Polycyclic Hydrocarbons

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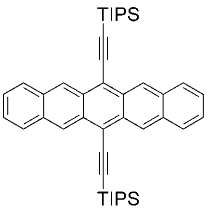
Indeno[1,2-b]fluorenes: Fully Conjugated Antiaromatic Analogues of Acenes**

*Daniel T. Chase, Bradley D. Rose, Sean P. McClintock, Lev N. Zakharov, and Michael M. Haley**

Dedicated to Professor Klaus Hafner

Conjugated hydrocarbons with extended polycyclic frameworks have fascinated chemists for more than a century.[1] Originally studied because of interest in the fundamental, intrinsic properties associated with such structures, more recent investigations have focused on utilization of these π-electron-rich compounds as materials in optical and electronic device applications.[2] Acenes such as pentacene and its derivatives (e.g., **1**)[3] have received the bulk of the renewed attention,[1c,d] but they unfortunately are prone toward oxidative degradation;[4] hence, there is demand for alternative, acene-like topologies. Although incorporation of heteroatoms is one possibility,[5] very recent studies by the groups of Saito, Kawase, and Tilley have reported improved syntheses of derivatives of dibenzopentalene (**2**), in which two five-membered rings have replaced the more traditional six-membered rings, as potential acene analogues.[6]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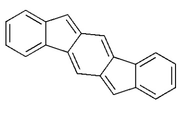
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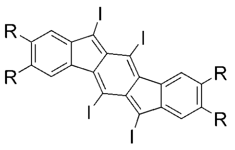
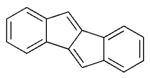

6, R = H, Dec, Dodec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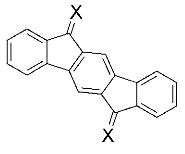
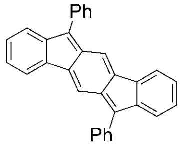

4, X = O
5, X = C(CN)$_2$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The indeno[1,2-b]fluorene skeleton (**3**), a 6-5-6-5-6 fused ring system also known as dibenzo[a,g]-*s*-indacene,[7] is an attractive structural motif in this regard. A fully conjugated indenofluorene (IF) should possess some remarkable characteristics: 1) Compounds like **3** have two fewer carbons than pentacene and thus two fewer π-electrons, making **3** formally antiaromatic (20 π-electrons). 2) Such molecules host a *para*-xylylene (*p*-quinodimethane) core, a reactive moiety that typically cannot be isolated because of its tendency to oligomerize/polymerize.[8] 3) The bonding picture of **3** should be interesting as the IF core can be viewed in several possible ways (e.g., a [20]annulene, a dibenzo-fused [12]annulene). 4) IFs do not possess any internal *s-cis* diene linkages, which could make them more resistant to the cycloaddition pathways that degrade acenes.

Although a number of molecules incorporate the indenofluorene core, nearly all bear substituents on positions 5 and 11 that either result in cross-conjugation (ketones **4**, olefins **5**)[9] or disrupt conjugation altogether (disubstitution, spirofusion).[10] Examples of fully conjugated species are extremely rare, as only four compounds have been reported to date. In 1994 Swager et al. prepared and characterized tetraiodides **6** but these rapidly oxidized to the corresponding diones upon exposure to air.[11] Very little is known about IF **7** prepared by Scherf et al. as the synthesis has not been disclosed; the only spectroscopic feature mentioned is a UV/Vis $\lambda_{\max}$ absorption of 543 nm.[12] Recently Kubo and co-workers prepared naphthalene-fused IFs. These molecules exhibited singlet biradical behavior, however, meaning that the dominant resonance structure has a benzene unit as the central six-membered ring; thus, the molecules cannot be considered fully delocalized.[13] Here, we disclose the synthesis of stable indenofluorenes **8a** and **8b**. We also report the X-ray crystal structure of **8a**, which unambiguously confirms the planar, fully conjugated state and provides a rare glimpse into the *p*-xylylene core. Also discussed are the optoelectronic profiles of **8a** and **8b**, as well as a cursory examination of their stability to photooxidative conditions in comparison to **1**.

