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Synthesis and Properties of Symmetric and Unsymmetric Dibenzothienopyrroles

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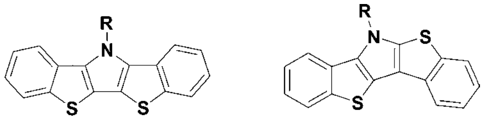
ABSTRACT



R = *n*-butyl, 4-hexylphenyl

Symmetrical and unsymmetrical heteroacenes containing thiophene and pyrrole rings were synthesized. The unsymmetrical heteroacene was synthesized in two steps involving an unexpected palladium catalyzed amination of alkyl or aryl amines with benzo[b]thiophene followed by a copper catalyzed coupling. The symmetrical heteroacene was obtained by a palladium catalyzed amination reaction and also by a copper catalyzed amidation reaction. The crystal structure, photophysical and electrochemical properties of symmetrical and unsymmetrical heteroacenes are described.

Key advantages of using organic materials for electronic applications are their easy accessibility in pure form, tunability of properties and easy fabrication.[1] Acenes such as pentacene[2] are common benchmarks in the field of organic electronics with a high mobility of $\sim$3 cm^2 V^{-1} s^{-1}. But pentacene and other higher acenes suffer from low environmental stability and poor solubility in common organic solvents which limits their practical applications.[3] Heteroacenes are π-conjugated ladder molecules, with heteroatoms (e.g., N, S, O, etc.) incorporated into the structures.[4] Some heteroacenes such as thieno[n]acenes,[5] pyrrole based indolocarbazole[6] and thiophene-benzene annulated acene[7] have been successfully tested for application as organic field effect transistors (OFET). Most of the heteroacenes reported in the literature are thiophene based symmetrical systems.[8] Unsymmetrical heteroacenes provide an inherent advantage of having a high dipole moment which is expected to provide dense packing and higher transport properties.[9] Synthetic strategies for a highly extended π system possessing more

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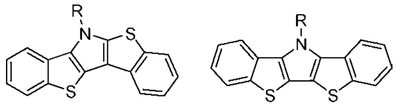
than four aromatic rings are limited.[10] Moreover, synthesis of unsymmetrical heteroacenes is challenging owing to the requirement of selective reaction conditions or a long synthetic route. Heteroacenes containing more than two different heteroatoms have also been reported[11] though only a few unsymmetrical heteroacenes are known.[9,12]

In this regard unsymmetrical heteroacenes **1**, and symmetrical heteroacenes **2** were synthesized (Figure 1).[13] Their properties, along with their molecular organization in the crystal lattice are presented in this study. Palladium catalyzed amination of 3-bromothiophene **3** with alkyl or aryl amine resulted in *N*-(alkyl/aryl)-*N*-(3′-thienyl)-3-aminothiophene **4**.[14] Under identical conditions, 3-bromobenzo[b]thiophene **5** failed to give *N*-(alkyl/aryl)-*N*-(3′-benzo[b]thienyl)-3-aminobenzo[b]thiophene **6** but yielded *N*-(alkyl/aryl)-*N*-(2′-benzo[b]thienyl)-3-aminobenzo[b]thiophene **7** (Scheme 1).

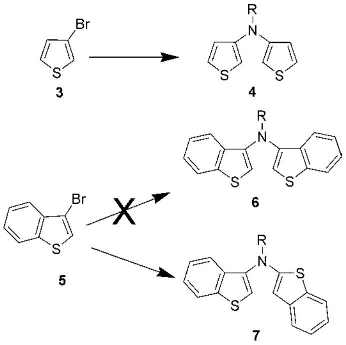


1 **2**

R = (**a**) *n*-butyl, (**b**) 4-hexylphenyl

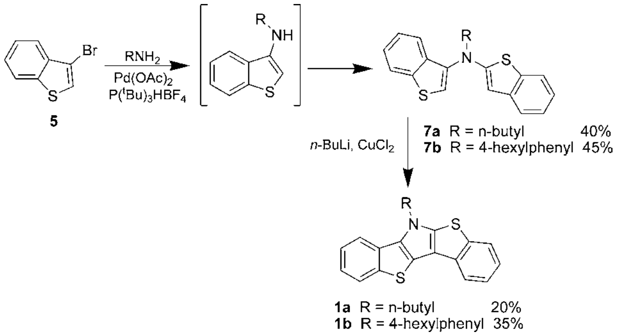
Figure 1. Structures of symmetric and unsymmetric heteroacenes.

