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Toward Singlet–Triplet Bistable Nonalternant Kekulé Hydrocarbons: Azulene-to-Naphthalene Rearrangement

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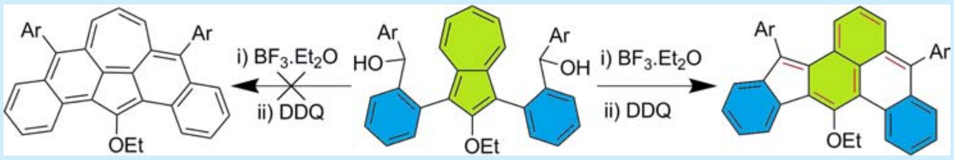
S *Supporting Information*



ABSTRACT: Recent developments of open-shell singlet diradicaloids motivated the search for stable singlet–triplet bistable nonalternant polycyclic hydrocarbons. During the synthesis of this type of molecule, such as the dibenzo-cyclohepta[*def*]fluorene **3**, an unexpected azulene-to-naphthalene rearrangement was observed at room temperature, which resulted in new nonalternant hydrocarbons **8a**/**8b** with a closed-shell singlet ground state. These studies provided insight into the unique chemistry of azulene and challenges for the synthesis of singlet–triplet bistable polycyclic hydrocarbons.

π-Conjugated polycyclic hydrocarbons (PHs) with an open-shell singlet diradical ground state have recently received much attention due to their unique electronic, optical, and magnetic properties and potential applications in materials sciences.[1] Our group and others have synthesized various relatively stable PHs with significant diradical character and have systematically investigated their fundamental structure-diradical character-physical property relationships.[2] Existence of Kekulé structure in PHs is usually considered to be indicative of the singlet ground state, and by far, most of the studied open-shell nonalternant PHs reported are singlet[1i,j,2a−c,f−l] rather than triplet due to a double spin polarization mechanism.[3] Malrieu et al. extended the Ovchinnikov rule[4] to the nonalternant PH skeletons considering that the S_z value of the most alternant spin distribution defines the spin multiplicity of the ground state (i.e., if the optimal $S_z = 1$, the state will be a triplet; if $S_z = 0$, the state will be singlet). Their theoretical calculations on nonalternant PHs, using both the geometry-dependent Heisenberg Hamiltonian and *ab initio* methods, found that the lowest singlet and triplet states for cyclohepta[*def*]fluorene **2** are nearly degenerate in their substantially different equilibrium geometries (**2-CS** and **2-OS**) with the two wells being separated by a significant energy barrier.[5] This finding eventually evolved the "singlet–triplet bistability" in nonalternant PHs. Early synthetic attempts to the derivatives of **2** have been so far unsuccessful,[6] with the exception of its dianion form $\mathbf{2}^{2-}$.[7] The reason for the instability has been attributed to the more stable triplet ground state, **2-OS**, due to the recovery of two aromatic sextets in the open-shell form in addition to an allyl radical.[8a] The more stable triplet ground state was indeed in good agreement with earlier predictions by Heilbronner.[8b]

To date, experimental demonstration of singlet–triplet degenerate Kekulé hydrocarbon is limited to *in situ* photochemically generated fluoranthene[9] derivatives, likely due to intrinsic instability. Notably, tetramethyleneethene (TME)[10] is a classic example with singlet–triplet states nearly degenerate; however, it is a non-Kekulé hydrocarbon. Our plan was to incorporate azulene into the PH framework to investigate the effect of its dipolar nature to the diradical character. We designed dibenzo-cyclohepta[*def*]fluorene (Figure 1), **3**, which can accept a Kekulé structure (**3-CS**) in singlet state, while exercise of Ovchinnikov rule supports a "singlet–triplet bistability" in **3** ($S_z = 1$, Figure 1), as it is an extended version of **2**. Similar to the literature,[8a] we theoretically found the ground state of **3a** (a potential singlet

