Pentacenes

Deutsche Ausgabe: DOI: 10.1002/ange.201508650
Internationale Ausgabe: DOI: 10.1002/anie.201508650

Stabilizing Pentacene By Cyclopentannulation

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Abstract: *A new class of stabilized pentacene derivatives with externally fused five-membered rings are prepared by means of a key palladium-catalyzed cyclopentannulation step. The target compounds are synthesized by chemical manipulation of a partially saturated 6,13-dibromopentacene precursor that can be fully aromatized in a final step through a DDQ-mediated dehydrogenation reaction (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone). The new 1,2,8,9-tetraaryldicyclopenta[fg,qr]pentacene derivatives have narrow energy gaps of circa 1.2 eV and behave as strong electron acceptors with lowest unoccupied molecular orbital energies between −3.81 and −3.90 eV. Photodegradation studies reveal the new compounds are more photostable than 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene).*

Higher acenes are known to readily undergo photoinduced oxidation, dimerization, or polymerization largely owing to a biradical character in the electronic ground state.[1–3] These decomposition pathways are undesirable because acene stability has been identified as a critical design parameter for their incorporation in electronic devices,[4] considering that acene-based devices have been found to fail as a result of decomposition of the active material.[5] To address this problem, useful strategies to stabilize acenes have employed ethynylation,[6–9] thiolation,[10–12] cyanation,[13,14] or bulky substituent incorporation[15–18] to access electronically modulated or sterically blocked structures.[19] Benzannulation, or higher ordered six-membered ring fusions, of the acene core is an alternative strategy to obtain stabilized compounds, yet the resulting electronic properties of these derivatives no longer possess the desirable acene character. For example, upon benzannulation of pentacene **1** to form dibenzo[*fg*,*qr*]pentacene **2**,[20] significant electronic modulation occurs and the molecule no longer behaves as an acene but rather as two electronically separated phenanthrene units (Figure 1). These properties can be easily rationalized by invoking Clar's aromatic sextet rule that says the resonance contributor with the most π sextets (that is, benzene-like moieties) is the most important contributor to the properties of the polycyclic aromatic hydrocarbon (PAH).[21] Although benzannulated **2** contains four isolated π sextets, a pentannulated acene core (for example as in **3**) alleviates this conjugation dilemma owing to the isolation of a double bond in the five-membered ring. From the Clar sextet representation, the electronic structure of **3** should be similar to that of a native pentacene with a single migrating π sextet (Figure 1). Owing to our recent interest in cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs),[22–26] we set out to prepare pentacene derivatives working under the hypothesis that the fusion of five-membered rings would minimize the biradical character at the central carbons leading to stabilized structures. Towards this new class of compounds, we demonstrate herein that cyclopentannulation of a partially unsaturated pentacene precursor followed by an aromatization step with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) leads to the formation of new pentacenes that are more stabilized than the well-known 6,13-bis(triisopropylsilylethynyl)pentacene (**4**; TIPS-pentacene). These molecules behave as strong electron acceptors and possess significantly decreased energy gaps.

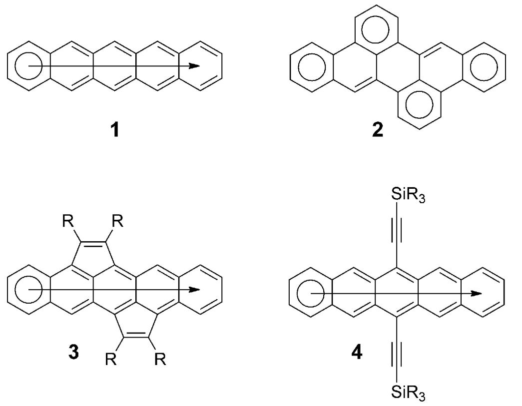

Figure 1. Pentacene structures. According to Clar's sextet rule, **1**, **3**, and **4** have a single migrating π sextet while **2** has four π sextets.