Scheme 1. Comparison of Reactivity of 3-Bromothiophene and 3-Bromobenzo[b]thiophene under Palladium Catalyzed Amination Condition



This unexpected reactivity formed the basis for the synthesis of unsymmetrical heteroacenes. When 3-bromobenzo[b]thiophene, was treated with half an equivalent of alkyl or aryl amine, **7a** or **7b** was obtained in 40−45% yield along with 3,3′-bibenzo[b]thiophene (20−30%) and 3-aminobenzo[b]thiophene (10−15%) (Scheme 2). A stepwise procedure also resulted in the same rearranged product **7**, possibly due to the rearrangement of N-functionalized 3-aminobenzo[b]thiophene under the coupling conditions (in the catalytic cycle). No such reaction has previously been reported for amination reactions in the literature. The rearrangement of a similar system, 3-bromo-2-nitrobenzo[b]thiophene is known for aromatic nucleophilic substitution with amines.[15] The 3,3′-dibenzo[b]thiophene was obtained from the oxidative coupling of **5**.[14] Reactions involving aryl amine resulted in higher yields due to the absence of a competing β-elimination pathway.[14a]

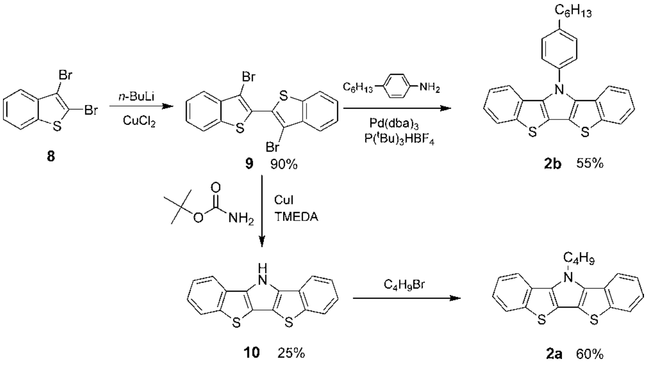
Scheme 2. Synthesis of **1a** and **1b**



Since the $Pd(OAc)_2/P(^tBu)_3$ catalyst system was successful in the amination of 3-bromothiophene, initially the same catalyst was used for the amination of 3-bromobenzo[b]thiophene.[14] Other catalysts such as $Pd_2(dba)_3/\pm$ BINAP, $Pd_2(dba)_3/P(^tBu)_3$, $Pd(OAc)_2/\pm$ BINAP, $Pd(OAc)_2/PCy_3$ were also employed and only product **7** was obtained, but in lower yield. Toluene and *o*-xylene were employed as solvents for the amination reaction and both solvents yielded the same amination products without significant difference in yield. The target compounds **1a** and **1b** were synthesized via cyclization of **7**, using butyl lithium and anhydrous cupric chloride.

As the palladium catalyzed amination reaction resulted in rearranged product, symmetrical heteroacenes were prepared by a different synthetic approach. Symmetrical heteroacenes **2a** and **2b** were synthesized from 2,3-dibromobenzo[b]thiophene **8**. The synthetic route leading to these compounds is represented in Scheme 3. Compound **9**[16] was synthesized from 2,3-dibromobenzo[b]thiophene by treatment with BuLi followed by addition of anhydrous $CuCl_2$.