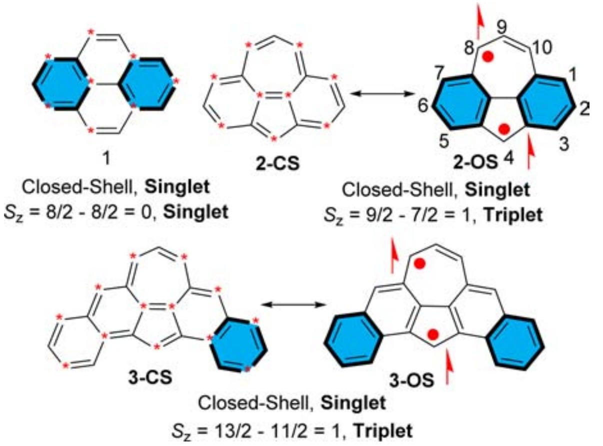


Figure 1. Prediction of the ground states of the alternant hydrocarbon pyrene **1** and the nonalternant Kekulé hydrocarbons **2** and **3** using Ovchinnikov rule.

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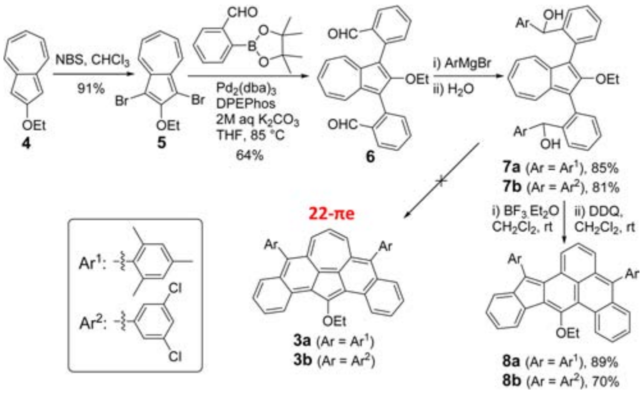
aromatic 22-πe system) to be triplet, which was 7.7 kcal/mol lower than the singlet state (Table S1 and Figure S23 in the Supporting Information (SI)). Intrigued by the theoretical results, we feel it is worth synthesizing **3** and studying the actual ground state.

In order to achieve the desired derivative of **3** (i.e., **3a**), we selected 2-ethoxy-azulene **4**[11] as the starting material in order to prevent any isomer formation during Lewis-acid catalyzed ring-cyclization step from the diol precursor **7a**/**7b** (Scheme 1).

Scheme 1. Synthetic Route to Derivatives 8a/8b



Regioselective bromination of **4** with *N*-bromosuccinimide (NBS) gave **5** in 91% yield, and Suzuki coupling between **5** and 2-formylphenylpinacolboronic acid ester afforded **6** in 64% yield. Treatment of **6** with excess of 2-mesitylmagnesium bromide generated the diol **7a** in 85% yield. The BF_3·Et_2O mediated ring cyclization of **7a** revealed the formation of a mixture of ring-cyclized dihydrogen-precursor and partly oxidized final product (Figure S16 in SI), which on subsequent treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (to ensure a complete dehydrogenation) produced a blue color solution, instantaneously. The final mesityl derivative was isolated as a stable blue solid, which showed the desired parent ion peak at an *m*/*z* value of 582.0023 under MALDI-TOF mass analysis (Figure S17 in SI). A well-resolved, sharp ^{1}H NMR signal (Figure S6 in SI) was observed for the blue solid, which, according to calculation,[5] might be indicative of the desired framework **3** as strong bond length alternation in the singlet state of **3a** may prevent it to show an average ^{1}H NMR signal (for a 22π-electron Hückel aromatic system). In fact, one can assign the ^{1}H NMR peaks with the help of 2D-COSY and NOESY spectra, considering the structure **3a**. Regardless of the clear NMR and mass spectral analysis, we felt an imminent need for crystallographic analysis to prove the final compound's molecular structure. Unfortunately, we were unable to get a single crystal for the mesityl derivative. So we changed the mesityl substituent to 3,5-dichlorophenyl unit.