The palladium-catalyzed cyclopentannulation chemistry utilized here is an extension of our recent work[26] that was rooted in the contributions of several other groups.[27–31] For this work, we needed to adapt the pentannulation synthetic method from an anthracene to a pentacene core. This new chemistry required the synthesis of 6,13-dibromopentacene, or a reactive surrogate, in place of the previously utilized 9,10-dibromoanthracene. Owing to the unknown nature of 6,13-dibromopentacene,[32] we turned to a pentacene precursor that could undergo known transformations to access the desired CP-PAH substructure and then could later be transformed into the desired pentacene derivatives. To accomplish

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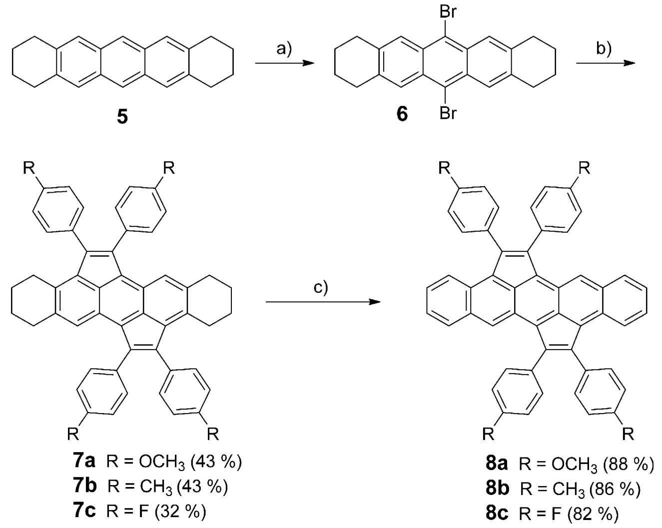
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201508650.

this goal, we synthesized 6,13-dibromo-1,2,3,4,8,9,10,11-octahydropentacene (**6**) from the previously known and partially hydrogenated pentacene **5** (Scheme 1).[33] This stable precursor contains an aromatic core that reacts as a substituted anthracene and therefore can undergo known chemical transformations related to that core.[32] We performed our newly optimized palladium-catalyzed cyclopentannulation between **6** and several diaryl acetylenes utilizing the catalyst system of $[Pd_2(dba)_3]$, $P(o\text{-Tol})_3$, and LiCl with KOAc as a base (Scheme 1; dba = dibenzylideneacetone, *o*-Tol = *ortho*-toluene).[26] Anthracene-based CP-PAHs with electron-rich (**7a**), mildly electron-rich (**7b**), and electron-poor (**7c**) substituents on the aryl rings were obtained in consistent yields of 32–43 %.



Scheme 1. Synthesis of CP-pentacenes: a) Br_2, CCl_4, RT; b) Ar—≡—Ar, $[Pd_2(dba)_3]$, $P(o\text{-Tol})_3$, KOAc, LiCl, DMF, 130 °C; c) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), benzene, 80 °C.

The resulting compounds have photophysical and electrochemical properties similar to previously prepared anthracene CP-PAH derivatives.[26] Each derivative (**7a–c**) formed emerald-green solutions in chloroform and their UV/Vis absorption spectra were almost identical (Figure 2; see also the Supporting Information), each having with a high-energy band ($\lambda_{abs} \approx 260$ nm), a mid-range band ($\lambda_{abs} \approx 416$ nm), and a broad charge-transfer band ($\lambda_{abs} \approx 590$ nm; Table 1). The cyclic voltammograms show that the compounds are irreversibly oxidized but give two reversible or quasi-reversible reductions (Figure 3). Both the onset of oxidation as well as that of the reduction waves vary with respect to the substituents, with the oxidation occurring at less positive potentials with the more electron-rich substituents ($R = OCH_3$) and the reduction waves occurring at less negative potentials with the more electron-poor (R = F) substituent (Table 1).

Conversion to the fully unsaturated 1,2,8,9-tetraaryldicyclopenta[*fg*,*qr*]pentacenes (**8a–c**) was conveniently accomplished by aromatization with four equivalents of DDQ. The effectiveness of this aromatization step to form **8a–c** is fascinating because we were unable to extend the method to access traditional 6,13-diarylpentacenes by means of DDQ aromatization of precursors formed following a Suzuki cross-coupling to **6**. The synthetic method described here is an alternative method to a recent report accessing internally fused, cyclopenta-fused pentacenes using a Scholl cyclodehydrogenation.[34] The method reported herein is more broadly applicable as a result of the inherent stability of the anthracene precursors and the broadened scope of substituents to include electron-withdrawing groups that were known to inhibit the Scholl reaction.

