Polycycles

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A Stable π-Conjugated Singlet Biradical

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π-Conjugated species, exclusively constructed by benzannulation of six-membered rings, span a dramatic space in reactivity, topology, and stability. When one examines such species, the difference in stability—increasing with the number of Clar sextets—is evident (Figure 1). While hexacene (**1**) is a sensitive green-black species, dibenzotetracene (**2**) and dibenzochrysene (**3**), featuring four Clar sextets each, are stable and display only weak absorbance in the visible region. A remarkable case is zethrene (**4**),[1] for which a mesomeric biradical resonance structure can be formulated, affecting only the butadiene unit. If one expands the zethrene motif by another butadiene moiety, one arrives at heptazethrene (**5**); it exhibits two Clar sextets in the quinoidal structure, topologically preventing the middle of the three six-membered rings from ever attaining a Clar sextet.

The mesomeric biradical structure, however, features a Clar sextet for this ring. If the gain in energy outweighs the presence of the two radical centers, these open-shell species could either be present as a singlet biradical or as a triplet biradical in the ground state.[2] Stable molecules with a singlet biradical ground state are rare, but sought for their unique optoelectronic and magnetochemical properties as well as promising application in spintronics.

In 1955, Clar et al. reported the synthesis of deeply red-colored zethrene. Acenaphthylene (**6**) dimerizes in a sodium chloride/aluminum chloride melt; zethrene rapidly photooxidizes under ambient conditions.[3] Modern approaches, either to **4** or its higher homologue **5**, proceed via (spontaneous) transannular cyclization of diynes or bis(diynes). Alternative nucleophilic addition of RM to a diketone with subsequent reduction employing $SnCl_2$ or via oxidative dehydrogenation of the dihydro precursor (Scheme 1) is feasible.[4] Experimentally, the butadiene-like character of zethrene is underlined by reaction with maleic imide in a Diels–Alder cycloaddition in the bay position.[5] Quantum chemical calculations, EPR measurements, and solid-state structures indicate that zethrene exhibits some singlet open-shell biradical character in its ground state (Figure 1).[6] In

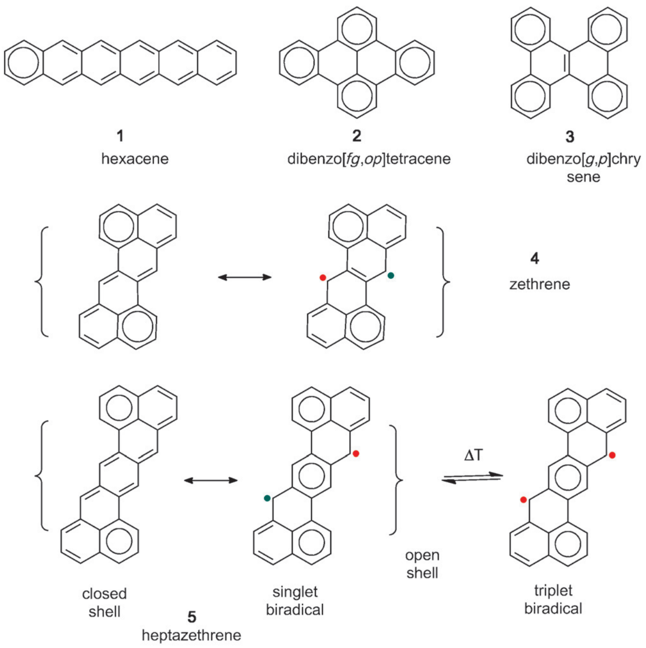
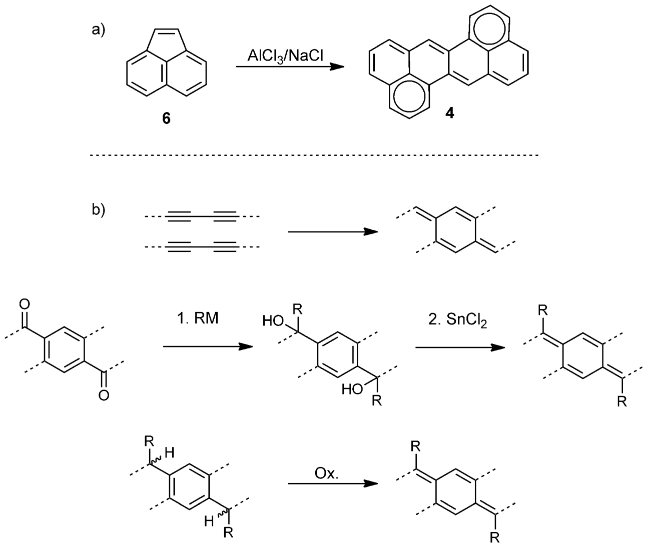


