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Dithieno-Fused Polycyclic Aromatic Hydrocarbon with a Pyracylene Moiety: Strong Antiaromatic Contribution to the Electronic Structure

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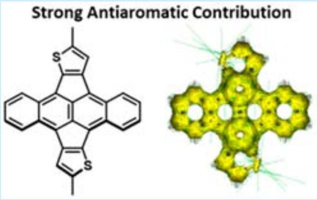
Supporting Information

ABSTRACT: A synthetic route to dithieno-fused CP-PAHs with a pyracylene segment is reported. A combination of experimental and theoretical studies revealed a strong contribution of antiaromatic character to the electronic structure of this dithieno-fused CP-PAH. Anisotropy of current-induced density (ACID) calculations indicated a significantly increased paramagnetic ring current on the two pentagonal rings, which is more prominent than that of the dibenzo-fused analogue. Furthermore, enhanced electron affinity and a consequently decreased HOMO−LUMO gap were observed for this dithieno-fused CP-PAH.



Polycyclic aromatic hydrocarbons (PAHs) with fully unsaturated pentagonal ring(s), the so-called cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs), have attracted substantial interest in account of their unusual properties, which include high electron affinity[1] and reactivity,[2] as well as due to their applications in materials science.[3] In particular, cyclopentadiene- or indene-fused structures have been generated on the periphery of a variety of π-skeletons, which include not only PAHs such as acenes,[4] pyrene,[5] and corannulene[6] but also porphyrins.[7] Such modifications induce significant perturbations of the electronic structure of the π-system and consequently the aromatic character. However, the change of the aromatic character of CP-PAHs has not been examined[8] as thoroughly as that of PAHs. Recently, Matsuo and co-workers have reported that the introduction of one thieno-fused moiety via a pentagonal ring on the periphery of a porphyrin derivative enhances the antiaromatic contribution to the electronic structure of the resulting π-extended porphyrin.[7a]

Among the reported CP-PAHs, pyracylene exhibits a considerable antiaromatic contribution to its electronic structure as well as a high electron affinity based on its 12π-electron framework (Figure 1a).[9] We have previously reported that tetrabenzo-fused pyracylene (TBP, 1) can be obtained from an efficient 2-fold Scholl cyclization of 5,11-diphenyltetracene (2) (Figure 1b).[10] TBP (1) exhibited an electron-deficient character that can be attributed to the contribution from the pyracylene segment. During our study on the electronic properties and aromaticity of CP-PAHs, we conducted a 2-fold Scholl cyclization of 5,11-dithienyltetracene (3) (Figure 1c). Although there are, to the best of our knowledge, no reports on a Scholl cyclization that realizes a thieno fusion via a fully unsaturated pentagonal ring, the symmetric Scholl cyclizations of 3 proceeded to afford dithieno-fused CP-PAH (i.e., 5), which contains a pyracylene segment. Herein, we report the synthesis and structural characterization of 5 as well as experimental and theoretical studies on its aromaticity. The obtained data indicate a distinct antiaromatic contribution to its electronic structure and an electron affinity that is higher than that of 1.

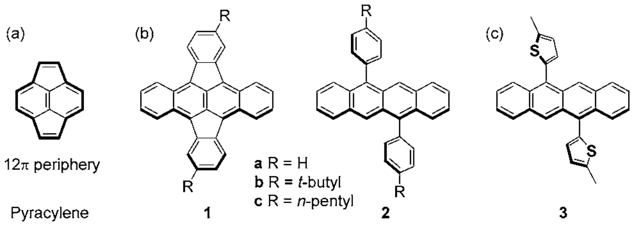


Figure 1. Chemical structures of (a) pyracylene, (b) previously reported CP-PAHs **1**,[10] which were obtained from a 2-fold Scholl cyclization of precursor **2**, and (c) 5,11-dithienyltetracene (**3**).

In this work, we used 5,11-dithienyltetracene (**3**) as a precursor because the introduction of a methyl group in each thienyl group effectively suppressed polymerization. Following our previous report for the synthesis of **1**,[10] we initially attempted the Scholl reaction of **3** with $FeCl_3$ as an oxidant, but these reactions only afforded insoluble black solids. When the dichlorodicyano-*p*-benzoquinone (DDQ)/TfOH system was used, symmetrically cyclized **5** could be isolated in 22% yield. Usin a *p*-chloranil/TfOH system, i.e., milder oxidation conditions, furnished **5** in improved yield (57%) (Scheme 1). Upon reducing the amount of oxidant, monocyclized **4** was obtained in 53% yield. It is noteworthy here that fusion of a thiophene ring via a fully unsaturated pentagonal ring by the Scholl reaction is unprecedented.[11] For that purpose, Pd-catalyzed cyclizations have been used so far.[2c,7a]

