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Soluble and Stable Heptazethrenebis(dicarboximide) with a Singlet Open-Shell Ground State

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S *Supporting Information*

ABSTRACT: A soluble and stable heptazethrene derivative was synthesized and characterized for the first time. This molecule exhibits a singlet biradical character in the ground state, which is the first case among zethrene homologue series. Exceptional stability of this heptazethrenebis(dicarboximide) raises the likelihood of its practical applications in materials science.

Singlet biradical polycyclic aromatic hydrocarbons (PAHs) bearing Kekulé structures have attracted increasing attention not only due to the passion for exploring their intrinsic electronic properties,[1] but also because of their promising applications in materials science,[2] molecular electronics, and information processing.[3] Some have been experimentally proven to be excellent two-photon absorption materials and ambipolar semiconductors.[4] However, because of their open-shell character, most singlet biradical species tend to be short-lived, thus obscuring their identification and applications. Recent progress on thermodynamically stable biradicals involve bis(phenalenyl) hydrocarbons which are stabilized by delocalization of unpaired electrons through a phenalenyl moiety [5] and a teranthene biradical whose stability stems from the formation of three additional Clar sextets.[6]

Computational studies predict a prominent biradical character for higher-order acenes[7] and zethrenes.[8] Zethrenes represent an attractive class of hydrocarbons with a fixed double bond embedded in the molecular skeleton, and its derivatives can potentially serve as semiconductors, near-infrared dyes,[9] and nonlinear optical chromophores.[10] However, challenges to obtain zethrene derivatives lie in synthetic difficulties and their poor stability. Recently, relatively stable 7,14-substituted zethrene derivatives[11] and a more stable zethrenebis(dicarboximide) (**1**) with smaller band gap[12] were synthesized and characterized, providing the first experimental data for zethrene species (Figure 1). Although calculations indicate a resonance between a closed-shell quinoid form and an open-shell biradical form for zethrene (Figure 1), none of those above-mentioned zethrene derivatives displays biradical features. The heptazethrene, which can be viewed as two phenalenyl moieties fused by one benzene ring, is predicted to possess a larger biradical character, consisting of energy balance between loss of the double bond and aromatic stabilization by the central aromatic benzene ring (Figure 1). In addition, heptazethrene will form one more Clar sextet in the biradical form, while zethrene will lose one Clar sextet upon resonance to biradical state. Thus, heptazethrene is more likely to display biradical character while at the same time is less stable and more difficult to make. Despite all theoretical studies, experimental evidence has not been available so far. An attempt to synthesize heptazethrene by Clar was not successful due to its extremely high reactivity.[13] In light of this background, we report the first synthesis of a stable and soluble heptazethrene derivative, a heptazethrenebis(dicarboximide) (**2**, Figure 1), with remarkable singlet biradical character in the ground state. Since the investigations of teranthene[6a] and bisanthene[14] raise the question of the crossover from a closed-shell form to an open-shell form in a homologue series of anthenes, herein we also address the comparison between **1** and **2** for better understanding of zethrene series and their biradical properties.

The design consideration of **2** originates from our previous experience that an electron-withdrawing dicarboximide with a bulky diisopropylphenyl group can effectively decrease the HOMO energy level of the zethrene core and suppress dye aggregation, providing enhanced stability and solubility.[12] In the meantime, as a narrow band gap is believed to be a precondition of the singlet biradical ground state, attachment of an imide on the heptazethrene core can narrow the band gap by generating a push−pull structure, thus making the singlet biradical form accessible. The synthesis of **2** is shown in Scheme 1, and an intramolecular coupling pathway was adopted toward the octadehydronaphthoannulene key intermediate **6**.[15] Successive Sonogashira coupling reactions between **3**[12] with trimethylsilylacetylene (TMSA) and then triisopropylsilylacetylene (TIPSA) gave **4**, which underwent selective deprotection and oxidative coupling to yield **5**. The careful choice of the alkyne coupling condition is essential at this stage because commonly used Glaser conditions with oxygen as oxidant failed or gave **5** in extremely low yield, indicating an oxygen-sensitive nature of the terminal alkyne. Alternatively, the Pd-catalyzed coupling reaction with *p*-benzoquinone as oxidant in the absence of oxygen led to improved yield.[16] Subsequent in situ deprotection and intramolecular alkyne coupling afforded the key intermediate **6**, which underwent simultaneous transannular cyclization to give the target compound **2** as a dark-green solid.

