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Thermal and Nickel-catalyzed Dimerization of Hexapentaene. Synthesis of Two [4]Radialenes with Planar, Stable Cyclobutadiene-like Geometry

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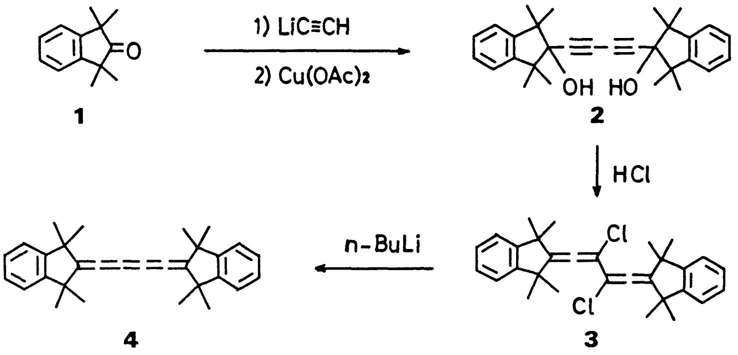
The thermal and nickel-catalyzed cyclodimerization of the hexapentaene produced two types of [4]radialenes. The X-ray structural analysis of the thermal dimer has shown that the molecule has a pinwheel-like structure with the exactly planar central four-membered ring.

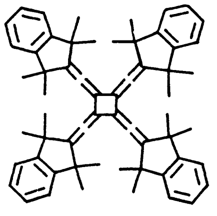
[4]Radialenes possess the potentially destabilizing cyclobutadiene-like arrangement of π-electrons. However, no [4]radialene has unusual resonance destabilization based on antiaromaticity. According to recent theoritical consideration,$^{1)}$ [4]radialenes suffer only a small resonance destabilization. Therefore, instability of the parent [4]radialene, which has been shown to have a planar structure based on the Raman and IR spectra, can be recognized by its high reactivity to dienophile and oxygen even at low temperature.$^{2)}$ Since [4]radialenes can bear various functional groups at the terminal positions, planar and stable [4]radialenes may serve as an interesting symmetrical framework for a molecular tweezer, a four-fold spacer, and an unique host molecule.

We recently reported the synthesis and molecular structures of various types of radialenes.$^{3,4)}$ We describe here the selective synthesis of two types of [4]radialenes by the thermal and nickel-catalyzed dimerization of [5]cumulene (hexapentaene) and the crystal structure of a novel, planar [4]radialene derivative.

Nickel-catalyzed cyclodimerization of tetraarylhexapentaene yields the head-to-head dimer.$^{5)}$ In contrast, reactions of hexapentaenes bearing bulky alkyl-substituents with $Ni(CO)_2(PPh_3)_2$ produce either the head-to-tail dimer or the dimers at the central double bond (i.e., the corresponding [5]radialenone and [4]radialene).$^{6)}$ Thus, the nickel-catalyzed dimerization of [5]cumulenes occurs regioselectively. In order to synthesize

[4]radialenes with bulky 1,1,3,3-tetramethylindane groups as terminal substituents, we carried out the thermal and nickel-catalyzed reactions of the [5]cumulene **4**.





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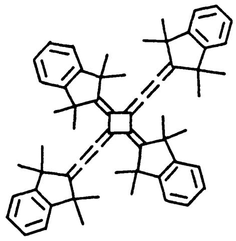

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The addition of acetylene to 1,1,3,3-tetramethyl-2-indanone **1**, followed by the oxidative coupling with $Cu(OAc)_2$ in pyridine-methanol gave the diol **2** in 70% overall yield. Treatment of **2** with hydrochloric acid in aqueous AcOH-dioxane afforded the dichloride **3** in 76% yield. The dechlorination of **3** with butyl lithium in THF resulted in the formation of the desired **4** in 96% yield.

The pale yellow plates of **4** have no melting point and begin to dimerize gradually at 240 °C. Thus, treatment of **4** under argon at 250-260 °C for 2 h gave the dimer **5**$^{7)}$ in 21% yield together with other unidentified products. The yield of **5**, however, can be increased by brief heating at higher temperature (51% at 270-275 °C for 5 min). The NMR spectra of **5** show that the dimerization occurs at the central cumulenic sp-sp bond. Therefore, the formation of tetravinylidenecyclobutane is favored in the thermal dimerization of **4**. In contrast to thermal dimerization, the nickel-catalyzed cyclodimerization of **4** gave the head-to-tail dimer **6**$^{8)}$ in 64% yield by treatment of **4** with 0.5 equiv. of $Ni(CO)_2(PPh_3)_2$ and 1 equiv. of PPh_3 in refluxing benzene under argon for 24 h.

To elucidate the exact molecular structure of [4]radialene with exocumulenic bonds, the crystal structure of **5** has been determined by the X-ray diffraction method.$^{9)}$ From the crystallographic data, the molecule **5** was revealed to locate on a crystallographic center of symmetry. Thus, the central four-membered ring of the molecule is exactly planar. Figure 1 shows the molecular projection of **5** onto the four-membered ring plane together with the important structural parameters. Figure 2 shows a van der Waals drawing of **5**. The figures stress a very characteristic feature of **5** with widely spread planar structure in its center, to which four benzocyclopentene substituents are approximately perpendicular with the puckered angles of around 10° in the cyclopentene rings. Therefore, the molecule has a very beautiful shape like a pinwheel or a cogwheel.