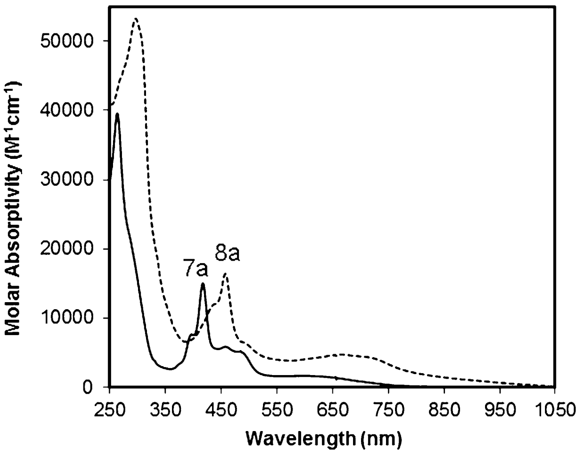


Figure 2. Representative UV/Vis absorption spectra of **7a** and **8a** in chloroform at room temperature. Remaining spectra are given in the Supporting Information.

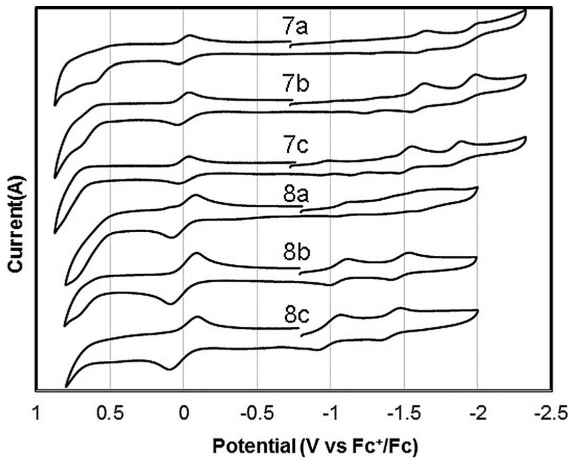


Figure 3. Cyclic voltammograms of 0.2 mм **7a–c** and **8a–c** (0.2 mм in THF) with 0.1 м tetrabutylammonium hexafluorophosphate as the supporting electrode, a glassy carbon working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 50 mV s^{-1}. Ferrocene (Fc) was added as the internal standard and referenced to 0 V.

The conversion from the anthracene (**7a–c**) into pentacene cores (**8a–c**) resulted in significant modulation of the optoelectronic properties, leading to significant shifts in the absorption bands and the occurrence of the reduction waves at less negative potentials. For example, the transition from **7a**

Table 1: Summary of the optoelectronic properties of **7a–c** and **8a–c**.[a–f]

Cmpd	$E_{ox/onset}$[a] [V]	$E_{red/onset}$[a] [V]	HOMO[b] [eV]	LUMO[b] [eV]	E-chem gap[c] [eV]	λ_{abs}[d] [nm]	Energy gap[e] [eV]	$\tau_{half\text{-}life}$[f] [min]
7a	0.48	−1.52	−5.28 (−5.31)	−3.28 (−3.07)	2.00 (2.24)	262, 417, 592	1.59	–
7b	0.56	−1.50	−5.36 (−5.41)	−3.30 (−3.10)	2.06 (2.31)	261, 415, 587	1.57	–
7c	0.63	−1.46	−5.43 (−5.58)	−3.34 (−3.24)	2.09 (2.34)	263, 416, 597	1.57	–
8a	0.51	−0.99	−5.31 (−5.33)	−3.81 (−3.66)	1.50 (1.67)	297, 458, 706	1.22	1614 ± 172
8b	0.55	−0.98	−5.35 (−5.41)	−3.82 (−3.69)	1.53 (1.72)	308, 455, 706	1.20	1063 ± 70
8c	0.65	−0.91	−5.45 (−5.54)	−3.90 (−3.80)	1.57 (1.74)	309, 456, 706	1.21	1106 ± 79

[a] Measurements taken at sample concentration of 0.2 mM and potentials measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Figure 3). $E_{ox/onset}$ is the onset of oxidation potential, $E_{red/onset}$ is the onset of reduction potential. [b] HOMO and LUMO values calculated on the basis of the oxidation of the ferrocene reference in vacuum (4.8 eV). B3LYP/6-311g(d,p) predicted values are in parenthesis. [c] Difference between the electrochemically calculated HOMO and LUMO values. [d] Wavelengths at which maximum absorption bands are detected. [e] Energy gap calculated by $E = hc/\lambda$, where h is Planck's constant and c is the speed of light. The $\lambda_{abs,onset}$ value is taken from the onset of absorption from the lowest energy band. [f] Average and standard deviation from three runs. TIPS-Pentacene (**4**) = 317 ± 18 min (see Figure 6).

