Organic device, Organic magnetism, Organic conductor

Synthesis and characterization of a novel polycyclic hydrocarbon containing a planar octagon

Department of Applied Chemistry, Graduate School of Engineering
Assistant Professor **Akihito Konishi** Researchmap https://researchmap.jp/a-koni?lang=en
Professor **Makoto Yasuda** Researchmap https://researchmap.jp/read0185253?lang=en
Department of Materials Engineering Science, Graduate School of Engineering Science
Associate Professor **Ryohei Kishi** Researchmap https://researchmap.jp/rkishi0017?lang=en

Abstract

For *ortho*-fused benzenoid hydrocarbons with three or more rings, replacing the three hexagons with a set of two pentagons and one octagon is also possible. Following this concept, we designed pentacyclic cyclooctadiindene with a 5–8–5 tricyclic skeleton. Five examples of cyclooctadiindenes were synthesized and characterized as stable closed-shell molecules.

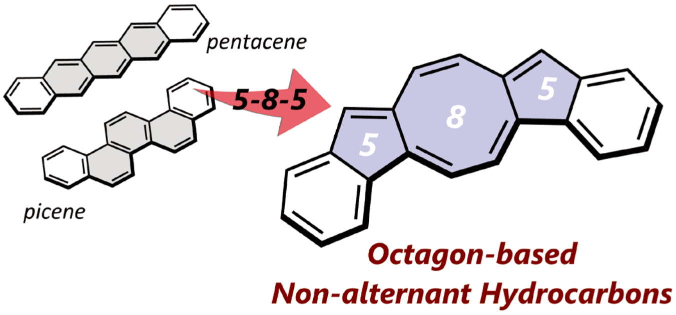
Background & Results

The chemistry of non-alternant hydrocarbons has recently experienced a considerable resurgence. As the relationship between naphthalene and azulene shows, an important design concept for a nonalternant framework is to replace the two hexagons of an alternant system with a pentagon and heptagon pair. For *ortho*-fused benzenoid hydrocarbons with three or more rings, another design for their nonalternant isomers is possible: replacing the three *ortho*-fused hexagons with a set of two pentagons and one octagon. However, in contrast to abundant azulenoid (5–7) nonalternant hydrocarbons, the related 5–8–5 tricyclic molecules are limited. Thus, nonalternant hydrocarbons containing an *ortho*-fused 5–8–5 tricyclic framework merit further exploration.

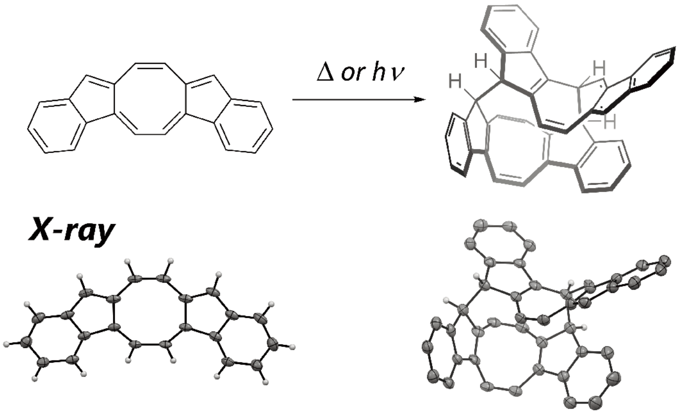
To unveil the electronic and structural effects of the 5–8–5 nonalternant framework on the π-extended backbone of *ortho*-fused hydrocarbons, we designed cyclooctadiindene. The target can enjoy the aromatic stabilization from the two hexagons. To confirm the hypothesis and unveil the electronic structure of cyclooctadiindene, we synthesized novel hydrocarbon as a nonalternant isomer of *ortho*-fused pentacyclic benzenoid aromatic systems, such as pentacene, and picene. Optoelectronic measurements clearly showed the nonalternant character. Heating or photoirradiation of a solution afforded a formal [6 + 4] cycloadduct. Theoretical calculations and mechanistic investigations revealed the occurrence of a stepwise formation of two C–C bonds, in which the hidden open-shell character emerges with the two molecules in close contact. The increased spatial overlap of the frontier orbitals and the reduction of the energy gap facilitate the diradical-based bond formations.

Significance of the research and Future perspective

The scientifically most important point of this work is the reactivity of the title compound. Heating or photoirradiating afforded a formal [6+4] cycloadduct. Theoretical calculations and mechanistic investigations revealed that the stepwise formation of C–C bonds proceeds via two-fold radical–radical couplings, in which the hidden open-shell character emerges when the two molecules are in close contact. The changes in the electronic configuration promote the formation of bonds based on diradicals. Our findings demonstrate that the open-shell electronic structure of a π-stacked arrangement can be adjusted, even when the open-shell characteristics of the monomer are negligible. Since tuning these open-shell characteristics is essential for developing efficient optoelectronic materials, our results can be expected to aid in establishing design strategies for innovative open-shell functional molecular materials derived from the condensed states of closed-shell nonalternant hydrocarbons.



Molecular structure of cyclooctadiindene



Dimerization of cyclooctadiindene with the X-ray structures

Patent	
Treatise	Konishi, Akihito; Kishi, Ryohei; Yasuda, Makoto et al. Synthesis and characterization of cycloocta[1,2-a:6,5-a′]diindene as an octagon-containing nonalternant isomer of pentacyclic benzenoid aromatic hydrocarbons with hidden diradical character that induces dimerization. Journal of the American Chemical Society. 2025, 147(20), 17281-17292. doi: 10.1021/jacs.5c03615
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