The biradical character of **2** was revealed by low-temperature ^{1}H NMR spectra (Figure 2). A solution of **2** in CD_2Cl_2 exhibited no resonance signals for the heptazethrene core in the aromatic region, while peaks began to emerge and sharpen upon cooling.

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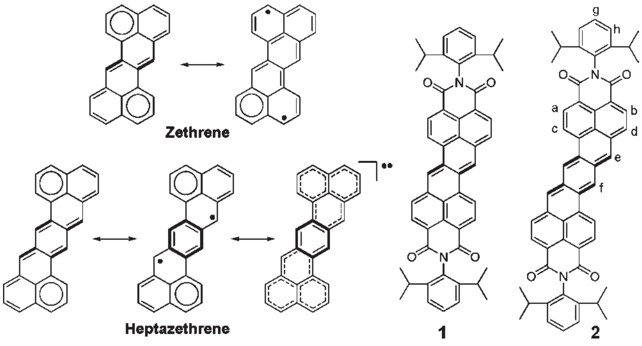
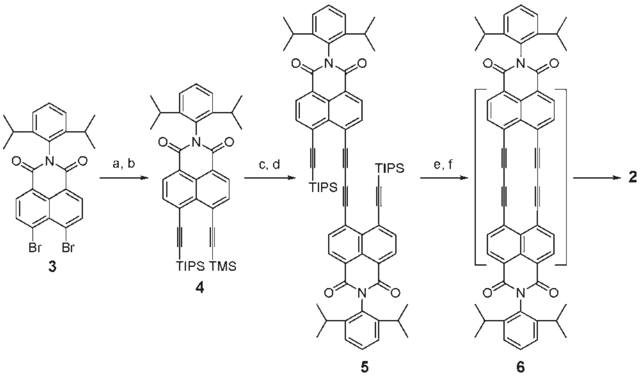


Figure 1. Resonance structures of zethrene and heptazethrene, and molecular structures of **1** and **2**.

Scheme 1[a]



[a] Reagents and conditions: (a) TMSA, 1 equiv, $PdCl_2(PPh_3)_2$/CuI, THF/Et_3N, rt, 70%; (b) TIPSA, 2 equiv, $PdCl_2(PPh_3)_2$/CuI, THF/Et_3N, 70 °C, 95%; (c) K_2CO_3, MeOH/THF, rt, 60%; (d) *p*-benzoquinone, $PdCl_2(PPh_3)_2$/CuI, diisopropylamine, toluene, 60 °C, 85%; (e) TBAF/THF, rt, 30 min; (f) $PdCl_2(PPh_3)_2$/CuI, toluene, rt, 1 h, 22% for two steps.

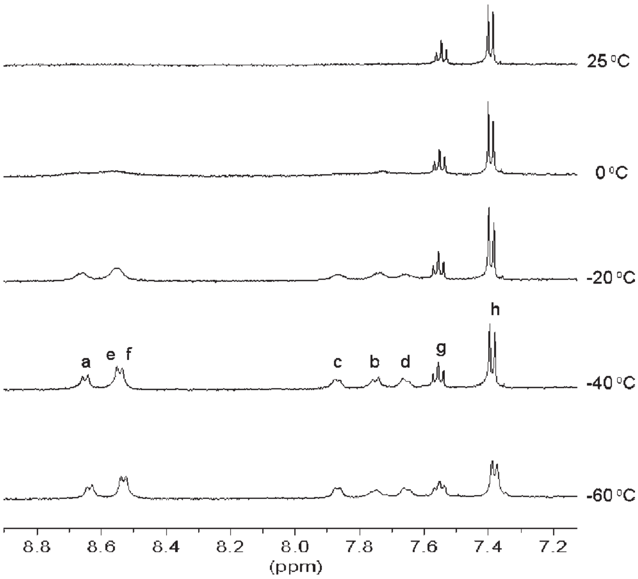


Figure 2. Variable-temperature ^1H NMR spectra of **2** in CD_2Cl_2 in aromatic region and assignment of aromatic protons. The resonance assignment referred to the structure shown in Figure 1.