Using a similar synthetic approach, we treated **6** with an excess of 3,5-dichlorophenyl magnesium bromide to get the diol **7b**, which was subsequently treated with BF_3·Et_2O (no purification was done) and then DDQ, to afford the desired 3,5-dichlorophenyl substituted final compound as a blue solid. Interestingly, X-ray crystallographic analysis of this blue compound revealed the formation of **8b**, having indeno-benzophenalene core (Figure 2a and Figure S24 in SI) instead of the desired hydrocarbon core **3**.[12] The ^{1}H NMR spectra of **8a** was consequently assigned, with the help of 2D-COSY and NOESY NMR (Figure S7 and S8 in SI), to possess the same hydrocarbon core of **8b**. It seems an unprecedented azulene-to-naphthalene rearrangement took place at room temperature!

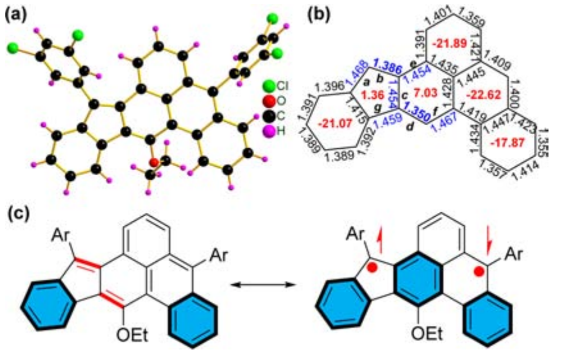


Figure 2. (a) X-ray crystallographic structure of **8b** (solvent molecule is omitted for clarity); (b) selected mean bond lengths and calculated NICS(1)zz values in the hydrocarbon core of **8b**; (c) resonance structures of nonalternant indeno-benzophenalene **8**.

Compound **8b** adopts a quasi-planar structure with the anthracene moiety rotated against the cyclopenta-fused phenyl moiety by 12.6° (Figure 2a and Figure S25 in SI). The 3,5-dichlorophenyl ring attached to the anthracene ring is rotated out of plane by about 87.7°, indicating negligible contribution to the π-delocalization. Another 3,5-dichlorophenyl ring, attached with the five-membered ring, is rotated out of plane by 39.4° due to smaller steric repulsion. The interplanar distance between two **8b** molecules was found to be 3.77 Å, revealing a weak $\pi-\pi$ interaction (Figure S25 in SI). Bond length analysis on the single-crystal structure of **8b** disclosed that the bonds *b* and *d* (*b*, 1.386 Å; *d*, 1.350 Å) are significantly shorter than that of bond *a*, *c*, and *f* (*a*, 1.468 Å; *c*, 1.454 Å; *f*, 1.467 Å), indicating an fixed *trans*-1,3-butadiene substructure (Figure 2b). In addition, the bonds *e* and *g* show typical $C(sp^2)-C(sp^2)$ single bond character (*e*, 1.454 Å; *g*, 1.459 Å). The nucleus independent chemical shift [NICS(1)-zz] calculation reveals weak to moderate antiaromatic nature of the central five- and six-membered rings, respectively, bearing the "diene" unit, whereas the other outer six-membered rings showed quite strong aromatic character (Figure 2b). All these data indicate a closed-shell ground state for **8b** and this is reasonable since the singlet diradical form can only recover one additional Clar sextet (Figure 2c). DFT calculations (at B3LYP/6-31G(d) and UB3LYP/6-31G(d)), by optimizing the crystal structure, found the triplet state of **8b** to be 16.88 kcal/mol (Table S1 in SI) higher than that of the singlet state with zero diradical character; thus strongly supporting a closed-shell singlet ground state, which is also in line with the sharp ^{1}H NMR spectra observed for **8a**/**8b** (Figure S6/S11 in SI).

