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Kinetically Blocked Stable 5,6:12,13-Dibenzozethrene: A Laterally π-Extended Zethrene with Enhanced Diradical Character

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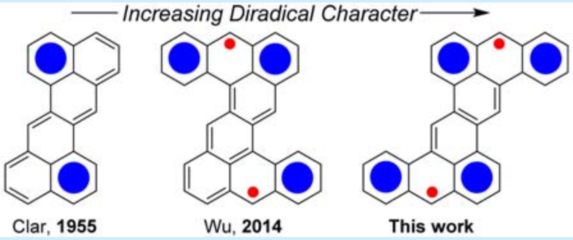
S Supporting Information

ABSTRACT: Although the ground-state and physical properties of zethrene and recently invented 1,2:8,9-dibenzozethrene have been well studied, the other dibenzozethrene isomer, i.e., 5,6:12,13-dibenzozethrene, remained unexplored. A short synthetic route to a kinetically blocked stable 5,6:12,13-dibenzozethrene derivative **5** is presented. The ground state is found to be open-shell singlet experimentally, and the theoretical y_0 was enhanced to 0.414, which corroborates nicely with the experimental and theoretical singlet−triplet energy gap.



The expansion of the open-shell π-conjugated polycyclic hydrocarbon (CPH)[1] empire has recently gained much attention because of its unique magnetic and electronic properties that make CPHs potential materials for nonlinear optics,[2] spintronics,[3] field effect transistors[4] and energy storage devices.[5] In recent years, various classes of stable open-shell singlet CPHs with diradical character have been reported, including biphenalenyls,[6] indenofluorenes,[7] anthenes,[8] π-extended p-quinodimethanes,[9] and zethrenes.[10] Parent zethrene was experimentally found to be closed-shell, and vertical π-extension of the central core through fusion of one benzene (heptazethrene) and one naphthalene (octazethrene) moiety leads to open-shell derivatives with increased diradical character (Figure 1).[10d,e] If parent zethrene is horizontally π-extended through fusion of two benzene rings at the upper and lower naphthalene sites, it leads to 1,2:8,9-dibenozethrene and 5,6:12,13-dibenzozethrene (Figure 1).[11] Among these zethrenes, 5,6:12,13-dibenzozethrene still remains unexplored, although its relevant higher order zethrene derivative, i.e., 5,6:13,14-dibenzoheptazethrene (Figure 1), was recently reported by our group.[10f] In 1963, Clar's synthetic attempt to 5,6:12,13-dibenzozethrene from corresponding dihydrogen precursor, via an oxidative dehydrogenation route, afforded a "very unstable green dibenzozethrene",[12] and thereafter, no attempt has been devoted to its isolation, likely due to lack of a well-defined synthetic approach.

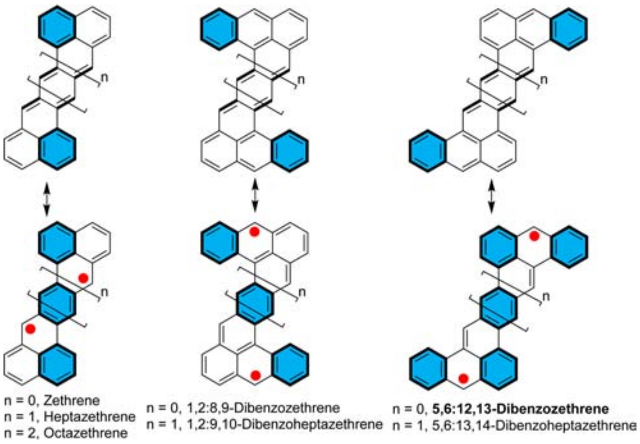


Figure 1. Closed-shell and open-shell canonical forms of zethrenes and higher order π-extended zethrenes.

Our previous calculation (UCAM-B3LYP/6-31G*) predicted the parent 5,6:12,13-dibenzozethrene as an open-shell singlet CPH with a diradical character (y_0) of 0.292 in the ground state,[11a] which may explain the observed high reactivity of the parent compound attempted by Clar. This is reasonable as we have shown that between two isoelectronic open-shell CPHs (1,2:9,10-dibenzoheptazethrene and 5,6:13,14-dibenzoheptazethrene), the one with the higher number of Clar's sextet shows higher diradical character in the singlet ground state.[10f] Therefore, kinetic blocking of the most reactive radical sites at the terminal zigzag edges with bulky substituents was necessary. We chose triisopropylsilylethynyl (TIPS) substituent as it will not only improve stability of the molecule 5,6;12,13-dibenzozethrene-TIPS (**5**) but also enhance solubility. Herein, we disclose a short-step synthesis of **5**, and for the first time in more than five decades, the ground state of the stable material can be thoroughly investigated by various experimental techniques, assisted by the density functional theory (DFT) calculations.

