals (see the Supporting Information), it is clear that a concerted [2+2] addition of TCNE at the γ-bond is forbidden by orbital symmetry, as also expected on the basis of the Woodward–Hoffmann rules for a four-electron system. We hypothesized that the addition of TCNE to cumulene **7** could occur through a stepwise mechanism that is sterically directed toward the γ-bond of the cumulene (Scheme 2). A subsequent retro [2+2]

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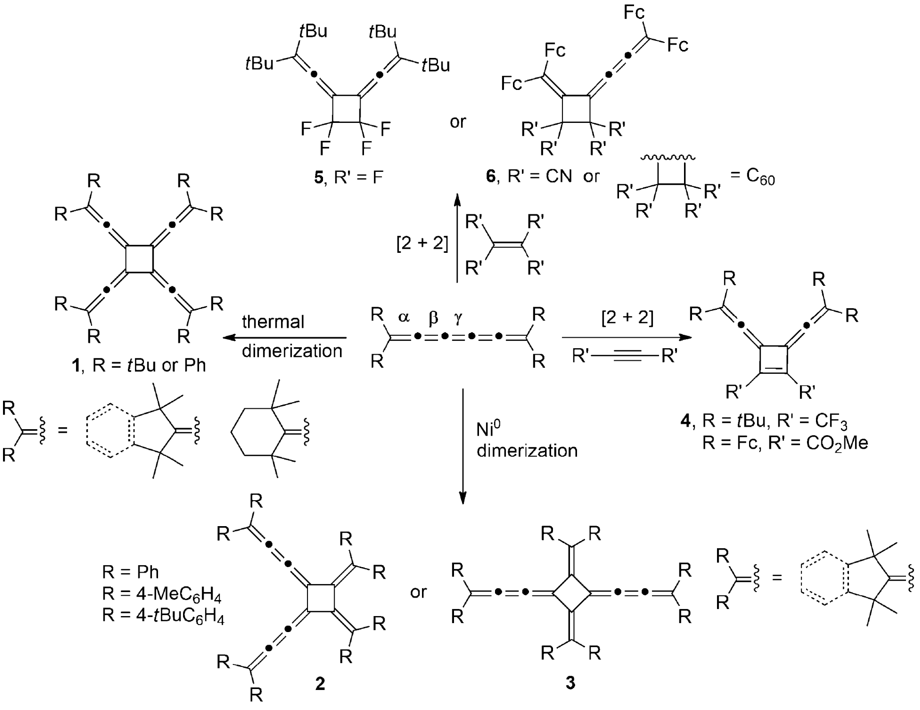
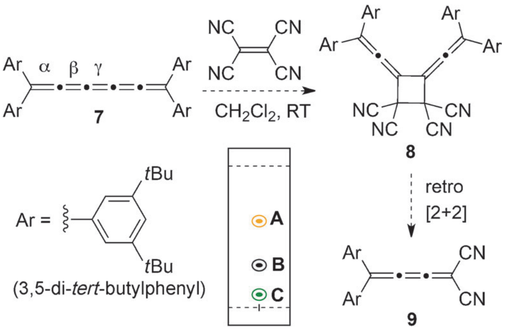


Scheme 1. Examples of cycloaddition reactions reported for [5]cumulenes; Fc: ferrocenyl.



Scheme 2. Hypothesized synthesis of **9**, by reaction of **7** with TCNE. Inset: schematic depiction of the TLC analysis of the reaction after 2 h; SiO$_2$, CH$_2$Cl$_2$/hexanes = 1:1. The identity of products **A**–**C** is described in the text.

reaction from **8** might then give **9**. This overall sequence would be a useful metathesis reaction to form polarized cumulene products such as **9**.[4]

Herein, we report the reaction of [5]cumulene **7** with TCNE. Although the desired product **9** is not isolated from this reaction, the resulting synthesis offers a number of equally intriguing and unprecedented cross-conjugated[15] structures, including two acyclic [4]dendralenes (after further bromination),[15,16] a cyclic [3]dendralene, and an electron-deficient [4]radialene.[15,17] The products and unusual reaction mechanisms are discussed with the help of five X-ray crystal structures and DFT calculations.

