Synthesis and Properties of Kinetically Stabilized Bis-periazulene Derivatives

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In polycyclic hydrocarbons (PAHs), the topological difference of the π-conjugation highly affects their electronic properties, such as aromaticity, redox ability and/or spin state.[1] For example, azulene, which is a non-alternant isomer of naphthalene, has engaged many chemists' attentions as a building block of π-extended molecules and as a great candidate of optoelectronics because of its deep blue color and polarized structure .[2] Bis-periazulene **1a**, a non-alternant isomer of pyrene, is theoretically predicted to be a Kekulé molecule with a triplet ground state due to a *m*-quinodimethane subunit.[3] Although many syntheses of **1a** or its derivatives have been attempted, they hve not been achieved due to the difficulty in forming odd-membered rings and the luck of sufficient kinetic stabilization.[4]

In order to unveil the electronic structures of bis-periazulene , including the actual ground state, we designed kinetically stabilized derivatives **1b–d** (Figure 1A). The desired molecules **1b–d** were successfully synthesized in 8 steps using indium-catalyzed cyclization as a key step to construct a seven-membered ring. The structures of **1b–d** were fully characterized by X-ray crystallographic analyses. The electronic and magnetic measurements, and quantum chemical calculations of **1b–d** indicated that bis-periazulene **1a** contains three aspects of π-conjugation: peripheral 14π-system (**1a-A**), charge-separated polarized structure (**1a-B**) and open-shell π-conjugations (**1a-C**, Figure 1B). Due to the three aspects of π-conjugation of bis-periazulene, the introduced aryl groups affect the energy gap between the lowest singlet and triplet states. The details of the molecular structure and physical properties will be presented.
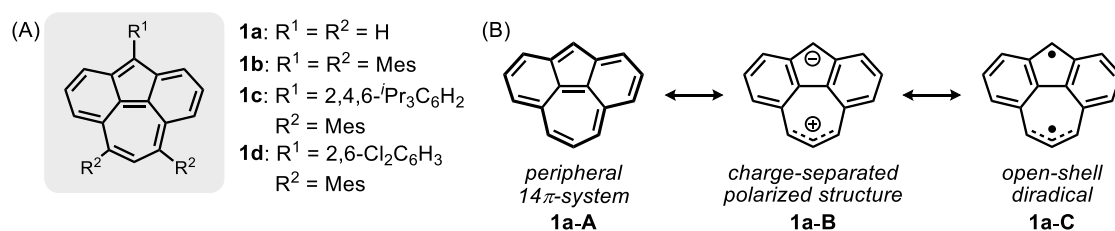

Figure 1. (A) Structure of bis-periaulene **1a-d**. (B) Resonance structure of bis-periazulene **1a**.

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