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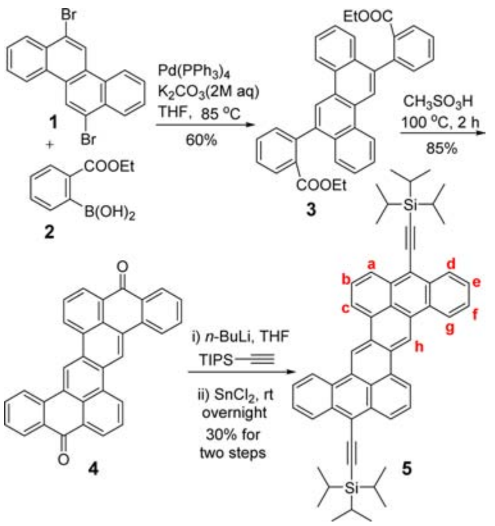
The synthetic route used to obtain the target molecule **5** is mainly based on a Friedel−Crafts acylation followed by reductive dehydroxylation approach (Scheme 1). The synthesis commenced with the Suzuki reaction between the commercially available 6,12-dibromochrysene **1** and 2-ethoxycarbonylphenylboronic acid **2** to give the diester **3**. Compound **3**, upon Friedel−Crafts acylation with methanesulfonic acid, underwent regioselective cyclization to give diketone **4**. Finally, diketone **4** was treated with excess TIPSLi (prepared by addition of *n*-BuLi in TIPS-acetylene at −0 °C in tetrahydrofuran (THF)) and subsequently quenched with $SnCl_2$ to afford compound **5** as a green solid in 30% yield for two steps.

Scheme 1. Synthetic Route to 5



Compound **5**, when subjected to ^1H NMR measurement (Figure 2a), revealed some broad signals at room temperature. The signals started to sharpen as the temperature was lowered to −40 °C, thus allowing assignment of the proposed structure with the help of 2D-COSY NMR measurements (Figure S4). This is a typical phenomenon mostly observed for open-shell singlet diradicaloids and can be explained by the existence of a significant amount of thermally populated triplet biradical species, which lies little higher in energy than the singlet diradical. Further, the formation of **5** was confirmed by high-resolution mass spectroscopy (see the SI) and crystallographic analysis (vide infra). A broad and featureless electron-spin resonance (ESR) signal with $g_e = 2.0028$ was obtained from solid-state ESR measurement at room temperature (Figure 2b), indicating the open-shell nature of **5**. The spin concentration was found to be 2.2% against 2,2-diphenyl-1-picrylhydrazyl (DPPH). To observe magnetic behavior with variable temperature and to calculate singlet−triplet energy gap (ΔE_{S-T}), superconducting quantum interference device (SQUID) measurements were done with the powder sample at 2−380 K (Figure 2c). According to the analysis, magnetic susceptibility increased after 225 K and fitting of the data using the Bleaney−Bowers equation[13] gave an exchange interaction energy ($2J/k_B$) of −2264.5 K (i.e., $\Delta E_{S-T} = -4.5$ kcal/mol). These experimental data strongly support that **5** is a singlet diradical in the ground state, which can be thermally populated to the triplet excited state at room temperature because of a small singlet−triplet energy gap.

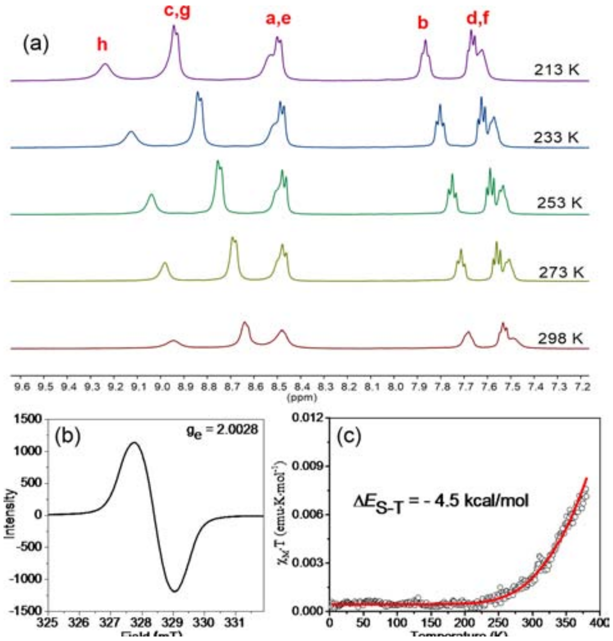


Figure 2. (a) VT ^1H NMR of **5** (aromatic region) in THF-d_8; the resonance assignment referred to the structure shown in Scheme 1; (b) ESR spectrum of **5** in solid form at room temperature; (c) $\chi T-T$ curve in the SQUID measurements of **5** as powder sample. The measured data were shown as circles, and the fitting curve was drawn by the Bleaney−Bowers equation with $g = 2.0$.

