

Fluoreno[4,3-*c*]fluorene: A Closed-Shell, Fully Conjugated Hydrocarbon

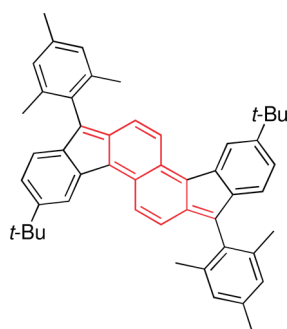
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ABSTRACT



The synthesis and optoelectronic properties of 24 π -electron, formally antiaromatic 4,11-di-*t*-butyl-1,8-dimesitylfluoreno[4,3-*c*]fluorene (FF) are presented. The solid-state structure shows that the outer rings are aromatic, while the central four rings possess a bond-localized 2,6-naphthoquinone dimethide motif (in red). The biradical character of FF is assessed experimentally and computationally; the results of which implicate a closed-shell ground state.

Conjugated hydrocarbons with extended polycyclic frameworks have fascinated chemists for over 125 years.¹ Such molecules have undergone a resurgence in interest over the last two decades because of their utilization as materials in optical and electronic device applications, such as organic field-effect transistors, photovoltaics, and light emitting diodes.² Large polycyclic aromatics have garnered considerable attention in this area due to π -orbital overlap of these electron-rich compounds in the solid state, which facilitates charge transport.³

Recently the syntheses of derivatives of *o*- and *p*-quinodimethane-containing indeno[2,1-*a*]fluorene⁴ and indeno-

[1,2-*b*]fluorene⁵ (IF) have been reported. These acene-like molecules show promise as electron transporting materials due to their relatively low-lying LUMO energy levels.⁶ In all cases, generation of the IF skeleton utilized a Sn(II)-mediated reductive dearomatization to furnish the quinodimethane core. We set out to probe the limits of this dearomatization reaction in larger arenes, such as naphthalene.

The feasibility of dearomatizing a larger system was first explored computationally by considering the energy required to form the product. We employedisodesmic reaction schemes and computationally determined the aromatic stabilization energies (ASE) of the basic indeno-[1,2-*b*]fluorene and fluoreno[4,3-*c*]fluorene core structures (IF **1** and FF **2**, respectively in Figure 1).⁷ The geometries

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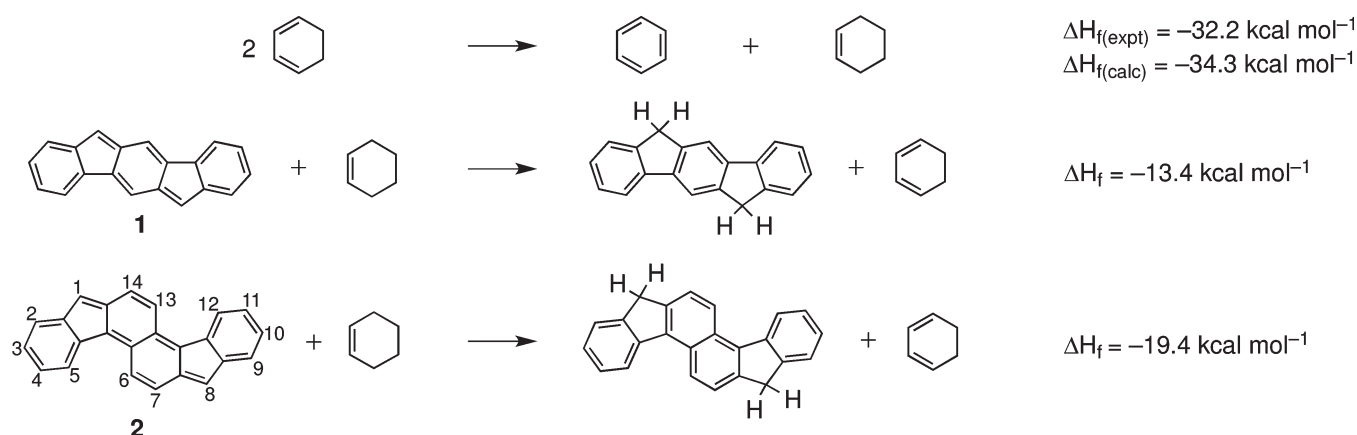