Initial attempts to access the tetraethynylated derivatives by Sonogashira cross-coupling of **6b** (prepared as previously described from the corresponding dehydrobenzo[12]annulene, Scheme 1),[11] with either phenylacetylene or (trimethylsilyl)acetylene proved to be problematic, affording complex mixtures of products. Instead, the syntheses of IFs **8a** and **8b** introduced the alkynes in a stepwise manner. Starting with known diiododiones **9a** and **9b**, again prepared from the dehydrobenzo[12]annulene,[11] cross-coupling with (triisopropylsilyl)acetylene (TIPSA) afforded diynes **10a** and **10b**, respectively. Addition of the lithiated acetylide of TIPSA and subsequent reduction of the intermediate diols **11a** and **11b** overnight using $SnCl_2$ in toluene at 80 °C provided **8a** and **8b**, respectively, in modest overall yield. Whereas the compounds are red in the solid state, solutions of IFs **8a** and **8b** exhibit a brilliant blue-purple color.

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[*] D. T. Chase, B. D. Rose, Dr. S. P. McClintock, Dr. L. N. Zakharov, Prof. M. M. Haley
Department of Chemistry & Materials Science Institute
University of Oregon, Eugene, OR 97403-1253 (USA)
Fax: (+1) 541-346-0487
E-mail: haley@uoregon.edu

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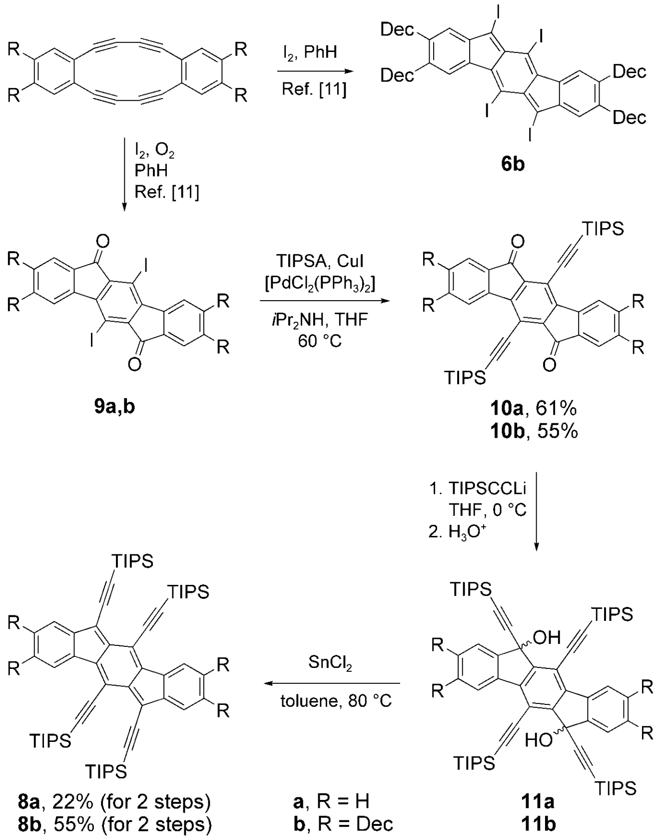

Scheme 1. Syntheses of **8a** and **8b**.

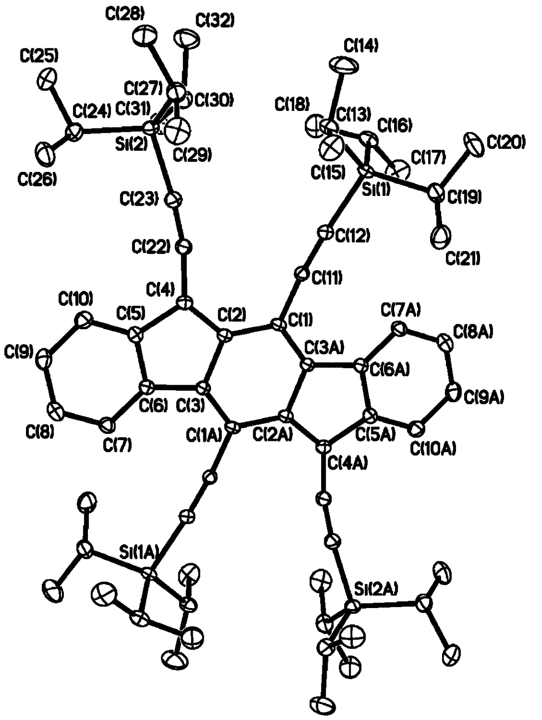

Figure 1. Molecular structure of indenofluorene **8a**; ellipsoids drawn at 30% probability level.

Table 1: Experimental and calculated bond lengths of indenofluorene **8a** and a structurally related *p*-xylylene molecule.

