ORGANIC LETTERS

2006
Vol. 8, No. 11
2385−2388

Synthesis and Cofacial π-Stacked Packing Arrangement of 6,13-Bis(alkylthio)pentacene

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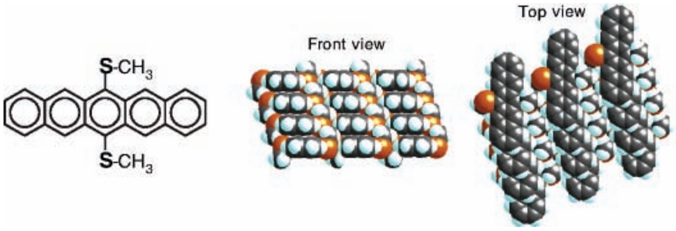
Received March 19, 2006

ABSTRACT



6,13-Bis(alkylthio)pentacenes directed toward organic field-effect transistors (OFETs) were synthesized by the ZnI_2-mediated reaction of *trans*-6,13-dihydroxy-6,13-dihydropentacene with alkylthiols, followed by the dehydrogenative aromatization of the resulting *trans*-6,13-bis(alkylthio)-6,13-dihydropentacenes with *p*-chloranil. The X-ray crystallographic analysis of 6,13-bis(methylthio)pentacene reveals that this compound is arranged as a result of cofacial π-stacking with S–S and S–π interactions.

Sulfur-containing aromatics are attractive candidates for organic semiconductors.[1,2] Pentacene is another promising candidate for organic semiconductors, especially organic field-effect transistors (OFETs).[3] It is generally recognized that the charge-carrier mobility in organic semiconductors depends on $\pi-\pi$ interactions between molecules. Acenes such as pentacene, however, tend to be susceptible to herringbone packing arrangements with minimal π-stacking,[4] although the herringbone-packed pentacene still holds the highest hole mobility among organic semiconductors.[3,5] Realization of a 2-D cofacial π-stacked packing arrangement of acenes may achieve greater charge-carrier transport

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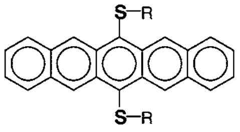
10.1021/ol060679x CCC: \$33.50

efficiency because this molecular ordering would permit good overlapping of the intermolecular π-orbitals.[3c,d,6] Thus, control of molecular orientation and arrangement is a very important subject for OFETs. Several groups have reported strategies for molecular design to achieve the cofacial π-stacked packing arrangement of acenes,[7−9] in which the introduction of aryl,[7c,d] bulky trialkylsilylethynyl,[8] or halogen groups[9] into acenes at the appropriate positions changes the packing structure from a herringbone to a cofacial π-stacking motif. Recently, we have demonstrated that S−S interactions assist a cofacial π-stacking of 9,10-bis(methylthio)anthracene.[10,11] Here, we report the synthesis of 6,13-bis(alkylthio)pentacenes (**3**) and the X-ray crystal packing structure of 6,13-bis(methylthio)pentacene (**3a**), wherein **3a** is arranged by cofacial π-stacking with S−S and S−π interactions.

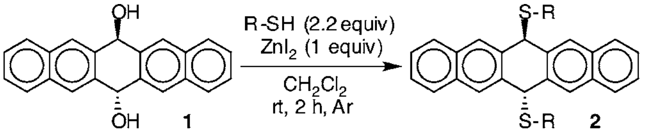


3a: R = CH_3
3b: R = n-C_5H_{11}
3c: R = n-C_8H_{17}
3d: R = $CH_2CH_2Si(CH_3)_3$
3e: R = Ph

The direct method for the synthesis of **3** may be the reaction of 6,13-dilithiopentacene with a dialkyl disulfide. However, 6,13-dilithiopentacene cannot be prepared. The reaction of 6,13-dihydropentacene with *n*-BuLi in the presence of TMEDA also did not generate 6,13-dilithio-6,13-dihydropentacene. We devised a general synthetic route to **3**, the key step of which utilizes the ZnI_2-mediated reaction of a benzylic alcohol with alkylthiol to provide a benzylic alkyl sulfide.[12]