The molecular structures of **3** and **5** were unambiguously determined by single-crystal X-ray diffraction analyses (Figure 2a). The obtained data show that the 2-fold cyclization induces significant bond length alterations. In particular, the interior bond *a* in **5** [1.362(5) Å] is substantially shorter than those of **3**

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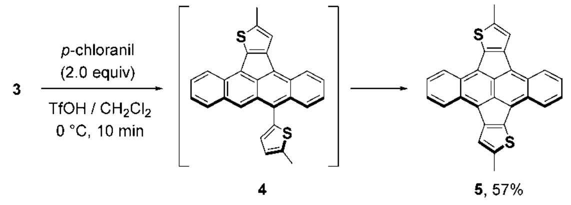
Scheme 1. Two-fold Scholl Cyclization of 5,11-Dithienyltetracene 3



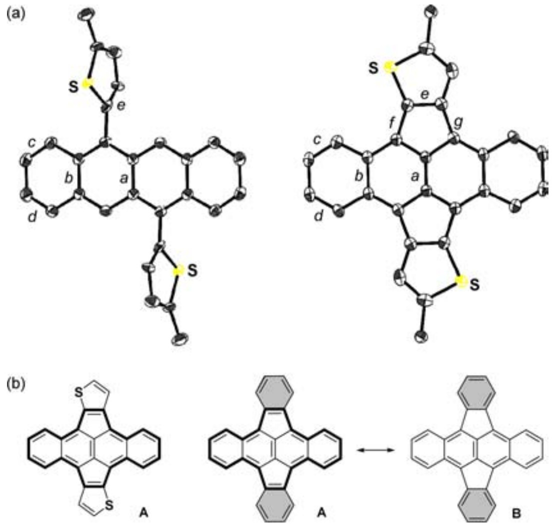


Figure 2. X-ray crystal structures of (a) **3** and **5**. (b) Selected resonance structures for the π-framework of **5** and **1**. Selected bond lengths (Å) for **3**: *a* 1.445(2); *b* 1.4399(18); *c* 1.3592(19); *d* 1.3549(19); *e* 1.410(7). Selected bond lengths (Å) for **5**: *a* 1.362(5); *b* 1.477(4); *c* 1.363(4); *d* 1.360(3); *e* 1.398(3); *f* 1.473(3); *g* 1.482(4).

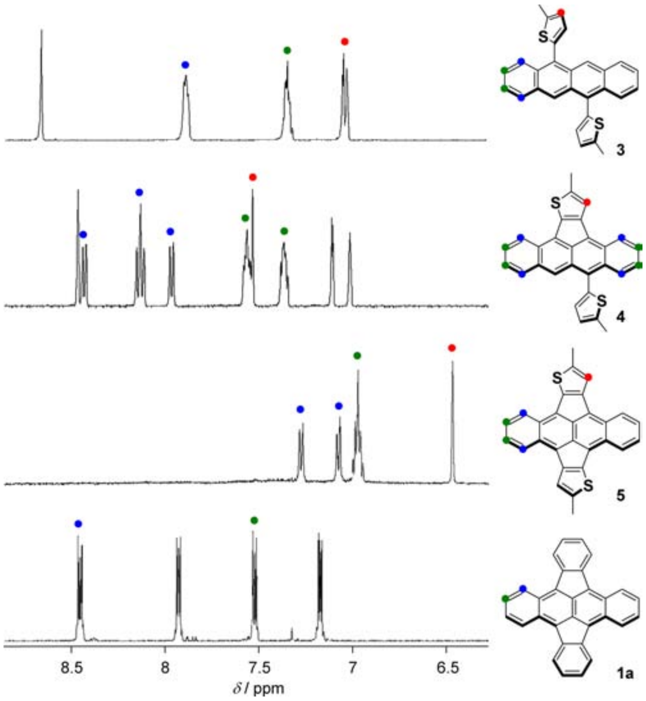


Figure 3. ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of **3**−**5** and **1a**.[10] Red, blue, and green dots indicate the assignment of the corresponding proton signals.

[1.445(2) Å] and **1b** [1.381(3) Å][10] and comparable to that of pyracylene [1.360 (3) Å)],[12] which indicates a localized double-bond character for bond *a* in **5**. Moreover, bond *b* in **5** [1.477(4) Å] is elongated with respect to that in **3** [1.4399(18) Å], and comparable to that in **1b** [1.474(2) Å].[10] It should be noted that bond *e* in **5** [1.398(3) Å] is considerably shorter than that in **1b** [1.438(2) Å],[10] which reflects the 2,3-thieno-fused structure. These data indicate that in **5** contributions from resonance structure **A** with a 20π-antiaromatic periphery should predominate (Figure 2b). This stands in sharp contrast to the structural features of **1** in which contributions from **B** predominate.[10] Consequently, **5** should contain a higher degree of antiaromatic contributions relative to **1**.