Bond	X-ray	DFT calcd[a]	SCF-MO calcd[b]	Thiele's hydrocarbon[c,d]
C1–C3A	1.374(3)	1.379	1.365	1.346
C1–C2	1.438(3)	1.444	1.457	1.449
C2–C3	1.457(3)	1.457	1.462	1.449
C2–C4	1.390(3)	1.396	1.371	1.381
C3–C6	1.470(3)	1.466	1.470	–[e]
C4–C5	1.470(3)	1.463	1.456	1.482
C5–C6	1.412(3)	1.417	1.411	–[e]
benzene (avg)	1.389(3)	1.398	1.402	–[e]

[a] Performed using Gaussian 03 at the B3LYP/6-311+G** level of theory. [b] Ref. [17]. [c] Ref. [15a]. [d] A more descriptive name is 3,6-bis(diphenylmethylene)-1,4-cyclohexadiene. [e] Not applicable.

Single crystals of **8a** suitable for X-ray diffraction were obtained by slow evaporation of a solution in hexanes. The molecular structure (Figure 1) reveals that the fused ring system is essentially planar (deviation rms = 0.013 Å).[14] The bulky TIPS-capped acetylenes are bent away from one another by 4–11° and are also bent out the plane of the 20-carbon-atom core by 3.5–4.0°. Our initial hypothesis regarding bond lengths consisted of two possibilities: 1) the overall antiaromaticity of the molecule would dominate, resulting in alternating long and short bonds throughout the entire ring system, that is, a [20]annulene; or 2) the benzene rings would stay fully delocalized and the *p*-xylylene unit would possess long and short bonds as typical for non-aromatic single and double bonds, that is, a dibenzo[12]annulene. Examination of the C–C bond lengths (Table 1) indicates that indeed there are alternating long (1.438(3) and 1.457(3) Å for C1–C2 and C2–C3, respectively) and short (1.374(3) and 1.390(3) Å for C1–C3A and C2–C4, respectively) bonds in the central *p*-xylylene core but the peripheral benzene bonds are relatively homogeneous (1.392–1.412 Å). Interestingly, this bonding situation closely resembles the X-ray data analyses of Thiele's and Chichibabin's hydrocarbons, two previously reported molecules containing crystallographically determined *p*-xylylene cores.[15]

To shed additional light, NICS(1) calculations for the desilylated analogue of **8a** afforded NICS values for the peripheral, five-membered, and central rings of −7.12, 1.84, and 0.02, respectively. The B3LYP/6-311+G**-optimized geometry of desilylated **8a** (Table 1) using Gaussian 03[16] provided bond lengths of 1.444, 1.457, and 1.379 Å for C1–C2, C2–C3, and C1–C3A, respectively, and 1.393 to 1.418 Å for bond lengths of the peripheral arene rings, values which nearly coincide with the crystallographic data. Lower level semi-empirical calculations by Kataoka and Toyota also confirm these findings.[17] Such good agreement between the experimental and computational data suggests that neither hypothesis is correct. Instead, **8a** should be considered a fully conjugated 20-π-electron hydrocarbon with fused *s-trans* 1,3-diene linkages across both the top and bottom portions of the carbon skeleton. The 1,4-diphenyl-1,3-butadiene bonding picture is also consistent in solution, as the ^{3}J values of the arene protons are within a narrow range of 7.44–7.55 Hz. As initially described by Günther et al.[18] and used extensively by

Mitchell et al.,[19] one can utilize these coupling constants to determine the bond alternance parameter, Q, which equals the ratio of the bond orders of the benzene C7–C8 and C8–C9 bonds (as shown in Figure 1) and thus reveals the nature of the ring current in the fused ring. As such, we obtain a Q value of 1.01, which is indicative of a nonaromatic fused ring, analogous to the NICS results.

The crystal packing of **8a** (Figure 2) loosely resembles the herringbone pattern often found in unsubstituted acenes such as pentacene. The presence of four interdigitated TIPS groups per indenofluorene expands this basic motif, yet the packing is sufficiently tight that no solvent molecules co-crystallize with **8a**. The major contacts in the unit cell are between the TIPS groups and the central IF ring with an average distance of 3.93 Å.

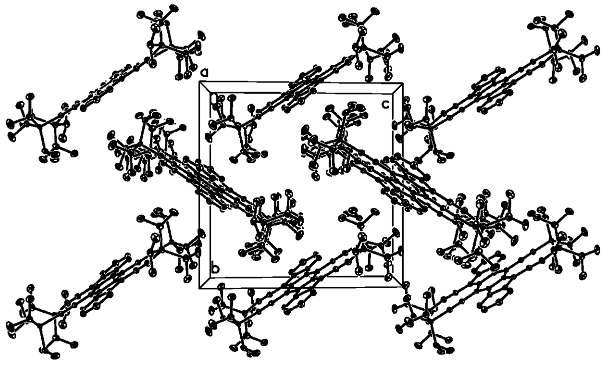

Figure 2. Crystal packing of **8a**.