The reduction of 6,13-pentacenequinone with $NaBH_4$ (4 equiv) in MeOH at room temperature gave *trans*-6,13-dihydroxy-6,13-dihydropentacene (**1**) in 77% yield.[13] The reaction of **1** with alkylthiols or thiophenol (2.2 equiv) in the presence of ZnI_2 (1 equiv) in CH_2Cl_2 at room temperature produced *trans*-6,13-bis(alkylthio)-6,13-dihydropentacenes (**2a**−**d**) or *trans*-6,13-bis(phenylthio)-6,13-dihydropentacene (**2e**), respectively, in good yields (Scheme 1). These compounds are freely soluble in $CHCl_3$. This reaction is applicable to a variety of thiols[14] and scarcely produces any of the cis isomer of **2**. In contrast, reaction of the dimesylate of **1** with n-$C_8H_{17}SNa$ (4 equiv) in CH_2Cl_2−DMF gave a mixture of **2c** and *cis*-**2c** in a 2:1 ratio (total 57% yield).

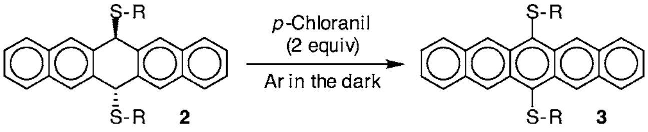
Scheme 1. Formation of **2** by a ZnI_2-Mediated Reaction of **1** with Thiols



2a: R = CH_3, 70% yield
2b: R = n-C_5H_{11}, 85% yield
2c: R = n-C_8H_{17}, 88% yield
2d: R = $CH_2CH_2Si(CH_3)_3$, 84% yield
2e: R = Ph, 73% yield

The final step in the synthesis of 6,13-bis(alkylthio)pentacenes (**3**) is dehydrogenative aromatization of **2**. The results are summarized in Table 1. With the goal of establishing the optimum conditions, **2c** (R = n-C_8H_{17}) was chosen as a test substrate (entries 3−5). All reactions were

Table 1. Formation of **3** by Dehydrogenative Aromatization of **2** with *p*-Chloranil



a: R = CH_3, **b**: R = n-C_5H_{11}, **c**: R = n-C_8H_{17},
d: R = $CH_2CH_2Si(CH_3)_3$, **e**: R = Ph

entry	R	solvent	temp/time (°C/days)	K_2CO_3 (10 equiv)	yield of **3** (%)
1	**a**	C_6H_6	60/3	yes	66
2	**b**	C_6H_6	60/2	yes	85
3	**c**	$CHCl_3$	40/3	no	40
4	**c**	C_6H_6	60/2	no	10
5	**c**	C_6H_6	60/2	yes	68
6	**d**	C_6H_6	60/2	yes	45
7	**e**	$CHCl_3$	40/2	no	79