The reaction of **7** with TCNE was carried out in CH$_2$Cl$_2$ at room temperature (Scheme 2). After 2 h, a "rainbow" of at least six products was apparent by TLC analysis. After several days, however, three predominant products (**A**, **B**, and **C**) had formed (Scheme 2). Purification by chromatography allowed the isolation of pure products **A** and **C**, although it was quickly clear that these products were neither **8** nor **9.**

The identity of product **A** was tackled first. A signal at *m*/*z* 979.6557 in the high-resolution ESI mass spectrum (positive mode) is consistent with the formula [**7** + TCNE + Na]$^+$ (C$_{68}$H$_{84}$N$_4$Na). The aryl region of the ^{1}H NMR spectrum shows triplets at 7.61, 7.53, and 7.49 ppm (integration ratio 1:1:2) and doublets at 7.29, 7.19, and 7.12 ppm (integration ratio 4:2:2). These signals are consistent with four di-*tert*-butylphenyl groups, but also confirm a loss of symmetry during the course of the reaction. There is a noteworthy resonance at 203.4 ppm in the ^{13}C NMR spectrum, while the IR spectrum reveals a weak signal at 1920 cm^{-1}; both observations suggest an allene moiety. Finally, overlaying a solution of **A** with either MeOH or EtOH afforded crystals, and struc-

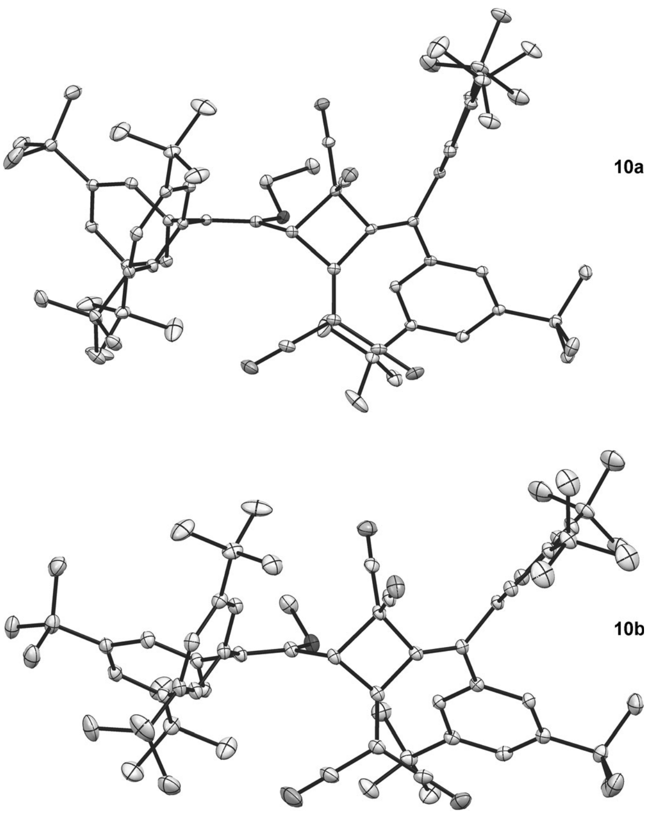
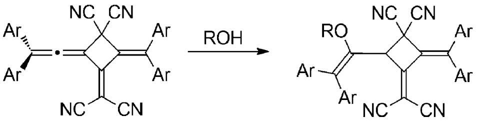


Figure 1. ORTEP representations (20% probability level) of compounds **10a** and **10b**.

tural analysis (Figure 1) showed that the resulting structures correspond to the ethyl and methyl enol ethers **10a** and **10b**, respectively. Thus, product **A** can be confidently assigned as cyclic [3]dendralene **11** [Eq. (1)].[18]

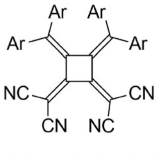


11 (product **A**)

10a R = Et (quant)
10b R = Me (quant)

(1)