The optoelectronic spectra of **8a** and **8b** are shown along with pentacene **1** in Figure 3. Similar to **1**, IFs **8a** and **8b** exhibit three low-energy absorptions (λ_{max}: 594 and 614 nm, respectively) but are blue-shifted approximately 50 and 30 nm, respectively. These optical data correspond to estimated HOMO–LUMO gaps of 1.98 and 1.91 eV for **8a** and **8b**, respectively, compared to 1.85 eV for **1**,[20] which agree quite well with the B3LYP/6-311+G**-calculated gap of 1.97 eV for the desilylated analog of **8a**. Unlike **1**, both **8a** and **8b** are non-emissive, which is usually the case with $[4n]$ π-electron systems.

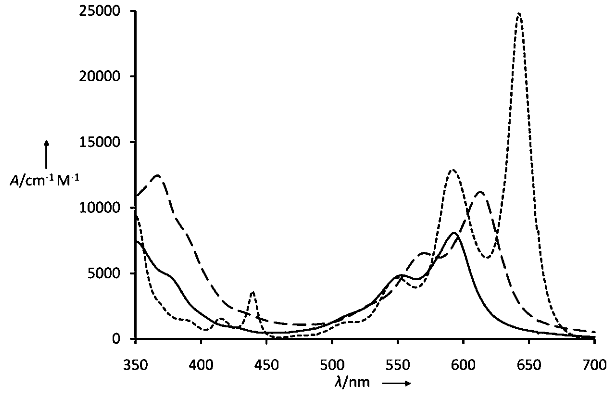

Figure 3. Electronic absorption spectra of **1** (-----), **8a** (——), and **8b** (– – –) in CH_2Cl_2.

The relative stabilities of **8a** and **8b** were also briefly examined. Initial testing by UV/Vis spectroscopy was performed under similar conditions as reported by Miller et al. but no degradation was observed in the time frame used for their pentacene studies (< 12 h).[4c] Instead, samples of **8a** and **8b** were allowed to stand in loosely capped volumetric flasks under air in the light, and periodic ^{1}H NMR measurements were made. While it was found that samples of **8a** and **8b** were stable on the order of a few weeks, the molecules eventually did degrade over the course of 2–3 months.

In summary, we have demonstrated the feasibility of fully conjugated, formally antiaromatic indenofluorenes. Through X-ray crystallography, we have also captured a rare glimpse of the p-xylylene core and confirmed the structure of **8a** by comparison to the other known molecules that contain this moiety. Examination of the optoelectronic properties of the IFs **8a** and **8b** unambiguously confirm that a clear comparison of fully conjugated indenofluorenes to pentacenes can be made with potentially superior stabilities. Future work will consist of exploring more efficient methodologies to generate the conjugated indenofluorene core along with investigating a larger variety of substitution motifs to better improve packing in the solid state as well as to provide a greater opportunity for detailed structure–property relationship studies.

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[14] X-ray data for **8a**: $C_{64}H_{92}Si_4$, $M = 973.74$, $0.26 \times 0.12 \times 0.05$ mm, $T = 173(2)$ K, monoclinic, space group $P2_1/c$, $a = 13.579(2)$ Å, $b = 15.042(2)$ Å, $c = 15.054(2)$ Å, $\beta = 97.502(3)°$, $V = 3048.6(8)$ Å^3, $Z = 2$, $Z' = 0.5$, $\rho_{calcd} = 1.061$ Mg m^{-3}, $\mu = 0.133$ mm^{-1}, $F(000) = 1064$, $2\theta_{max} = 50.00°$, 29004 reflections, 5357 independent reflections [$R_{int} = 0.0554$], $R1 = 0.0453$, $wR2 = 0.1092$ and GOF = 1.103 for 4217 reflections (491 parameters) with $I > 2\sigma(I)$, $R1 = 0.0651$, $wR2 = 0.1273$ and GOF = 1.103 for all 5357 reflections, max/min residual electron density $+0.338/-0.274$ e Å^3. CCDC 787154 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[20] The optical HOMO–LUMO gap of **8a** and **8b** were determined as the intersection of the x axis and a tangent line that passes through the inflection point of their lowest-energy absorption.