X-ray quality crystals of **5** can be obtained by cooling a saturated THF solution of **5** at 0 °C for 2 days. Compound **5**, co-crystallized with THF, has a planar structure with a slight deviation of TIPS groups from the core plane. Molecular packing of **5** shows a one-dimensional polymeric chain structure through intermolecular $\pi-\pi$ (or spin−spin) interactions with significant overlap (with roughly four rings) between two neighboring molecules of **5**. Close contacts between edge-carbon atoms with a short distance of 3.267 Å was observed, which may hint at moderate intermolecular spin−spin interactions. Bond length analysis on the single-crystal structure of **5** (Figure 3a) showed that $C(sp^2)=C(sp^2)$ bond lengths in *b*, *c*, *d* are 1.368, 1.418, and 1.438 Å, which are longer than typical C=C bond lengths in olefins (1.33−1.34 Å), suggesting the weakening of the double-bond character. At the same time, the shortening of the C−C bond distance in $a = 1.418$ Å is indicative of some partial double-bond character, showing a larger contribution of diradical resonance form as compared to the closed-shell form. The calculated nucleus-independent chemical-shift (NICS(1)zz) values for **5** show highly aromatic character for terminal benzene rings of the anthracene moiety (−21.45 and −18.06 ppm), indicating greater contribution of the diradical resonance form in the singlet ground state.

DFT calculations (using CAM-B3LYP/6-31G**) for **5** predicted that energy of the singlet diradical state is 4.46 and 6.52 kcal/mol lower than the energy of the triplet biradical and singlet closed-shell states, respectively. The theoretical singlet−triplet energy gap is also in agreement with the experimental value (4.5 kcal/mol) obtained by SQUID measurement. The singlet diradical character was calculated to be 0.414 based on the computed natural-orbital occupation numbers at the same level of theory. The y_0 of **5** is higher than parent 5,6:12,13-dibenzozethrene,[11a] seemingly due to the more extended

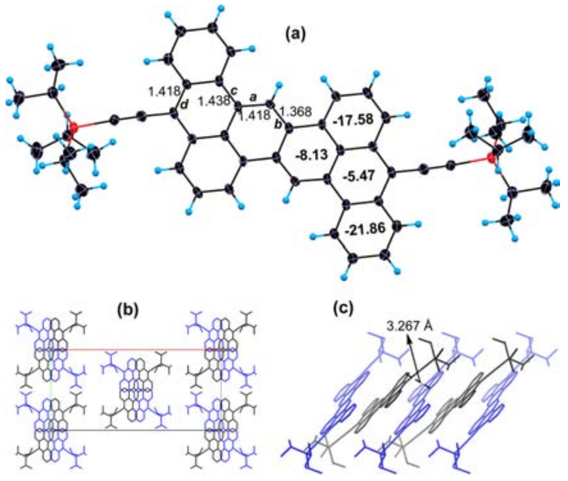


Figure 3. (a) X-ray crystallographic structure of **5** with selected bond lengths (Å) and calculated NICS(1)zz values. (b) 3-D packing structure from top view. (c) Side view showing close contact between two molecules; hydrogens and solvent molecules are omitted for clarity.

delocalization to acetylene counterparts. For comparison, under the identical level of calculation, the parent 1,2:8,9-dibenozethrene isomer has a smaller diradical character of 0.13.[11a] Our theoretical calculation is indeed in good agreement with the observed signal broadening in NMR and featureless ESR signal at the room temperature. The calculated frontier molecular-orbital profiles of α and β spins were shown to have a typical disjointed nature for the ground-state singlet diradical, and the spin densities are evenly delocalized over the whole π-conjugated framework (Figure 4).

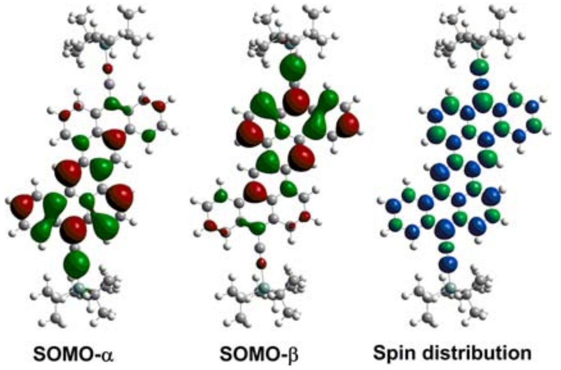


Figure 4. Calculated (UCAM-B3LYP/6-31G**) frontier molecular orbital profiles for the α-spin and β-spin and spin density distribution of the singlet diradical **5**.