Figure 1. Calculated ASE using electronic and zero point energies from B3LYP/6-311+G(d,p)//B3LYP/6-31G(d). Compound **2** is shown with IUPAC numbering scheme.

were optimized with DFT using the B3LYP/6-31G(d) method⁸ as utilized in Gaussian 09,⁹ and then single point energies and frequency calculations were performed with the same method using the larger 6-311+G(d,p) basis set. This method was verified against benzene, the usual standard, yielding a computed ASE value of $-34.3 \text{ kcal mol}^{-1}$, whereas the experimentally determined ASE is $-32.2 \text{ kcal mol}^{-1}$ from the enthalpies of formation (ΔH_f).¹⁰ The ASE of IF **1** is surprisingly small at $-13.4 \text{ kcal mol}^{-1}$, 38% the ASE of benzene. However, the ASE for the expanded FF **2** is $-19.4 \text{ kcal mol}^{-1}$, which is expected relative to **1** since naphthalene has about 1.7 times the ASE of benzene. These results indicated that the synthesis of **2** should be possible. Although **2** is formally antiaromatic with a total of 24 π -electrons, nucleus-independent chemical shifts (NICS(1)_{zz}) calculations¹¹ (see Supporting Information) reveal that only the peripheral benzenes are diatropic and that the inner rings are very weakly paratropic and/or atropic, similar to **1**.

A second possibility we considered was that the fluorenofluorene might have an open-shell (biradical) configuration (e.g., **2'**, Figure 2). Recently a variety of extended

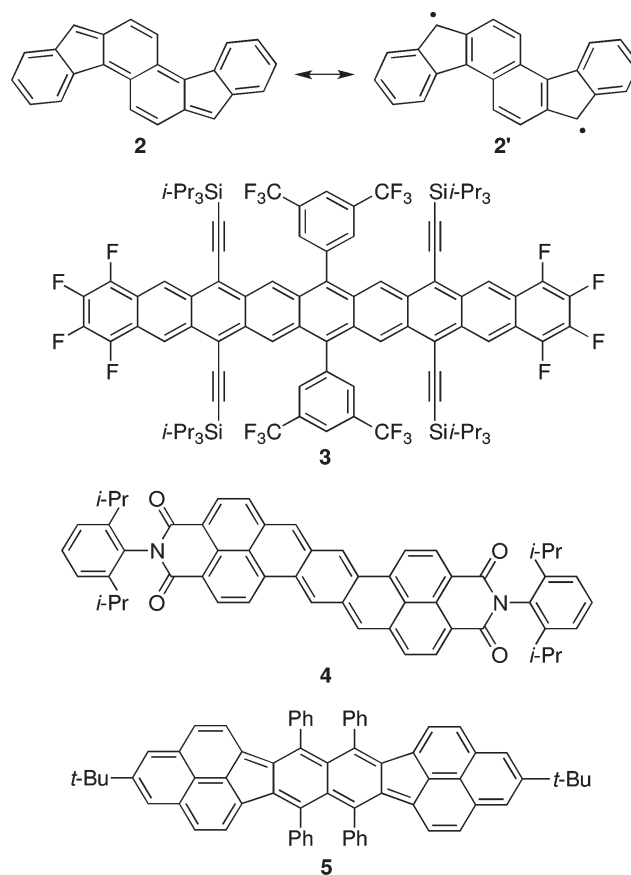


Figure 2. Closed-shell and OS forms of **2** and recently reported molecules **3–5** that show significant biradical character.

polycyclic π -systems have been described that exhibit a singlet open-shell (OS) ground state (e.g., **3**) and thermally