This notion is also consistent with the ^{1}H NMR spectra of **3**−**5** and **1a**,[10] measured in CD_2Cl_2 (Figure 3). The observed signals were assigned based on DFT calculations[13] at the GIAO-B3LYP/6-311G**//B3LYP/6-31G* level of theory (Figure S7). A comparison of the data for **3**−**5** revealed that signals associated with the aromatic protons shift upfield after the second cyclization, while such a trend was not observed after the first cyclization. For example, the singlet signal for the fused thiophene rings in **5**, marked with a red dot in Figure 3, is upfield shifted ($\Delta\delta$ = 1.1 ppm) compared to that in **4**. The aromatic signals of **5** are shifted upfield even compared to those of **1a**, which reflects the substantially decreased aromaticity of **5**. In particular, protons of **5** that are located in the close vicinity of the pentagonal rings (marked with blue dots) exhibit more pronounced upfield shifts ($\Delta\delta$ = 1.4 and 1.2 ppm) than those marked with green dots in **5** ($\Delta\delta$ = 0.5 ppm) with respect to those in **1a**. This result implies that, compared to **1a**, the dithieno-fused structure in **5** induces a strong paramagnetic ring current in the two pentagonal rings.

In order to obtain a better insight into their aromatic character, nucleus-independent chemical shifts (NICS)[14] were calculated for model structures **3′**−**5′**, in which the methyl groups were replaced with hydrogen atoms (Figure 4a). Even though the changes in the NICS(0) values after the first cyclization are small, both the negative values for the hexagonal rings and the positive value for the two pentagonal rings become more positive in **5′** with respect to those in **4′** after the second cyclization. The increase of the positive value at the two pentagonal rings in **5′** (+23.8) is particularly interesting, as it is indicative of a strong antiaromatic contribution to the

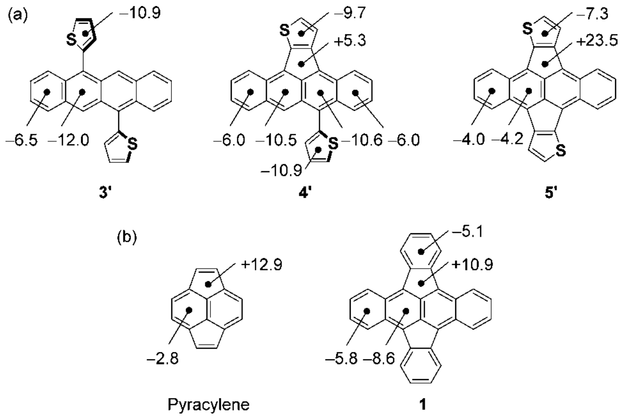


Figure 4. NICS(0) values for (a) model compounds **3′**−**5′** and (b) pyracylene as well as **1a** (values calculated at the HF/6-311+G**//B3LYP/6-31G* level of theory).

electronic structure. It should also be noted that the value for the pentagonal rings in **5′** is much higher than the corresponding value in **1a** (+10.9)[10] and pyracylene (+12.9)[10] (Figure 4b).

Subsequently, we calculated the anisotropy of current-induced density (ACID)[15] (Figure 5). ACID plots illustrate diamagnetic and paramagnetic ring currents as clockwise and counterclockwise ring currents, respectively. When the ACID plots for **4′** and **5′** with one and two pentagonal rings, respectively, are compared, counterclockwise paramagnetic ring currents are evident on the two pentagonal rings in **5′**, while such a current is virtually absent in the pentagonal ring in **4′** (Figure 5a). Similar counterclockwise ring currents were obtained for the two pentagonal rings in pyracylene and **1a** (Figure 5b), although they are not as pronounced as those in **5′**. The results for **5′** suggest a strong antiaromatic contribution to the electronic structure and thus corroborate the experimental and theoretical results, i.e., the upfield shifts of the ^{1}H NMR signals and positively increased NICS(0) values in the two pentagonal rings for **5** relative to those of **1a**.[10]