At −40 °C, all peaks from heptazethrene backbone became clear and could be reasonably assigned according to integration values and the chemical environment of protons. This phenomenon was also observed in phenalenyl-based biradicals and teranthene biradical, resulting from a thermally excited triplet species which is slightly higher in energy than the singlet biradical state.[5,6] A THF solution of **2** showed no ESR signal at room temperature, presumably due to too many antiparallel couplings of unpaired electrons and cancellations of magnetic moments. On the other hand, the zethrenebis(dicarboximide) **1** exhibited sharp ^1H NMR signals at room temperature as a result of a larger singlet−triplet energy gap and smaller amount of triplet species, which is common for most closed-shell Kekulé hydrocarbons.

Theoretical calculations were conducted to further interrogate the biradical character of molecule **2**. The geometry was first optimized by the CAM-B3LYP[17] method using the Gaussian09 suite of programs.[18] The HOMO and LUMO of **2** obtained from the closed-shell solution can serve as a reference, which indicates an extended delocalization through the heptazethrene core, and shows that the central *p*-quinodimethane unit possesses the largest HOMO and LUMO coefficients (Figure 3), suggesting the most reactive site. As expected, further analysis performed with the STABLE=OPT keyword[19] revealed the instability of the restricted wave function. The reoptimization was carried out to achieve an unrestricted and symmetry-broken solution accordingly. The resulting structure with spin contamination of $\langle S^2 \rangle = 1.017$ was located to be 5.8 and 7.5 kcal/mol more stable than the closed-shell and the triplet biradical forms, respectively. These observations confirm that the ground state of **2** is open-shell singlet. The small singlet−triplet energy gap indicates that the radicals are bonded very weakly, similar to other singlet open-shell hydrocarbons.[5,6] Interestingly, the spin densities are homogeneously distributed through the whole heptazethrene molecule, including the carbonyl groups in **2** (Figure 3). This is slightly different from Kubo's benzoquinoid and naphthoquinoid *bis*phenalenyls,[5] in which the spins are mainly delocalized among the two phenalenyl units. In addition, detailed bond length analysis on the central six-membered ring reveals a quinoid character in closed-shell form and an aromatic benzenoid character in singlet and triplet biradical states (Figure S5 in the Supporting Information (SI)), indicating that the biradicals are stabilized by aromatization. For comparison, the same calculations for **1** were also conducted, and it was confirmed that **1** favors a singlet closed-shell ground state, which is 10.8 kcal/mol more stable than its triplet biradical state.

Compound **2** exhibited excellent solubility in common organic solvents due to the attachment of bulky 2,6-diisopropylphenyl groups. The absorption spectra of **1** and **2** in chloroform are shown in Figure 4. Compound **1** showed a well-resolved *p*-band with maximum absorption at 648 nm along with a shoulder band at 596 nm, corresponding to 0−0 and 0−1 electronic transitions, which is also typical for other closed-shell PAHs such as rylenes.[20] For **2**, the absorption spectrum displayed four bands from the far-red to the near-infrared region with maxima at 827, 747, 701, and 641 nm, and a similar band structure was also observed for teranthene derivative and quinoidal oligothiophenes.[6a,21] The weak, lowest-energy band most likely originates from the presence of a low-lying excited singlet state dominated by a doubly excited electronic configuration (H, H→L, L).[21] Variable-temperature absorption spectral measurements were conducted in dichloromethane (Figure S4, SI), and with decrease of temperature, absorbance of bands at lower energy

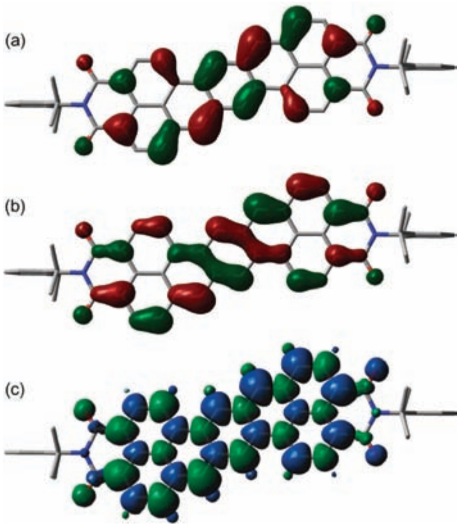


Figure 3. (a) HOMO, (b) LUMO, and (c) spin densities of **2**. The calculations were performed at CAM-B3LYP level of theory. Blue and green surfaces represent α- and β-spin densities, respectively.