Scheme 3. Synthesis of **2a** and **2b**



Herein, pyrrole fusion was achieved by employing a recently reported amidation procedure.[17] Cyclization proceeded with concomitant hydrolysis and gave **10** in 25% yield. Heteroacene **10** was then alkylated with butyl bromide to yield **2a**. Compound **2b** was synthesized by palladium catalyzed double N-arylation of 4-hexylaniline with 3,3′-dibromo-[2,2′]bibenzo[b]thiophene **9**.[18] It is notable that our entire synthetic route leading to five ring fused systems involves only two steps. The synthesized hetereoacenes were characterized by NMR spectroscopy (^{1}H and ^{13}C), elemental analysis and X-ray crystallography. These compounds are soluble in common organic solvents such as hexane, chloroform, toluene, ethyl acetate and methanol.

Single crystals of compounds **1a**, **1b** and **2b** suitable for single crystal X-ray diffraction studies were obtained by slow evaporation from a chloroform solution. The crystal packing of symmetric and asymmetric heteroacene are compared. Structural analysis indicated that these heteroacenes are planar and their molecular packing in the crystal lattice is shown in Figure 2. The bond length of N−C(Ph) in unsymmetrical compound **1b** is similar (1.43 Å) to symmetrical compound **2b** (1.44 Å). The pendant phenyl group in **1b** and **2b** are twisted by an angle of 46.7° and 81.8°, with respect to the acene plane. This may be due to unsymmetrical electron cloud distribution in **1b** or steric interactions between the ortho hydrogen atoms of the terminal benzene rings in **2b.** Heteroacene **1a** packs in an edge-to-face manner, leading to a sandwiched herringbone arrangement with a distance of 3.54 Å between sandwiched molecules. In the case of **1b,** the molecules form π-stacked dimers which interact with the dimers of adjacent columns by S···H (2.87 Å) interactions. The sulfur atom *anti* to the pyrrole nitrogen is involved in this interaction. The molecular packing, which is a critical parameter to consider for applications,[19] is influenced by the substituents on the nitrogen atom of the pyrrole ring. In the case of symmetrical molecule **2b**, a molecular dimer is formed by short S···S contacts (3.3 and 3.6 Å). Such dimers are well separated by a pendant phenyl group and the alkyl chain attached to it. In short, packing in the symmetrical acene (**2**) is mainly effected by S···S contact whereas in the case of an unsymmetrical acene (**1a**,**b**) packing is dominated by S···H interaction.

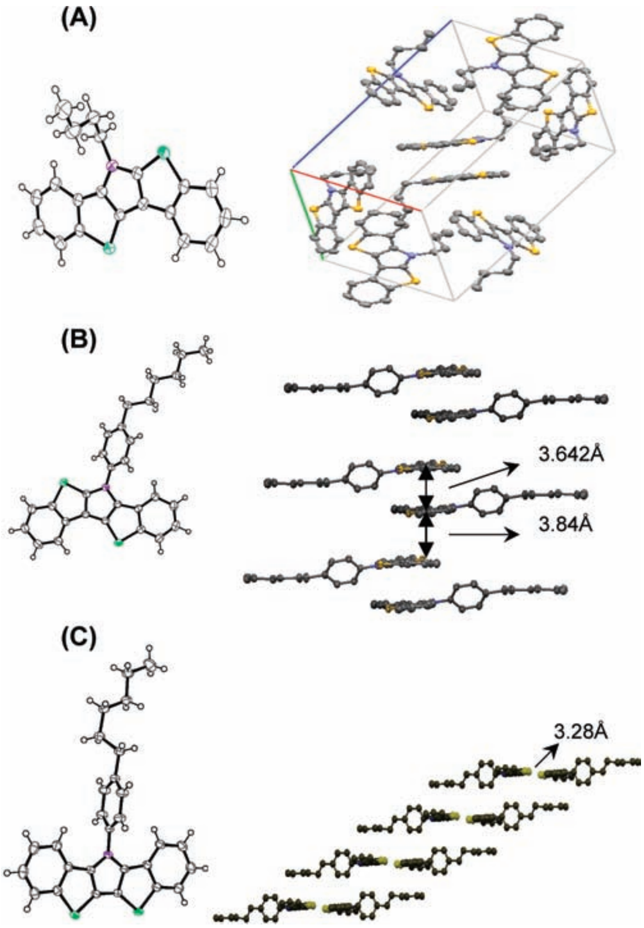


Figure 2. ORTEP drawings and packing of (A) **1a**, (B) **1b** and (C) **2b**.