Figure 1. Overview of benzannulated six-membered polycyclic hydrocarbons and resonance structures of heptazethrene.



Scheme 1. a) Zethrene synthesis by Clar et al. b) Different synthetic approaches to zethrene and its (substituted) higher homologues.

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contradiction to Hund's rule, the singlet biradical ground state is energetically preferred to the triplet biradical state for zethrene and its homologues as a consequence of double spin polarization (DSP).

Three strategies work to stabilize zethrene-type molecules:

a) topologically correct enlargement of the aromatic π-system to increase resonance and number of Clar sextets,
b) attachment of both conjugating but also fairly bulky substituents to sterically shield radical centers, and
c) attachment of electron-accepting functional groups.

Strategy a: Comparing zethrene and heptazethrene, the formation of an additional Clar sextet promotes the singlet biradical ground state in the latter species. This concept was expanded to the benzannulation of heptazethrene at the edge positions (compounds **7** and **8**).[7] Precise positioning of the annulated benzene rings stabilizes the biradical structure through two additional Clar sextets (Figure 2).[8] On going from **7** to **8**, the radical character y_0 increases from $y_0 = 0.31$ to $y_0 = 0.58$. The extent of biradical character is expressed as a percentage, obtained from quantum chemical calculations. Although not intuitively derived, this comparison lets us grasp the degree of the contribution of radicals to the electronic "landscape" of zethrene types.

Strategy b: When substituents are attached at the reactive sites (radical positions) of heptazethrene, triisopropylsilyl-(TIPS)-acetylene substituents stabilize the molecular structure to such an extent, that a closed-shell quinoidal moiety is preferred.[9] On the other hand, sterically demanding and out-of-plane rotated mesitylene groups promote biradical character. In Figure 2, two substituted heptazethrenes display strong biradical character of $y_0 = 0.31$ for **9** and closed-shell character for **10** with $y_0 = 0.16$.[5] In both cases, the compounds were sufficiently stable for full characterization; protection of the radical centers is important.

Strategy c: In 2011, Wu et al. reported enhancement and stabilization of open-shell singlet biradical ground state of a heptazethrene derivative by electron-poor dicarboximide substituents.[10] Although EPR measurements exhibited no resonance, calculations and NMR-spectroscopy gave evidence for the existence of a singlet biradical ground state for **11** (Figure 2).

Wu et al. described "super-heptazethrenes" which take advantage of both steric protection and topological mapping; these organic molecules display the highest biradical character to date ($y_0 = 0.71$), higher than that of octazethrene ($y_0 = 0.36$) and nonazethrene ($y_0 = 0.5$) as calculated by DFT. The mesomeric structures underline the stability of the delocalized biradical as the molecule gains one (radical in the bay position) or two (radical at the zig-zag edge position) complete Clar sextets. The extension of the π-electron system and the stabilization of the radical position with electron-withdrawing groups allowed full characterization of **13** by NMR and UV/Vis spectroscopy, cyclic voltammetry, and EPR spectroscopy. The half-life of **13** is around 4.5 h in the presence of air and light.