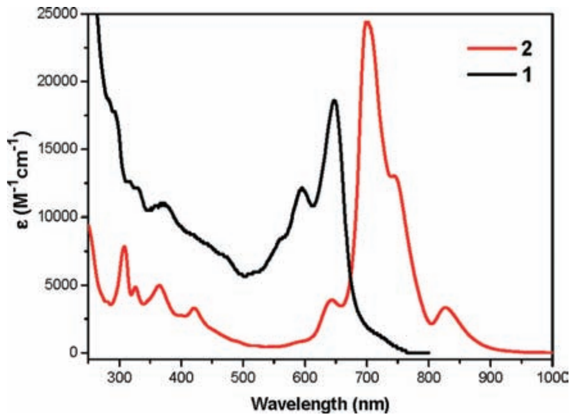


Figure 4. Absorption spectra of **1** and **2** in chloroform.

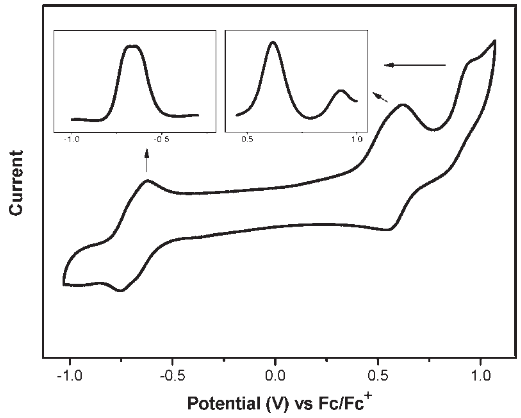


Figure 5. Cyclic voltammogram of **2** in dichloromethane with 0.1 M Bu_4NPF_6 as supporting electrolyte, Ag/AgCl as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s. (Inset) Differential pulse voltammograms of **2**.

(827 and 747 nm) increased, while the optical density for the bands at higher energy (701 and 641 nm) decreased, indicating a slight shift of the equilibrium between different species presumably including singlet species together with a small amount of triplet species. Moreover, **2** does not show any photoluminescence but **1** exhibits a moderate fluorescence quantum yield of 50%,[12] further indicating the biradical character of **2**. The cyclic voltammogram of **2** exhibited one reversible two-electron oxidation wave at E_{ox}^{1} = 0.62, one quasi-reversible one-electron oxidation wave at E_{ox}^{2} = 0.93 and two very close reversible one-electron reduction waves at E_{red}^{1} = −0.65 V and E_{red}^{2} = −0.69 V (vs Fc/Fc$^+$) (Figure 5). A low HOMO−LUMO band gap was determined as 0.99 eV for **2**, 0.55 eV smaller than that of **1**. This observation provided further evidence that a small band gap is one of the crucial preconditions in forming a singlet open-shell ground state.

Outstanding chemical and photostability were observed for **2**, making it one of the most stable singlet biradical PAHs known so far. The half-life time of **2** in chloroform exposed to ambient air and light conditions was found to be as long as 6 days (Figure S3 in SI). Such a high stability can be mainly ascribed to the attachment of strong electron-withdrawing imide groups, which can lower the high-lying HOMO energy level of the parent heptazethrene. In fact, a relatively low lying HOMO (−5.22 eV) was determined for **2** by cyclic voltammetry, indicating a high oxidation resistance. The impressive stability of the biradical form can be explained by (1) recovery of aromaticity in the central six-membered ring, (2) large-extent delocalization of the biradicals, and (3) stabilization of radicals by the electron-withdrawing imide groups. Since the delocalization and electron-withdrawing effects are similar in **1** and **2**, but **1** barely showed biradical character, we believe that the aromatic linker in the middle is the major contribution to the biradical stability of heptazethrene. However, considering that the aromatic stabilization energy of one more benzene ring is ~90 kJ/mol, which can by no means fully compensate the cleavage of C−C π-bond energy of ~270 kJ/mol,[22] the delocalization and electron-withdrawing effects of imides will still play key roles in stabilizing the biradical.

In conclusion, a stable heptazethrene derivative **2** was synthesized and well-characterized for the first time. Attachment of electron-withdrawing dicarboximide groups is proven to be an efficient approach toward soluble and stable open-shell PAHs, which is very important for further studies on their optical/electronic properties and practical applications. Our research also provided the first experimental proof on the singlet biradical character of zethrenes, an intriguing class of well-defined graphene fragments. Synthesis and investigation of higher-order zethrenes are currently underway in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and characterization data of all new compounds, theoretical calculation data, photostability test, variable-temperature UV−vis−NIR spectral measurements, and complete ref 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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