The most notable characteristic of product **C** is its color, which changes from orange when adsorbed on silica gel to green in the solid state.[19] UV/Vis spectroscopy indicates that product **C** also shows solvatochromism. Specifically, the UV/Vis spectrum shows a broad low-energy absorption with $\lambda_{max} > 700$ nm (see the Supporting Information) that ranges from $\lambda_{max} = 720$ nm (cyclohexane) to $\lambda_{max} = 771$ nm ($CHCl_3$), characteristic of an intramolecular charge-transfer absorption.[20] The ESI MS signal at m/z 979.6576 ($[M+Na]^+$) is analogous to that observed for product **A** (i.e. compound **11**). The aryl region of the ^{1}H NMR spectrum for product **C**, however, shows two sets of signals, namely, only two unique aryl groups and a structure with twofold symmetry. Furthermore, no resonance that is consistent with an allenic sp-hybridized carbon atom is found in the ^{13}C NMR spectrum. Ultimately, X-ray crystallography identified the structure of product **C** as radialene **12** (Figure 2). The rectangular structure of **12**[21] suggests a donor–acceptor (push-pull) interaction between the dicyanovinyl acceptor and the electron-rich bis(dialkylaryl)vinyl groups, with shortened C1–C2 bond lengths of 1.469(2) Å and lengthened C1–C1′ and C2–C2′ bonds (1.494(3) and 1.504(3) Å, respectively). This is concurrent with elongation of the alkylidene bonds C1–C4 and C2–C3 (1.36–1.37 Å) relative to those in other [4]radialenes.[22] The rigid structure of **12** is helical in the solid state, and perhaps configurationally stable in solution because of restricted rotation of the aryl groups.



12 Ar = 3,5-$tBu_2C_6H_3$
(product **C**)

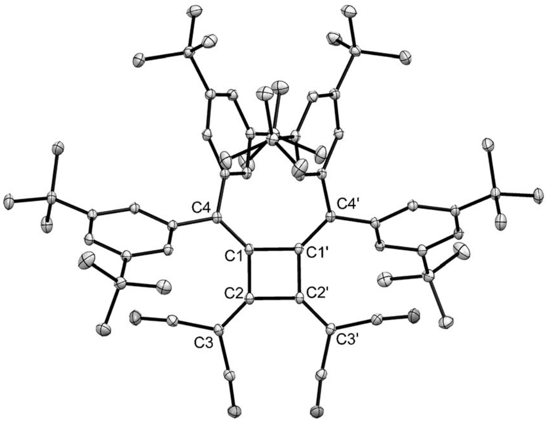
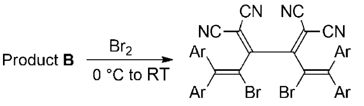


Figure 2. Molecular structure and ORTEP representation (20% probability level) of radialene **12** (product **C**). Selected bond lengths [Å]: C1-C1′ 1.494(3), C1-C2 1.469(2), C2-C2′ 1.504(3), C2-C3 1.362(2), C1-C4 1.370(2).

The identification of **11** and **12** (products **A** and **C**, respectively) is, in principle, consistent with intermediate **9** being formed during the reaction of **7** with TCNE. As the study progressed, it became clear that product **B** (Scheme 2) is not stable, and transforms to products **A** and **C** in a ratio of about 9:1 over time, on warming, or concentration of the reaction mixture. Thus, our attention turned to identification of product **B**. Viehe and co-workers[23] had shown that polarized [3]cumulenes could be efficiently trapped by reaction with bromine. Thus, product **B** was isolated at low temperature and treated with bromine at 0 °C in a solution of $CHCl_3$ [Eq. (2)]. The product of this reaction is, however, the symmetrical and stable [4]dendralene **14**, as established by X-ray crystallography (Figure 3). Compound **14** is not, unfortunately, a product that is easily linked to the presence of [3]cumulene **9** during the reaction of **7** with TCNE.