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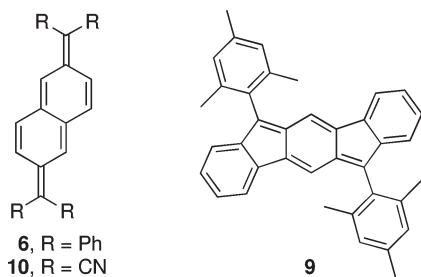
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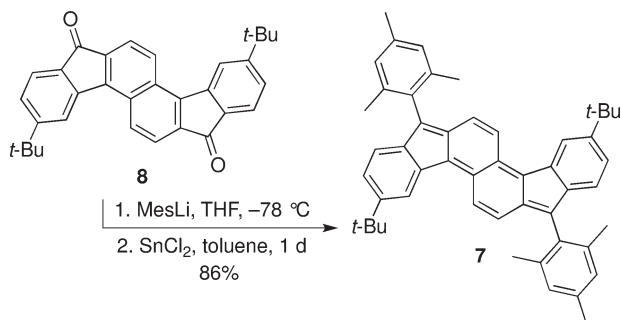
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accessible triplet states (e.g., **4**, **5**).¹² We therefore considered an OS singlet and triplet state for **2** using symmetry broken UB3LYP; the OS singlet energy was corrected using the approximate spin projection method.¹³ Using known 2,6-quinodimethylnaphthalene **6**¹⁴ as a test case, the calculated triplet state was estimated at 15.4 kcal mol⁻¹ above the OS singlet, which is in reasonable agreement with the experimentally determined value of 12.6 ± 2.0 kcal mol⁻¹.¹⁵ For **2** the closed-shell and OS singlet were calculated to be essentially the same energy. The square of the OS spin expectation value was miniscule ($\langle S^2 \rangle = 0.0001$), reinforcing that **2** should have a closed-shell ground state. The calculated triplet state for **2** is 16.1 kcal mol⁻¹ above the singlet.



Of the three possible fluorenofluorene variants that yield Kekulé hydrocarbons, we chose to experimentally investigate **7** since the requisite dione synthon **8** is a known molecule that can be prepared in seven steps from commercially available 2,6-dimethylnaphthalene.¹⁶ We also felt that inclusion of mesityl groups would enhance the kinetic and thermodynamic stability of **7**. Gratifyingly, treatment of **8** with mesityllithium followed by reduction with SnCl₂ in toluene at room temperature yields fully conjugated **7** in 86% yield (Scheme 1). Unlike the IF derivatives, elevated temperatures for this reaction led to

Scheme 1. Synthesis of 4,11-Di-*t*-butyl-1,8-dimesitylfluoreno[4,3-*c*]fluorene **7**



significant decomposition. Deep-blue solutions of **7** exhibited no line broadening in the proton NMR spectrum (i.e., no triplet character) upon heating to 160 °C (see Supporting Information), and the EPR spectrum of the powder and solution sample showed no triplet signal.

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Structurally similar **6** exhibited no biradical character in the EPR spectrum below 180 °C.¹⁵ Pure **7** is remarkably stable—the NMR spectrum showed no decomposition upon prolonged heating at 160 °C, and thermogravimetric analysis revealed less than 5% decomposition by ca. 350 °C. Another sample that was kept in CDCl₃ open to the atmosphere and exposed to ambient light exhibited by NMR only trace amounts of decomposition after 1 month.

The lowest energy transition in the absorption spectrum of **7** (Figure 3) appears at 649 nm, compared to a λ_{max} of 516 nm for dimesityl-IF **9**.^{5c} These values correspond to optical energy gaps of 1.79 and 2.29 eV, respectively,¹⁷ which clearly show the effect of inclusion in the core of the second six-membered ring and its two double bonds.

