



Synthesis and characterization of bis-periazulene: Unprecedented pyrene's structural isomer

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Abstract

Bis-periazulene (cyclohepta[*def*]fluorene), which is an un-known pyrene isomer, was synthesized as kinetically protected forms. Its triaryl derivatives exhibited the superimposed electronic structures of peripheral, polarized, and open-shell π -conjugated systems. In contrast to previous theoretical predic-tions, bis-periazulene derivatives were in the singlet ground state. Changing an aryl group controlled the energy gap between the lowest singlet–triplet states.

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. The pursuit of the non-alternant isomers of pyrene, which has seven possible non-alternant isomers, has been the most significant related project. Through enormous dedication by many pioneering works, six of the seven possible non-alternant isomers of pyrene have been isolated and characterized as stable aromatic molecules, differentiating themselves from pyrene in terms of optoelectronic properties. However, the only unsynthesized isomer, bis-periazulene (cyclohepta[*def*]fluorene), had remained an uncharacterized hydrocarbon until 2022, despite many synthetic and theoretical investigations since it was first reported in 1955. We successfully synthesized and characterized the kinetically protected derivatives, the remaining non-alternant isomer of pyrene. Triaryl-substituted derivatives exhibit singlet ground states, contrary to previous theoretical predictions.

Significance of the research and Future perspective

Despite many previous efforts, the synthesis and characterization of bis-periazulene have not been realized. Previous theoretical studies have offered an intriguing hint that bis-periazulene has a triplet open-shell ground state. Presumably, the high reactivity of bis-periazulene due to an *m*-quinoidal subunit has made isolation and characterization inaccessible. In this work, details of the synthesis and physical properties of the triaryl derivatives of bis-periazulene are described. The triaryl derivatives, in which three ortho-disubstituted aromatic groups were used to kinetically stabilize the reactive sites, were realized via an eight-step synthesis from the fluorene derivative. The synthesized triaryl derivatives were successfully isolated in their crystalline forms and characterized by X-ray analysis. Contrary to previous theoretical predictions, the determined molecular geometry and the observed magnetic behaviors exhibited singlet open-shell ground states. At the present stage, it is unclear why the determined ground state is a singlet state, regardless of the previous theoretical studies, but the introduced substituents may affect the lowest singlet–triplet energy gap. Changing a substituent enabled us to control the energy gap between the lowest singlet–triplet states, which is a rare example of ordinary polycyclic hydrocarbons. Notably, our study demonstrated that bis-periazulene contained three aspects of π -conjugation: pe-

ripheral, charge-separated, and open-shell π -conjugations. These characteristics of bis-periazulene are not shared by the previously reported polycyclic systems that contain azulene-subunit(s).

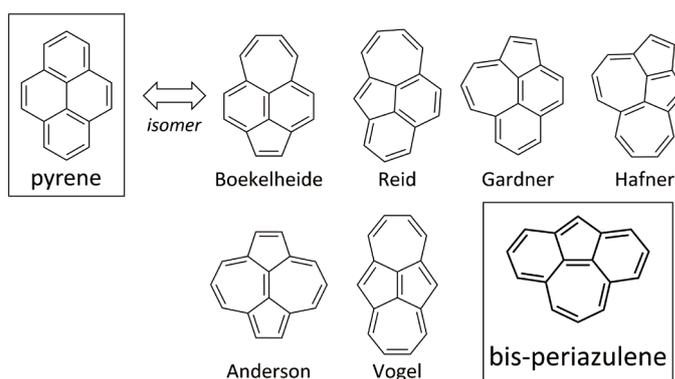


Fig1. Bis-periazulene as a one of the non-alternant isomers of pyrene

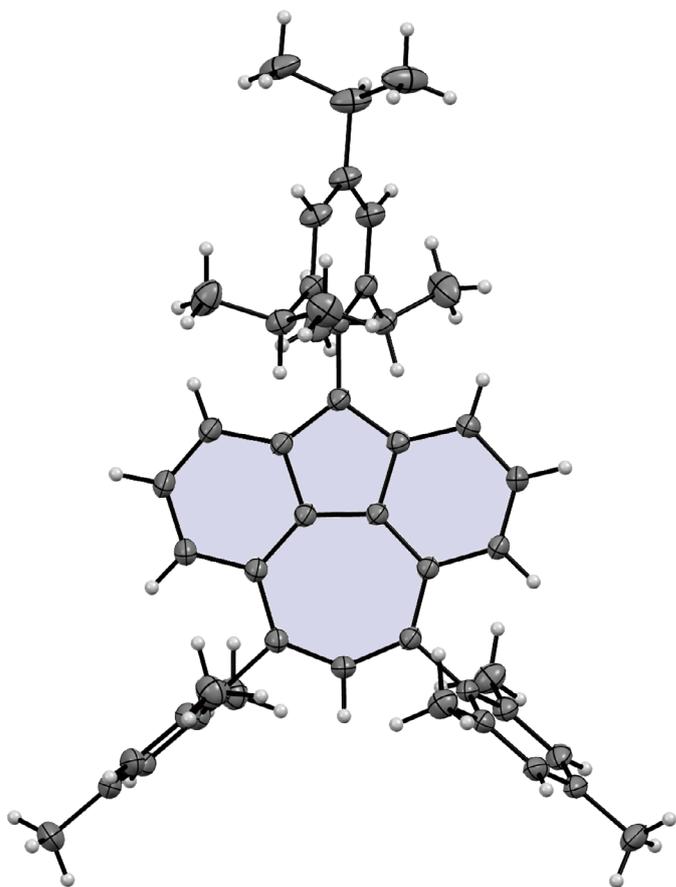


Fig2. Molecular structure of the synthesized bis-periazulene derivative

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Keyword

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non-alternant hydrocarbon, azulene, open-shell character