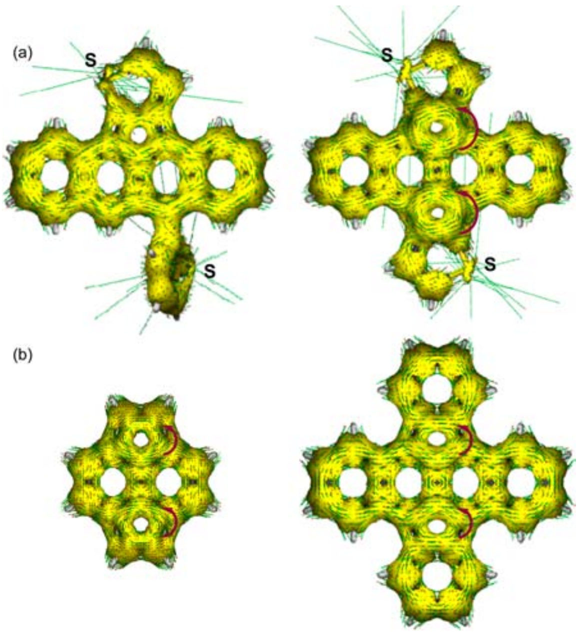


Figure 5. ACID plots for (a) **4′** and **5′** and (b) pyracylene and **1a** (HF/6-311+G**//B3LYP/6-31G*).

In order to elucidate the electronic properties, cyclic voltammograms and absorption spectra were measured for **5**, and the data are summarized in Table 1 together with those for **1c** for comparison. In the oxidation region, **5** exhibited an irreversible wave (E_{onset} = −0.02 V vs Fc/Fc$^+$), which is negatively shifted (ΔE_{onset} = 0.44 V) with respect to that of **1c** (E_{onset} = +0.42 V).[10] This difference was largely ascribed to the dithieno-fused structure. The shape of the oxidation wave of **5** was broad but reproducible for several cycles in the range of +0.5 to −1.5 V (Figure S6), which is similar to the behavior of **1**[10] and thus indicative of aggregation. In the reduction region, **5** exhibited two reversible reduction waves ($E_{1/2}$ = −1.21 and −1.68 V). The first reduction potential of **5** is shifted to more positive value (ΔE = 0.09 V) compared to that of **1c** ($E_{1/2}$ = −1.30 V), indicating that the electron affinity of **5** is higher than that of **1c.** The strong antiaromatic contribution in **5** can be attributed to the change in electron affinity, which overrules the effect of two electron-rich thiophene rings. The absorption spectrum of **5** showed the longest wavelength absorption at $\lambda_{\max}$ = 608 nm (log ε = 4.01), which is similar to that of **1c** ($\lambda_{\max}$ = 613 nm, log ε = 4.45), even though **5** should possess a narrower HOMO−LUMO gap than **1c**. TD-DFT calculations on **1c** and **5** at the CAM-B3LYP/6-31G*//B3LYP/6-31G* level of theory suggested that the transition with a predominant contribution from the HOMO → LUMO is forbidden in **5**, while it is allowed in **1c**. Thus, the observed absorption band for **5** should be assigned to a π−π^* transition with a major contribution from the HOMO−1 → LUMO, which is consistent with the similar $\lambda_{\max}$ values observed for **1c** and **5** (Figure S9 and Tables S1 and S2).

Table 1. Electrochemical and Optical Data for 1c and 5

	oxidation potential[a]	reduction potential[a]		absorption[b]	
compd	E_{onset} (V)	$E_{1/2}^{1}$ (V)	$E_{1/2}^{2}$ (V)	$\lambda_{\max}$ (nm)	log ε
1c	+0.42	−1.30	−1.76	613	4.45
5	−0.02	−1.21	−1.68	608	4.01

[a] In CH_2Cl_2. Supporting electrolyte: 0.1 M [$(n\text{-Bu})_4N$][PF_6]. Scan rate: 100 mV s^{-1}. Internal standard: Fc/Fc$^+$. [b] In toluene.

In summary, we have synthesized a dithieno-fused CP-PAH (**5**) that contains a pyracylene moiety via the symmetric 2-fold Scholl cyclization of 5,11-dithienyltetracene (**3**). A single-crystal X-ray diffraction analysis of **5** revealed distinct structural similarity to pyracylene on account of the introduction of two thieno-fused structures. On the basis of the experimental and theoretical results, **5** exhibits a strong contribution of antiaromatic character to its electronic structure. ACID calculations for **5** indicate substantially increased paramagnetic ring currents on the two pentagonal rings, which are more prominent than those in tetrabenzo-fused pyracylene (**1**). Thiophene-fused **5** exhibited an enhanced electron affinity and thus a decreased HOMO−LUMO gap compared to **1**. Further studies on thiophene-fused CP-PAHs containing pyracylene moieties for applications in low-band gap materials are currently in progress in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03819.

Experimental and computational details (PDF)
Crystallographic data for **3** (CIF)
Crystallographic data for **5** (CIF)

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Notes

The authors declare no competing financial interest.

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