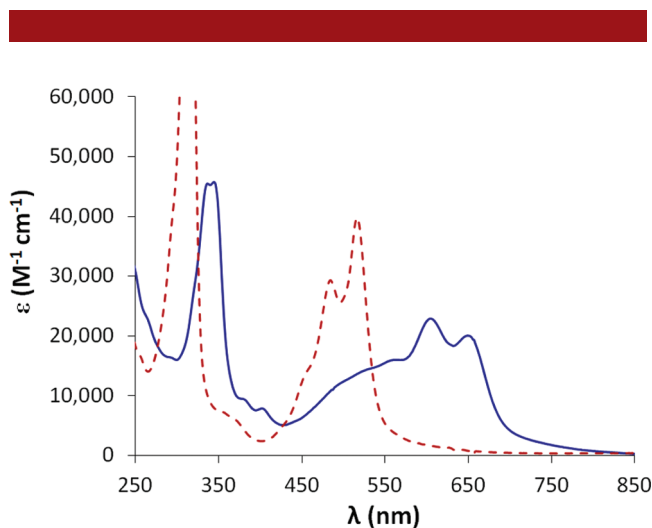


Figure 3. Electronic absorption spectra of **7** (solid blue) and **9** (dashed red) in CH₂Cl₂.

The cyclic voltammetry (CV) data for **7** exhibit redox amphoterism with two reversible reductions and two oxidations—the first oxidation reversible and the second quasi-reversible (Figure 4). The first reduction half wave potential is -0.87 V and the second -1.29 V, whereas the first oxidation half-wave potential is 0.82 V and the second 1.27 V.¹⁸ The electron affinity of **7** is higher than that of **9**, which has a first reduction half-wave potential of -1.12 V.^{5c} The LUMO energy of **7** was estimated at -3.77 eV from CV,¹⁹ an exceptionally low-lying LUMO for a polycyclic hydrocarbon that does not contain electron-withdrawing groups. This corresponds to an electrochemical energy gap of 1.69 eV, which agrees well with the optically determined value.

Compound **7** cocrystallized with benzene by slow evaporation, yielding single crystals suitable for X-ray diffraction. The molecular structure is shown in Figure 5, and relevant bond lengths are given in Table 1. The crystal

(17) The optical band gap was determined by taking a tangent line from the maximum of the first derivative for the lowest energy transition.

(18) For comparison, the potential references were changed from Fc/Fc⁺ to SCE, as described in: Connolly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.

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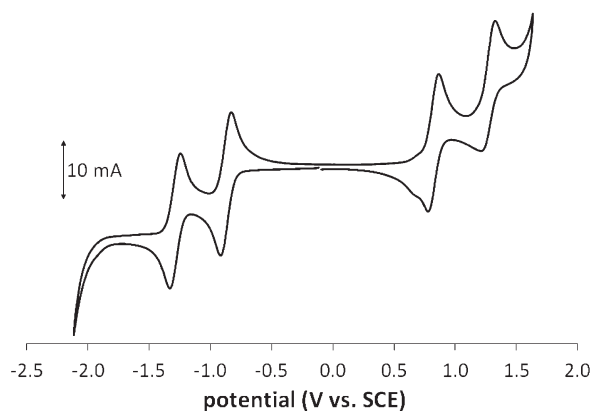


Figure 4. CV data for **7**. Data was recorded in a CH_2Cl_2 solution of 1 mM analyte and 0.1 M Bu_4NOTf using a scan rate of 50 mV s^{-1} . The working electrode was a glassy carbon electrode with a Pt coil counter electrode and Ag wire pseudoreference. Values reported as the half-wave potential (vs SCE) using the Fc/Fc^+ couple (0.46 V) as an internal standard; see reference 18.

structure of $7 \cdot (\text{C}_6\text{H}_6)$ establishes the closed-shell ground state due to the discrete, alternating short (1.356–1.378 Å) and long (1.410–1.433 Å) bond lengths. The B3LYP/6-31G(d) minimized structure of **7** accurately replicates the bond length alternation in central rings and near homogeneity for the outer six-membered rings. To the best of our knowledge, this is the first structural elucidation of a neutral 2,6-naphthoquinone dimethide; the crystal structure of **5** revealed a naphthalene-like core expected for an open-shell biradical.^{12a} The X-ray data for the anion of structurally similar **10** with methyltriphenylphosphonium counterion had a 2:1 stoichiometry and possessed longer bond lengths for the C(4)–C(5) double bond (Table 1) than neutral $7 \cdot (\text{C}_6\text{H}_6)$.²⁰ These differences are attributable to the negative charge distributed across the two independent molecules of **10**.