to **8a** resulted in bathochromically shifted absorption bands with the most dramatic being in the charge-transfer band onset that shifted from about $\lambda = 750$ nm (at the lower energy side of the onset) to over 1000 nm (Figure 2). Each of the pentacene derivatives had nearly identical UV/Vis absorption spectra with solution-based energy gaps of about 1.2 eV and showed variation only in the molar extinction coefficients (see the Supporting Information). All derivatives studied here were nonfluorescent, a property common to many CP-PAH compounds (see the Supporting Information).[35–37] The cyclic voltammograms (Figure 3) demonstrate how **8a–c** are significantly easier to reduce (by circa 0.5 eV) compared to **7a–c** giving lowest unoccupied molecular orbital (LUMO) energies of −3.81 to −3.90 eV (Table 1). In contrast, the highest occupied molecular orbital (HOMO) energies were very similar between the anthracene and pentacene derivatives. This result was confirmed by DFT calculations that show HOMO contours of **7a** and **8a** similar in energy with the majority of the electron density migrating between the five-membered rings in the core and two aryl substituents that are diagonal to each other (Figure 4). Conversely, the LUMO contour of **8a** is significantly different in relation to **7a** as it has electron density spread onto two additional six-membered rings. The HOMO and LUMO distributions of **8a–c** are therefore significantly different than traditional pentacene derivatives which leads to the absence of the known "fingerprint" vibronic fine structure in the UV/Vis absorption spectra.

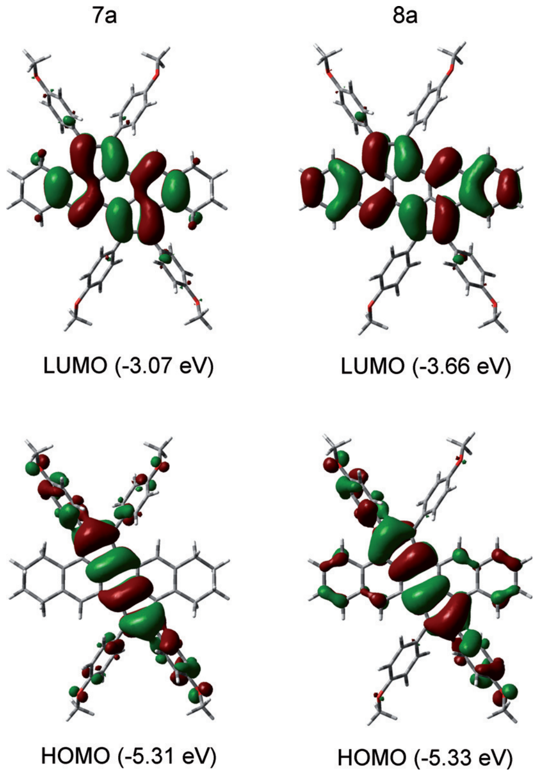


Figure 4. B3LYP/6-311 g(d,p) DFT-calculated HOMO and LUMO contours of **7a** and **8a**.

Single crystals of **8a** suitable for X-ray diffraction were grown by slow evaporation of a chloroform solution.[39] The molecular structure (Figure 5) reveals the central carbon framework is very similar to pentacene with a completely planar arrangement of fused benzene rings. The five-membered rings are coplanar with the pentacene core; however, the four appended aryl groups distort from planarity owing to their steric congestion in agreement with the DFT-calculated structures. The specific crystallographically determined and DFT-calculated bond lengths of **8a** were summarized and compared to pentacene (see the Supporting Information). Overall, the bond lengths show similar trends to pentacene with alternating short and long bond-length character near the terminal rings. Notable differences include a shorter C6–C8 bond, which is consistent with an indacene fragment,[38] and a more significant absolute value of alternation between the shorter and longer bonds on the outer ring. Nevertheless, this crystal structure demonstrates that the general bond orders are consistent between the cyclopenta-fused pentacene and traditional pentacene derivatives. With regards to the crystal packing, the perpendicular arrangement of the fused benzene rings hinders π stacking with the molecules ordering into a pseudo-herringbone-like arrangement.

