

Synthesis of Redox-Active Macrocyclic Dehydroannulenes Stabilized by Surrounding Rigid σ -Frameworks

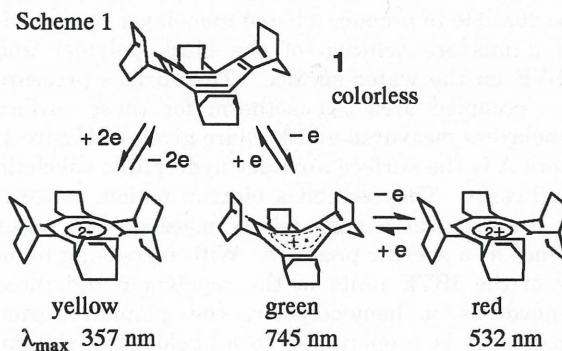
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The transition-metal catalyzed oxidative coupling has been applied to 2,3-diethynyl- and 2-bromo-3-ethynylbicyclo[2.2.2]octenes to give a series of macrocyclic conjugated polyenynes, i.e. dehydroannulenes. The X-ray crystallography has demonstrated that the hexadecahydro[18]annulene has a completely planar π -system while that of the tetradecahydro[16]annulene system is considerably bent. These π -systems are characterized by ready and highly reversible redox behaviors as examined by the use of cyclic voltammetry.

Keywords: π -conjugation / macrocycles / X-ray structure / CV / oxidative coupling / Pd catalysis

The highly conjugated π -electronic systems are of particular interest from the viewpoint of their possible applicability for functionality materials. Fundamental studies on the redox properties of these systems are important since the redox behaviors can trigger various physicochemical events that are required for application of these materials.

Previous studies in our group demonstrated that a cyclooctatetraene fully annelated with bicyclo[2.2.2]octene units (**1**) is redox active, affording not only a 10- π aromatic dianion but cation radical [1] and dication [2], which are the first examples of cationic species of cyclooctatetraene stable at room temperature. While the neutral compound is colorless, each of the ionic species exhibits deep colors



characteristic to their ionic state as shown in Scheme 1.

Now this work has been extended to the synthesis

ORGANIC MATERIALS CHEMISTRY — High-Pressure Organic Chemistry —

Scope of Research

Fundamental studies are being made for creation of new functional materials with novel structures and properties and for utilization of high pressure in organic synthesis. The major subjects are: synthetic and structural studies on novel cyclic π -systems; chemical transformation of fullerene C_{60} ; utilization of carbon monoxide and dioxide for organic synthesis under the transition-metal catalysis.



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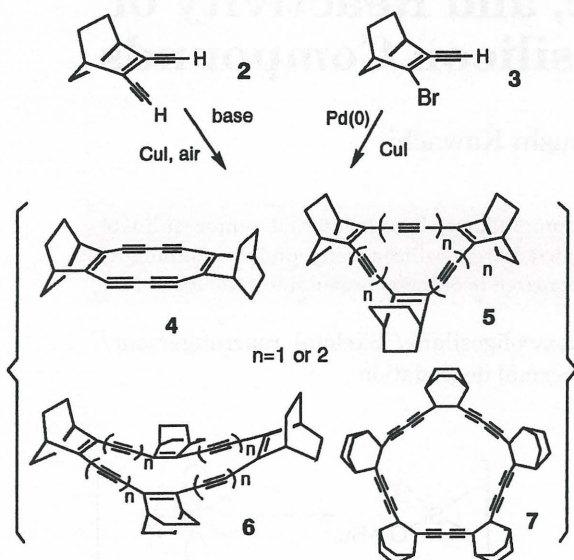
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Scheme 2



of compounds with more expanded π -systems, i.e., a series of dehydroannulenes containing the bicyclo[2.2.2]octene frameworks.

As shown in Scheme 2, the oxidative coupling of enediyne **2** and careful separation using GPC afforded a series of cyclomers, the dehydroannulenes, **4** (red crystals, 15%), **5** (n=2) (orange needles, 55%), **6** (n=2) (yellow solid, 0.6%), and **7** (red-brown crystals, 2%). Also the Pd-catalyzed coupling of enyne **3** gave trimer **5** (n=1) (red crystals, 22%) and tetramer **6** (n=1) (yellow needles, 9%).

The X-ray crystallography clearly demonstrated the presence of a planar π -conjugated system in **5** (n=2) and a bent and bond alternating cyclohexadeca-1,5,9,13-tetraene-3,7,11,15-tetrayne system in **6** (n=1) as shown in Figure 1.

The redox behaviors on these macrocyclic π -systems were examined by the use of cyclic voltammetry to give the results summarized in Table 1. Several

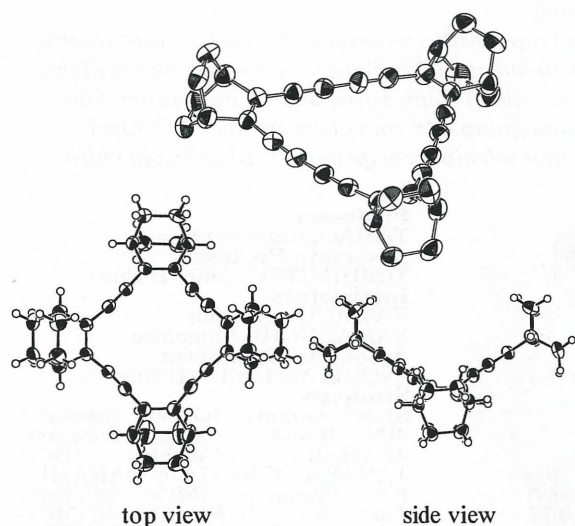


Figure 1. X-Ray crystal structures of **5** (n=2) (top) and of **6** (n=1) (bottom).

Table 1. Redox Potentials of Annulenes **4**, **5**, and **6**^a.

Compd	E_{ox}^2	E_{ox}^1	E_{red}
4		(+0.93) ^b	-1.67
5 (n=1)	(+0.99) ^b	+0.54	-1.93
6 (n=1)	(+0.88) ^b	+0.62	-1.96
5 (n=2)		(+1.21) ^b	-1.87
6 (n=2)			-1.53

^a In PhCN with 0.1 M TBAP; sweep rate 0.1 V s⁻¹.

^b Peak potential of the irreversible peak.

characteristic features emerge from these data. For example, both of the antiaromatic 4n π -electronic systems **5** (n=1) and **6** (n=1) undergo ready and completely reversible one-electron oxidation at remarkably low potential such as +0.5 ~ +0.6 V vs Ag/AgNO₃. Particularly in comparison with its mother compound having no substituent, the redox potentials of the hydrocarbon **5** (n=1) are cathodically shifted in general, reflecting the electron-donating tendency of the annelated bicyclo[2.2.2]octene units. It is also to be noted that, in spite of such electronic effects of the bicyclic frameworks, the expansion of the π -conjugated system is reflected in the occurrence of reversible one-electron reduction, which was not observed in the case of corresponding cyclic π -systems without acetylenic bonds.

Further study is now under way to elucidate the possibility of these macrocyclic polyenyne to exhibit selective complexation ability with metal ions or with specific organic molecules.

References

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