14 (26% from **7**)

(2)

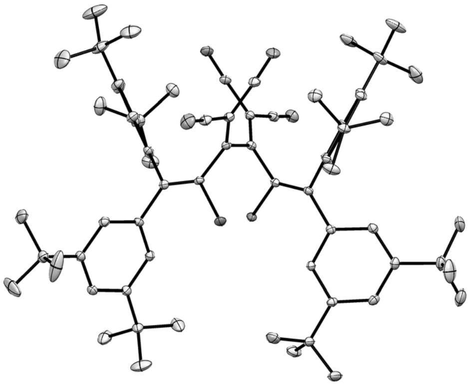
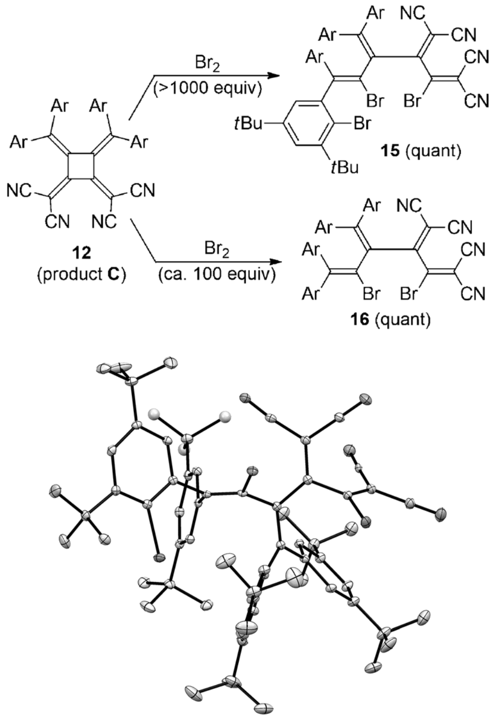


Figure 3. ORTEP representation of **14** (20% probability level).

It was hypothesized that dendralene **14** could be formed from the reaction of Br_2 with radialene **12**, which might be produced in situ from product **B**. Therefore, a test reaction was carried out in which radialene **12** was treated directly with excess bromine (Scheme 3). This reaction does not give the dibromoadduct **14**, but rather [4]dendralene **15**, an isomeric analogue of **14** (bromination of one aryl ring is also observed). The structure of **15** was confirmed by X-ray crystallography. The use of less bromine gave a single product, which was identified tentatively as [4]dendralene **16**.[24]

With the identity of product **B** not yet confirmed, direct isolation and characterization was attempted. The reaction of **7** and TCNE was conducted over 24 h at −25 °C. The desired product **B** was purified by column chromatography using $CDCl_3$, with the column temperature maintained



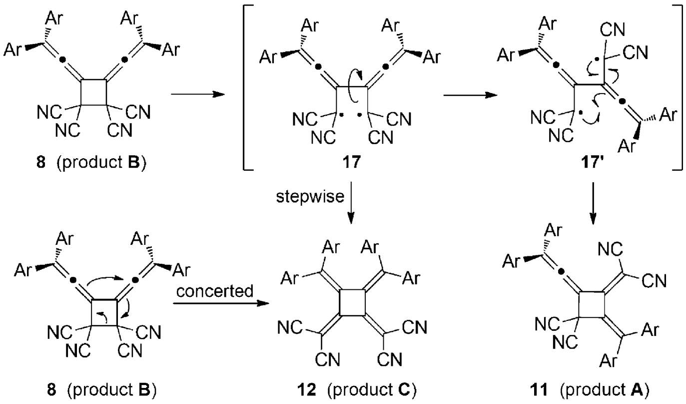
Scheme 3. Top: Bromination of radialene **12** (product **C**); bottom: ORTEP representation of **15** (20% probability level); Ar = 3,5-di-*tert*-butylphenyl.

between −20 and 0 °C (by using a jacketed column). The fractions containing product **B** were stored at low temperature (i.e. on dry ice) to prevent conversion into **A** and **C**. The combined $CDCl_3$ fractions (ca. 250 mL) were reduced to less than 1 mL under vacuum, and NMR spectra were acquired. The ^{1}H NMR spectrum shows only one set of signals representative of the 3,5-di-*tert*-butylphenyl group, namely a broad singlet (suggesting a triplet) at 7.39 ppm and a doublet at 7.16 ppm. These signals indicate a highly symmetrical structure for product **B**. More significantly, the ^{13}C NMR spectrum shows the signal corresponding to an allene at 203.6 ppm, as well as that of an sp^3-hybridized carbon atom at 42.9 ppm. Combined with ESI MS analysis, which shows a signal at m/z 979.6575 ($[M+Na]^+$), these data support that product **B** can be assigned as compound **8** (Scheme 2).[25]