The UV–vis absorption spectral pattern of **8a** matches well with that of **8b** (Figure 3a), thereby confirming that they have the same indeno-benzophenalene core. A broad absorption band from 400 to 800 nm was observed, with multiple not-well-resolved peaks. Time-dependent DFT calculations predicted the lowest energy HOMO → LUMO transition at λ_{max} = 628.1 nm (oscillator strength, f = 0.3548, Table S3 in SI) for **8b** (Figure S22 in SI), which is in agreement with the experimentally found λ_{max} = 599 nm. A slightly red-shifted absorption of **8b** (Figure 3a) compared to **8a** (λ_{max} = 588 nm) is indicative of some contribution from the 3,5-dichlorophenyl ring to the π-delocalization of the hydrocarbon core, in addition to inductive effect. The optical energy gap (E_g^{opt}), estimated from the lowest

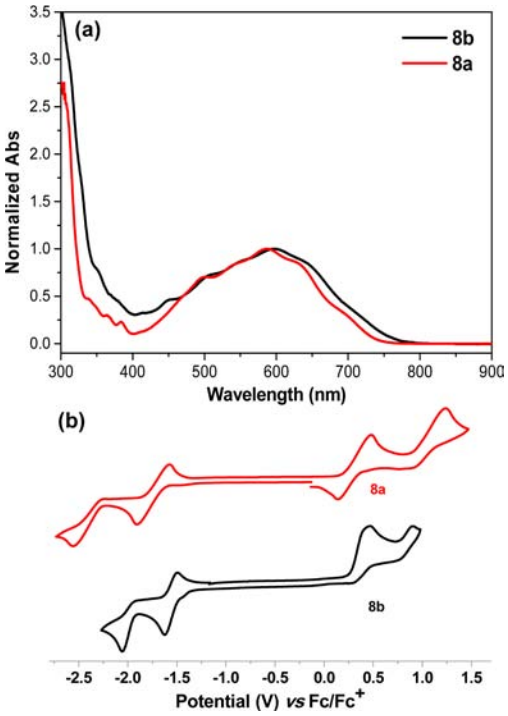
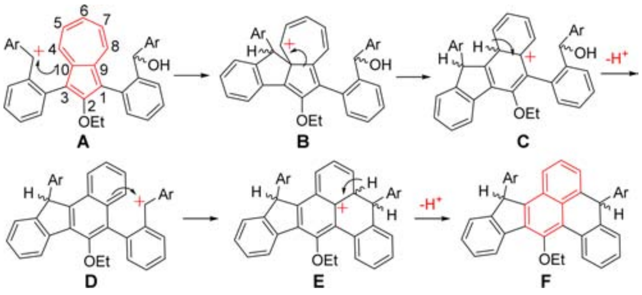


Figure 3. (a) Normalized UV−vis absorption spectra of **8a** and **8b**; (b) cyclic voltammogram for **8a** and **8b** on a gold disk electrode in dichloromethane and TBAPF$_6$ at 100 mV s^{-1}.

Scheme 2. Plausible Mechanism for the Azulene-to-Naphthalene Rearrangement during the BF$_3$·Et$_2$O Mediated Cyclization of 7a/7b



energy absorption onset of **8b**, was estimated to be 1.60 eV, which is slightly lower than the E_g^{opt} = 1.67 eV for **8a**.

Compound **8a** showed two quasi-reversible oxidation waves with half-wave potentials at $E_{1/2}^{ox}$ = 0.31 and 1.04 V. Two quasi-reversible reduction waves with half-wave potentials at $E_{1/2}^{red}$ = −1.70 and −2.36 V (vs ferrocene/ferrocenium (Fc/Fc$^+$)) (Figure 3b and Figure S20 in SI) were also observed. The HOMO and LUMO energy levels, estimated from the onset potentials of the first oxidation and reduction waves were found to be −4.98 and −3.18 eV, respectively, resulting in an electrochemical energy gap (E_g^{ec}) of 1.80 eV. Compound **8b** underwent three quasi-reversible oxidation waves with two very close half-wave potentials of $E_{1/2}^{ox}$ = 0.33 and 0.40 V and another at $E_{1/2}^{ox}$ = 0.81 V (Figure 3b and Figure S20 in SI). A reversible reduction wave with $E_{1/2}^{red}$ = −1.54 V, and another quasi-reversible reduction wave with $E_{1/2}^{red}$ = −1.99 V were also observed. The HOMO and LUMO energy levels were estimated to be −5.07 and −3.34 eV, respectively, resulting in a reduced E_g^{ec} = 1.73 eV compared to that of **8a**. Theoretically calculated HOMO and LUMO energy levels are summarized, in Table S2 (SI).