The stabilities of **8a–c** were tested in comparison to the known TIPS-pentacene derivative **4** by photodegradation in an oxygenated THF solution under ambient light irradiation (Figure 6).[5] The resulting decomposition half-lives (Table 1) were obtained by monitoring the disappearance of the

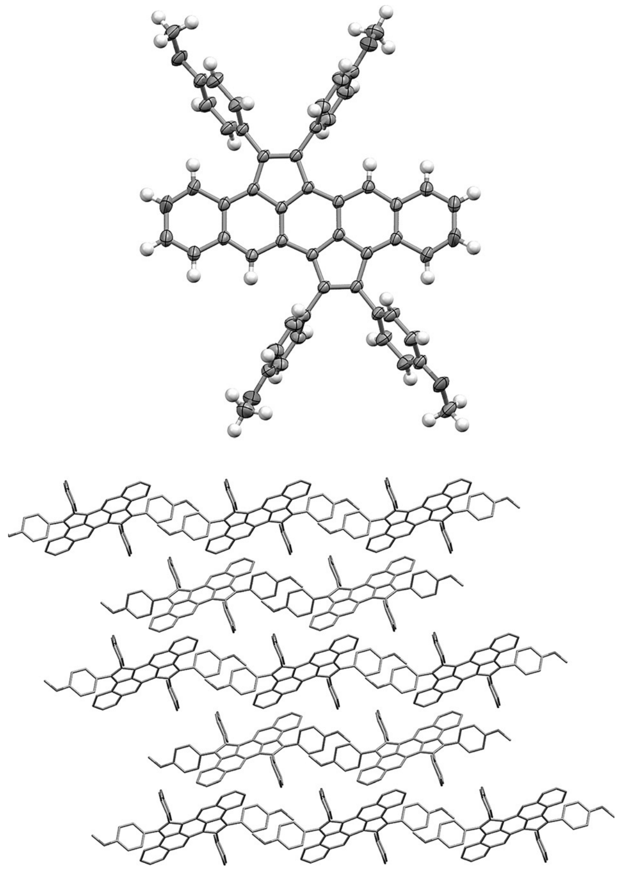


Figure 5. Crystal structure (top) and packing (bottom) of **8a**.[39]

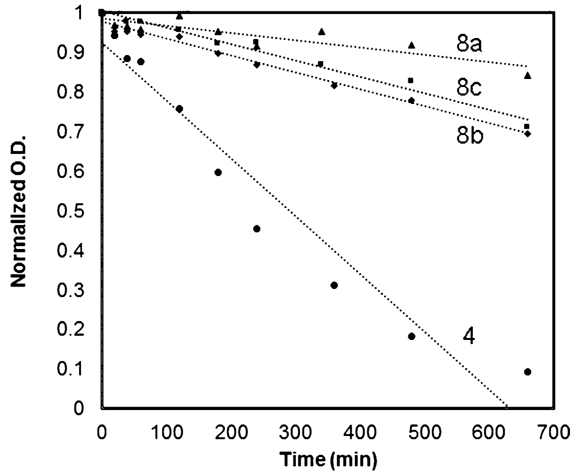


Figure 6. A single photodegradation run of TIPS-pentacene **4** and CP-pentacenes **8a–c** at 15 μм. Experiment ran in triplicate and half-life average values given in Table 1. O.D. = optical density.

absorption band at $\lambda = 455$ nm over time (Supporting Information). Compounds **8a–c** were found to be considerably more stable than **4** with half-lives on the order of 1063–1614 minutes, whereas **4** had a half-life of 317 minutes. In addition, **8a–c** showed no decomposition in the solid state when kept for over a year in the absence of light. These results clearly demonstrate the stabilizing effect of the cyclopenta fusion on the acene backbone and are consistent with the previous report of internally fused CP-PAH pentacenes.[34] The additional stability could be attributed to electronic factors or added steric congestion at the central rings which is known to minimize the rate of decomposition of pentacenes.[15–18]

In conclusion, we have presented a unique synthetic pathway that utilizes easily accessible and stable intermediates to access externally fused, cyclopenta-fused pentacene derivatives. The key to the described chemistry is chemical manipulation of a hydrogenated pentacene precursor followed by aromatization to the final acene by reaction with DDQ. The described cyclopentannulation strategy offers opportunities to access even higher ordered acenes, a topic we are currently pursuing, and contributes to the growing number of planar CP-PAH-based materials.[37]

Acknowledgements

This work was supported by a National Science Foundation CAREER grant (CHE-1352431).

Keywords: acenes · conjugation · organic electronics · palladium · polycyclic aromatic hydrocarbons

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 15762–15766
Angew. Chem. **2015**, *127*, 15988–15992

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[39] CCDC 1424587 (**8a**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Received: September 15, 2015