A proposed mechanism for the conversion of **8** into **11** and **12** is shown in Scheme 4.[26] Homolytic cleavage of the central $(NC)_2C{-}C(CN)_2$ bond gives intermediate **17**, which is stabilized by allylic delocalization of the unpaired electrons. Cyclization of rotamer **17′** then affords [3]dendralene **11**. Radialene **12** can also be formed from **8** in a stepwise mechanism, via intermediate **17**. However, neither a concerted reaction that converts **8** directly into **12** nor a two-step four-electron electrocyclic ring closing/opening can be ruled out.[27]

DFT calculations show that a reaction of **7** with TCNE to give **8** (product **B**), followed by rearrangement to **11** and **12** (products **A** and **C**), is in excellent agreement with predictions based on stability (Figure 4), namely, compounds **11** and **12** are clearly more stable than **8**. Interestingly, the inclusion of van der Waals corrections in the density-functional calculations gives enhanced stabilization of products **8**, **11**, and **12** compared to calculations without this correction. This observation is easily rationalized by the fact that the products are stabilized by intramolecular dispersion interactions between the aryl groups. The computed energies also explain why **9** is not observed, given that a metathesis reaction from **8** to **9** is significantly endothermic when dispersive interactions are included. In the absence of dispersion corrections, the formation of **11** and **12** is still preferred over **9**, although the differences are less pronounced.

In summary, we have presented the reaction of TCNE and a tetraaryl[5]cumulene (**7**) that affords mainly the novel vinylidene cyclobutane **8**, which contains two exocyclic allene groups. Compound **8** can be isolated at low temperature and characterized spectroscopically, although in solution at room temperature it converts into cyclobutane **11** and the electron-deficient radialene **12**. [4]Radialene **12** has an interesting electronic absorption approaching the near-IR region that appears to originate from a charge-transfer transition. The



Scheme 4. Proposed mechanism for the conversion of **8** into **11** and **12** (products **B**, **A**, and **C**, respectively); Ar = 3,5-di-*tert*-butylphenyl.

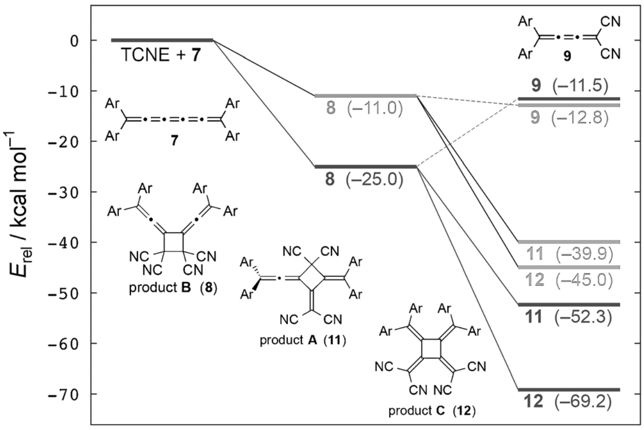


Figure 4. Computed energies (kcal mol^{-1}) of the products **8** (product **B**), **11** (product **A**), **12** (product **C**), and the hypothesized product **9** relative to that of the reactants TCNE + **7**. Calculations based on DFT including (black) and without (light gray) dispersion interaction corrections (see the Supporting Information for computational details).

importance of X-ray crystallography in mechanistic investigations is highlighted by this study, as five major products of this study have been identified by X-ray crystallographic analysis (compounds **10a**, **10b**, **12**, **14**, and **15**).

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Keywords: cumulenes · cycloaddition · dendralenes · radialenes · TCNE

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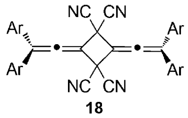
[25] Formation of the head-head dimer **18**, cannot be ruled out, but no evidence for supporting formation of **18** has been observed to date.



18

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