A plausible mechanism for the formation of **8a**/**8b** instead of **3a**/**3b** could be an, hitherto unknown, *ipso*-type electrophilic substitution through the 9 (or 10) carbon of the azulene unit in **7a**/**7b** (Scheme 2). Due to the dipolar character of the azulene, the electrophilic substitution reaction usually goes to the electron-rich five-membered ring, in particular, the 1,3-positions as we saw the bromination of **4** exclusively produced **5**. However, in the **7a**/**7b**, the 1,3-positions are now substituted by phenyl groups, and the as-formed cation **A** in the presence of Lewis acid (BF$_3$·Et$_2$O) will prefer an electrophilic attack to the neighboring 9 (or 10)-position to form a five-membered ring in **B** rather than to the 4 (or 8)-position to form a six-membered ring.[13] Then a ring opening occurred through a nucleophilic attack from the five-membered ring to the carbocation followed by a proton removal in **C**, affording the indeno-naphthalene intermediate **D**.[14] Then a Lewis-acid catalyzed Friedel−Crafts alkylation of aromatic naphthalene produced the dihydrogen-precursor **F**, which eventually afforded the indeno-benzophenalene core **8a**/**8b** through DDQ mediated oxidative-dehydrogenation. It is worthy to mention that the interconversion of one aromatic azulene to another aromatic naphthalene, considered as a rare type of reaction, was usually reported to be accomplished by static thermolysis at 400 °C or flash vacuum thermolysis above 800 °C,[15] and lately by microwave reaction at 300 °C on graphite surface.[16] A variety of intramolecular and radical-promoted mechanistic pathways for such rearrangement had been proposed and been theoretically extensively investigated.[17] Theoretical investigations found that the intramolecular route for azulene-to-naphthalene rearrangement requires an activation barrier of ≥81 kcal mol^{-1}, whereas a lower energy (≥24 kcal mol^{-1}) radical pathway is also feasible.[17d] However, our finding of Lewis-acid catalyzed room temperature interconversion of azulene-to-naphthalene via a carbocationic intermediate is noteworthy, and by far the most convenient approach as no harsh condition is required.

In conclusion, while synthesizing the singlet−triplet bistable nonalternant azulene-based hydrocarbons **3a**/**3b**, we observed an unexpected azulene-to-naphthalene rearrangement during the BF$_3$·Et$_2$O catalyzed electrophilic cyclization at room temperature. Per our knowledge, this is also the first report of hydrocarbons **8a**/**8b** with an indeno-benzophenalene core, which can also be classified as nonalternant PH with singlet closed-shell ground state. Our research revealed a unique azulene chemistry and provided insight into the challenging synthesis of singlet−triplet bistable nonalternant PHs. Nevertheless, different strategies to synthesize cyclohepta[*def*]fluorene derivatives are still underway 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.5b03028.

Experimental details, NMR and mass spectra, DFT calculation details (PDF)
Single crystal data (CIF)

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Notes

The authors declare no competing financial interest.

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(12) X-ray quality crystals were grown by slow diffusion of acetonitrile in the benzene solution of **8b**. Crystallographic data for **8b**: $C_{44}H_{28}Cl_4O$, M_w = 714.46; triclinic; space group = $P\bar{1}$; a = 11.3831(3) Å, b = 11.7165(3) Å, c = 12.5092(3) Å; α = 77.777(2)°, β = 83.900(2)°, γ = 89.052(2)°; V = 1621.27(7) Å^3; Z = 2; density (calcd.) = 1.464 Mg m^{-3}; R_1 = 0.0583 [$I > 2\sigma(I)$], wR_2 = 0.1372 (all data). CCDC no. 1425805.

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