The X-ray structures of [4]radialenes hitherto determined have the puckered four-membered ring, because of the steric repulsion between the neighboring substituents on the exo-cyclic double bonds.[4,10] An extension of the double bonds of [4]radialenes to the allenic bonds in **5** releases the severe steric repulsion between the neighboring substituents. No significant short contact shorter than 4 Å was found between the methyl groups in tetramethylindane parts.

Molecular models show that the radialene framework of **6** can have a planar structure with D_{2h}-symmetry, instead of a puckered structure with C_{2v}-symmetry. The Raman spectrum of **6** shows a very strong cumulenic absorption at 1995 cm^{-1}, while the IR spectrum shows a very weak one at 1955 cm^{-1}. Therefore, a planar radialene framework with D_{2h}-symmetry may be expected for the structure of **6**. All benzene rings in **6** are situated at the same horizontal axis. This provides a unique example of regular arrangment of four benzene rings at fixed positions of [4]radialenes.

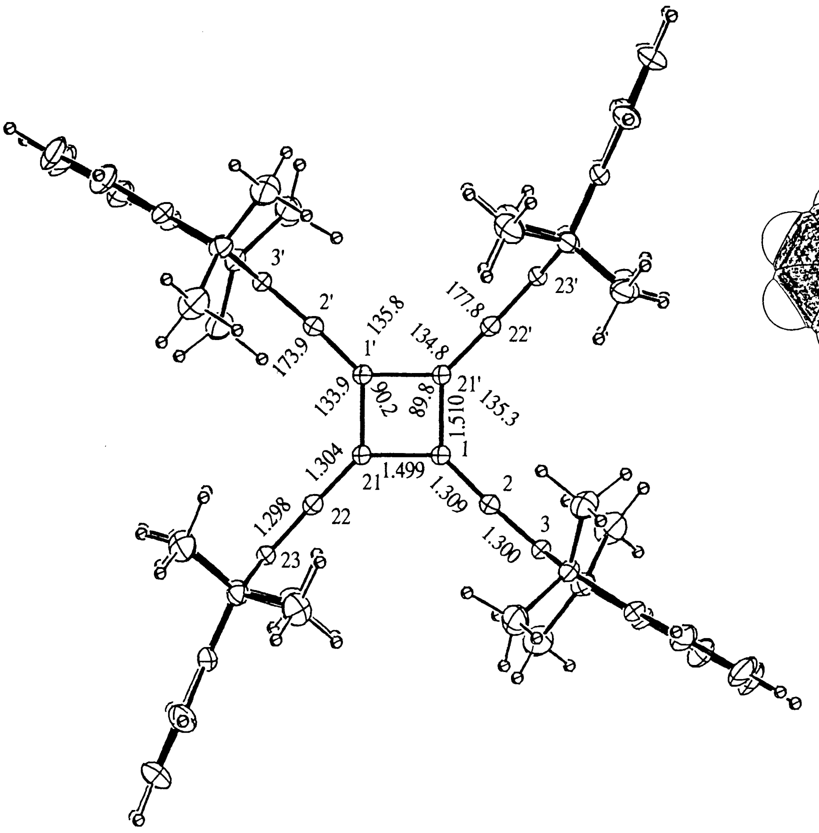

Fig. 1. Molecular structure of **5**.

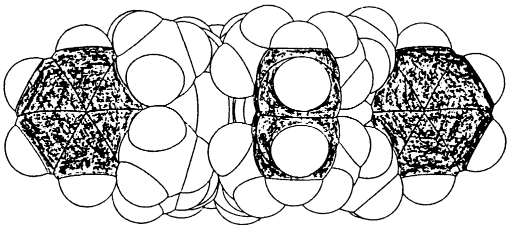

Fig. 2. A space-filling drawing of **5** (side view). The darkened parts represent benzene ring carbons.

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7) **5**: colorless prisms, mp 331-333 °C; MS: m/z 784 (M^+); ^{1}H-NMR (400 MHz, CD_2Cl_2/CS_2 = 1/4) δ = 1.35 (s, 48H), 6.99-7.04 (AA', 8H), 7.06-7.11 (BB', 8H); ^{13}C-NMR (100 MHz, CD_2Cl_2/CS_2 = 1/4) δ = 31.58, 48.16, 112.54, 122.38, 127.21, 134.17, 148.49, 189.78; Raman (KBr): ν = 1978, 1948 cm^{-1}.

8) **6**: yellow needles, mp 365-367 °C; MS: m/z 784 (M^+); ^{1}H-NMR (500 MHz, CD_2Cl_2/CS_2 = 1/4) δ = 1.58 (s, 24 H), 1.78 (s, 24H), 7.08-7.20 (m, 16H); IR (KBr): ν= 1955 (vw) cm^{-1}; Raman (KBr): ν= 1995 (vs), 1635 (s), 1615 (w), 1590 (w) cm^{-1}.

9) Crystal data of **5**: $C_{60}H_{64}$, M_r = 785.2, triclinic, space group $P\bar{1}$, a=13.285(1), b=8.513(1), c=11.694(1) Å, α =98.02(1), β =96.69(2), γ =80.63(1)°, V=1286.2(3)$Å^3$, Z=1, ρ_{calcd}=1.013 g cm^{-3}. X-Ray intensity data were measured with nickel-filtered CuKα radiation using a crystal with dimension of 0.2x0.2x0.3 mm^3. A total of 3809 reflections were collected up to 2θ=120°, of which 2955 had $|F_o| > 3\sigma(F_o)$ and were used in the refinement. The intensity data were corrected for Lorentz and polarization effects but not for absorption [μ(CuKα)=4.0 cm^{-1}]. The crystal structure was solved by SHELXS-86 and refined by XRAY-76. The final R and R_w indices were 0.061 and 0.088, respectively.

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