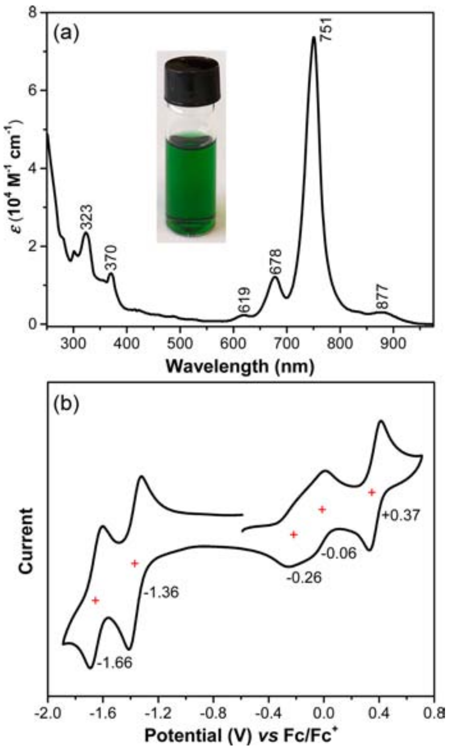


Figure 5. (a) UV−vis−NIR absorption spectra of **5** (inset: photo for the solution in DCM); (b) cyclic voltammogram of **5** in DCM with 0.1 M Bu_4NPF_6 as supporting electrolyte, Ag/Ag$^+$ as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and the scan rate at 100 mV/s. The potential was externally calibrated by an Fc/Fc$^+$ couple.

A solution of **5** in dichloromethane showed an intense absorption peak at λ_{max} = 751 nm, together with a small shoulder band on lower energy side (λ_{max} ∼ 877 nm) due to the admixing of a doubly excited electronic configuration (H, H → L, L) in the ground state (Figure 5a), a typical trait of singlet diradicaloids.[14] A concentrated solution of **5** is green. The nonfluorescence behavior is also in agreement with the diradical nature of **5**. The optical energy gap (E_g^{opt}), calculated from the lowest energy absorption onset, is found to be 1.30 eV. Despite the large diradical character, compound **5** is quite stable in the solid state even in the presence of air and light, while its solution in dichloromethane, under ambient conditions, decays with a half-life ($t_{1/2}$) of 33 h (Figure S5). This is comparable to the half-life of isoelectronic octazethrene-TIPS with similar diradical (theoretical) character.[10e]

The cyclic voltammogram of **5** (Figure 5b) shows three reversible oxidation waves with half-wave potentials at $E_{1/2}^{ox}$ = −0.26, −0.06, and 0.37 V against the ferrocene/ferrocenium (Fc/Fc$^+$) couple. Along with this, two reversible reduction waves with half-wave potentials at $E_{1/2}^{red}$ = −1.36 and −1.66 V vs (Fc/Fc$^+$) were also observed. Using the onset potentials for the first oxidation (−0.33 V) and reduction (−1.28 V) waves, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were calculated to be −4.47 and −3.52 eV, respectively, resulting in a low electrochemical energy gap of 0.95 eV. By looking at the multistage reversible oxidation waves, a stepwise chemical oxidation has been conducted using $SbCl_5$ at room temperature in dichloromethane. This sequential oxidation leads to radical cation (λ_{max} = 866 nm) and dicationic species (λ_{max} = 728 nm) at additions of 3 and 12 equiv of $SbCl_5$, respectively (Figure S8).

In conclusion, a kinetically blocked stable and soluble 5,6:12,13-dibenzozethrene derivative **5**, a long overlooked extended zethrene derivative, was successfully synthesized and fully characterized using various experimental techniques. With the assistance of DFT calculations, the ground state was confirmed to be an open-shell singlet with moderate diradical character (y_0 = 0.414). Unlike the usual vertical π-extension from zethrene to heptazethrene to octazethrene, here we have shown that rational π-extension through lateral conjugation also could be a feasible route toward designing new open-shell

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diradicaloids in singlet ground state. In addition, our approach toward diradicaloid **5** was a short-step synthesis with easy purification, and its nice crystalline behavior and packing in the solid state make compound **5** a potential open-shell singlet candidate for organic field effect transistors. This is currently under investigation in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01196.

Experimental details; NMR and mass spectra; DFT calculation details; single-crystal data (PDF)

X-ray data for **5** (CIF)

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Notes

The authors declare no competing financial interest.

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