The UV−vis spectra of **1** and **2** in $CHCl_3$ are shown in Figure 3. All unsymmetrical compounds showed similar absorption properties with λ_{max} at 266 and 323 nm and an absorption onset at 343 nm. The symmetrical compounds showed absorption peaks at 263 and 326 nm with an absorption onset at 360 nm. The absorption maxima of symmetrical heteroacenes are red-shifted compared to those of unsymmetrical heteroacenes indicating a better conjugation in **2**. The bandgap estimated from absorption onset was found to be 3.62 and 3.44 eV for **1** and **2** respectively. The relatively lower band gap of **2** compared to **1** also suggests a better delocalization of π electrons in **2**.

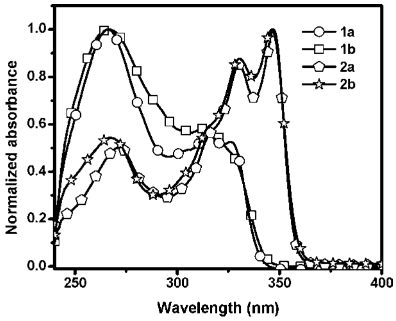


Figure 3. UV−vis spectra of heteroacenes **1** and **2**.

Electrochemical properties of the compounds **1** and **2** were investigated using cyclic voltammetry with Ag/AgCl as the reference electrode. Electrochemical data and energy levels are summarized in Table 1. All heteroacenes exhibit similar electrochemical behaviors with reversible oxidation waves. Compound **1a** showed an oxidation peak maximum at 1.19 V with an onset potential around 0.87 V, while **1b** showed an oxidation peak at 1.17 V with an oxidation onset of 0.94 V. The oxidation peaks of **2a** and **2b** were found at 1.14 and 1.25 V. HOMO energy level of **1a** and **1b** calculated from the oxidation onset potential using the empirical formula

Table 1. Photophysical and Electrochemical Data of Compounds **1** and **2**

compound	λ_{abs}/nm (in $CHCl_3$)	E_{ox} (V)	$E_{ox}{}^{onset}$ (V)	band gap[a] (eV)	E_{HOMO} (eV)	E_{LUMO}[b] (eV)
1a	266, 323	1.19	0.87	3.62	−5.25	−1.63
1b	266, 323	1.17	0.94	3.62	−5.32	−1.7
2a	263, 326, 346	1.14	1.01	3.44	−5.39	−1.95
2b	263, 326, 346	1.25	1.13	3.44	−5.51	−2.07

[a] Calculated from onset wavelength in absorption spectra. [b] Derived from bandgap and the HOMO.

$E_{HOMO} = -(E_{ox}{}^{onset} + 4.38)$ eV[20] are comparable (−5.25 and −5.32 eV). As the reduction peaks are out of our scan range, the LUMO energy levels are calculated from the HOMO energy level and the optical band gap. Unlike unsymmetrical compound **1b**, symmetrical compound **2b** is influenced considerably by an aryl substituent, which leads to a noticeable difference in oxidation potential and oxidation onset.

In summary, we report a two-step synthesis and characterization of symmetrical and unsymmetrical heteroacenes containing both pyrrole and thiophene rings. These acenes are highly soluble and stable at ambient conditions. Further studies on the reactivity of benzo[b]thiophene substrates under palladium catalyzed coupling conditions and incorporation of these compounds in OFET application are in progress in our labaratory.

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Supporting Information Available: Experimental procedures, Spectroscopic data, ^1H and ^{13}C spectra, cyclic voltammograms of all compounds and crystal data in CIF format and crystal packing of **1a**, **1b** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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