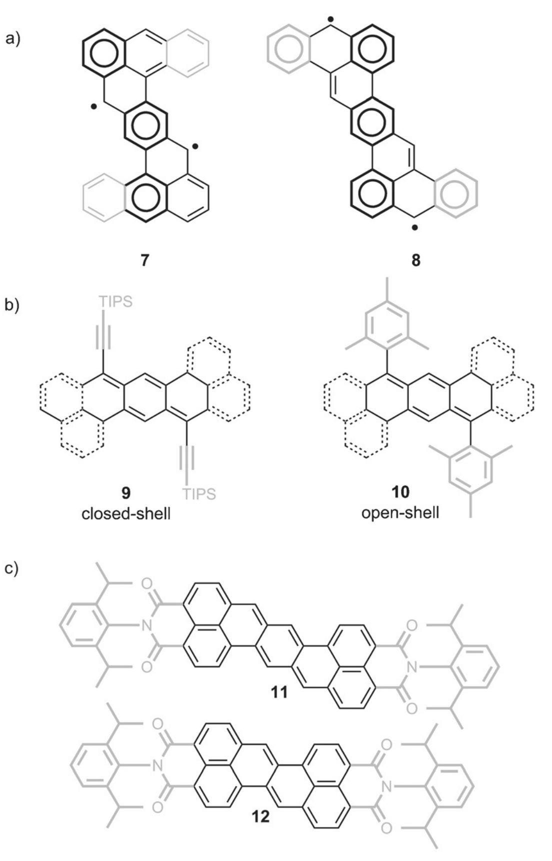

Figure 2. The three concepts used to stabilize zethrene-type molecules in their singlet biradical ground state. a) Extention of the π-system as well as attachment of b) sterically demanding grounds and c) electron-withdrawing groups.

In conclusion, the recent developments demonstrate that a clever combination of topology and electron-accepting aromatic substituents, placed in strategic positions, where the

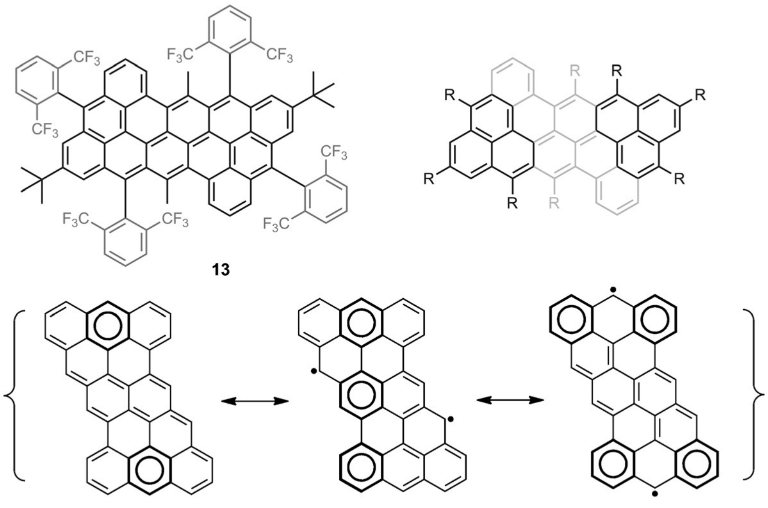

Figure 3. Wu's super-heptazethrene **13** and its resonance structures. The phenalene motif has been marked in the carbon framework to underline its tendency to form biradicals.

radicals' unpaired electron density is largest, lead to stable biradical or biradicaloid species. In a clever approach, Wu et al. have modified the zethrene system into a species, which they call super-heptazethrene (Figure 3). It is a large aromatic hydrocarbon, in which, upon going from the closed-shell singlet state to the biradical state, one or two additional Clar sextets form, and therefore the said biradical(oid) states are stabilized. These types of stabilized species are highly interesting and attractive for a variety of applications including as molecular magnets, as molecular units for data storage, and in the larger sense for the budding field of organic spintronics. The construction principle is relatively straightforward and consists of the clever attachment of two phenalene units to a suitable scaffold. This concept will attract great attention and lead to a number of spectacular novel structures with promising properties.

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