Table 1. Select Bond Lengths [Å]

bond ^a	7 (calc) ^b	$7 \cdot (\text{C}_6\text{H}_6)$ (X-ray)	10 (a) ^c	10 (b) ^c
C(1)–C(2)	1.359	1.356(6)	1.38	1.34
C(1)–C(5a)	1.446	1.433(6)	1.40	1.45
C(2)–C(3)	1.429	1.410(6)	1.46	1.47
C(3)–C(4)	1.455	1.433(6)	– ^d	– ^d
C(3)–C(6)	1.386	1.378(6)	1.42	1.38
C(4)–C(5)	1.387	1.377(6)	1.50	1.43
C(5)–C(5a)	1.479	1.459(6)	1.43	1.44

^a Numbering scheme for **7** (Figure 5) was applied **10**(a) and **10**(b).
^b RB3LYP/6-31G(d) minimized structure. ^c See ref 20. ^d Not reported.

Compound **7** is an intriguing addition to the molecular canon. In contrast to similar compounds that exhibit

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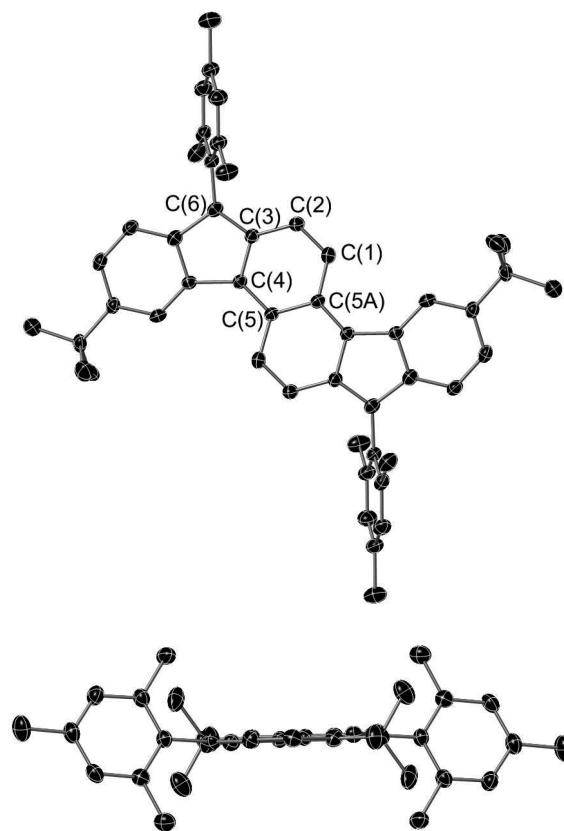


Figure 5. ORTEP showing top and side views of $7 \cdot (\text{C}_6\text{H}_6)$; solvent molecule and hydrogens omitted for clarity. Ellipsoids drawn at the 30% probability level.

considerable biradical character, the lack of a radical stabilizing motif (e.g., phenalenyl unit in **5**) leads to a closed-shell ground state for **7**.^{12a,b} The redox amphoterism in the CV data suggests potential as an ambipolar electronic material, similar to IF **9**,^{5c} and the unusual thermal and photochemical stability of **7** bode well for such applications. We are currently exploring use of the Sn-mediated dearomatization for the preparation of even larger, expanded π -conjugated polycyclic hydrocarbons.

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Supporting Information Available. Experimental and computational details; NMR spectra and X-ray cif file of **7**; and complete ref 9. This material is free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.