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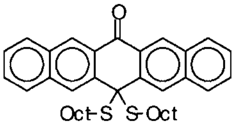
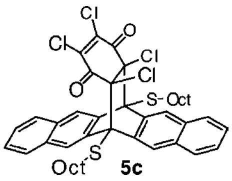
carried out under an argon atmosphere in the dark. *p*-Chloranil (2 equiv) was the best dehydrogenative aromatization reagent for **2c**.[15] In entry 3, the reaction of **2c** with *p*-chloranil in $CHCl_3$ at 40 °C for 3 days gave **3c** in 40% yield, along with 6,13-dihydro-13,13-bis(*n*-octylthio)pentacen-6-one (**4c**: 42% yield) as a rearrangement product[16] and the Diels–Alder adduct of **3c** with *p*-chloranil at the 6,13-positions (**5c**: 16% yield). In benzene at 60 °C for 2 days (entry 4), although overreactions toward **4c** and **5c** were almost inhibited, the reaction gave **3c** in 10% yield, together with *cis*-**2c** and recovered **2c**, wherein *cis*-**2c** had no reactivity with respect to *p*-chloranil. The use of K_2CO_3 as an additive was effective in inhibiting the formation of undesirable *cis*-**2c**.[17] Thus, the best result for the synthesis of **3c** (entry 5: 68% yield) was obtained under the conditions of **2c**, *p*-chloranil (2 equiv), and K_2CO_3 (10 equiv) in benzene at 60 °C for 2 days. On the basis of this procedure, **2a**, **2b**, and **2d** were transformed into **3a** (entry 1: $R = CH_3$, 66% yield), **3b** (entry 2: $R = n\text{-}C_5H_{11}$, 85% yield), and **3d** (entry 6: $R = (CH_2)_2Si(CH_3)_3$, 45% yield), respectively. The transformation of **2e** into **3e** (entry 7: R = Ph, 79% yield) was carried out in $CHCl_3$ because hardly any **4e** and **5e** were produced. Compounds **3a** and **3e** are less soluble in $CHCl_3$ and benzene (ca. 0.3 mg/mL at room temperature), whereas **3b**–**d** are freely soluble in these solvents. The UV–vis spectrum of **3c** in CH_2Cl_2 showed $\lambda_{max} = 617$ nm, which is red-shifted by 39 nm relative to λ_{max} of pentacene.[8d,18] Under both air and room light, **3a**–**e** in solution gradually decomposed to 6,13-pentacenequinone. In contrast to pentacene,[18] without lights, **3a**–**e** can be handled and purified under air.[19]


4c


5c

Single crystals of 6,13-bis(methylthio)pentacene (**3a**) suitable for X-ray diffraction analysis were obtained by allowing a hot solution of **3a** in 1,2,4-trichlorobenzene under an argon atmosphere in the dark to slowly cool to room temperature. The X-ray crystal packing structure of **3a** reveals that **3a** is arranged by cofacial π-stacking along the *a* axis with S–S and S–π interactions (Figures 1 and 2).

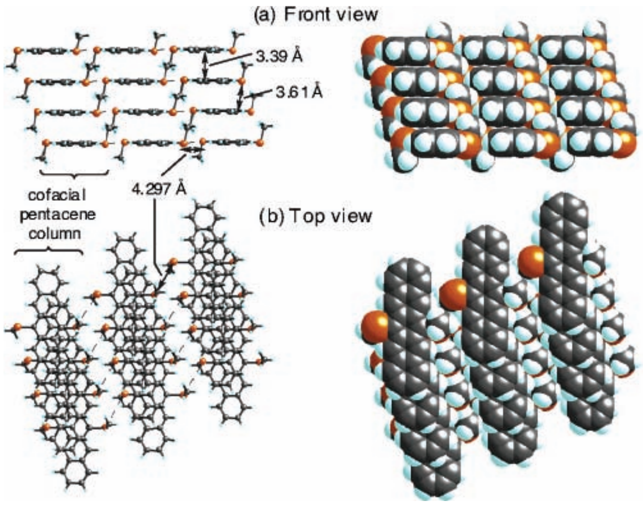


Figure 1. 2-D network sheet of **3a** in the crystal structure: (a) front and (b) top views.

Figure 1 shows one 2-D network sheet of **3a**. The pentacene ring of **3a** forms the pentacene column through a slipped-cofacial π-stacking motif along the *a* axis,[8b,10] with a face-to-face pentacene–pentacene distance of 3.39 Å. The pentacene rings in one column are slipped relative to each other along the long molecular axis by 3.64 Å and along the short molecular axis by 1.19 Å. This molecular ordering would permit good overlapping of the intermolecular π-orbitals of the pentacene rings. There is no S–S interaction (5.128 Å) in the pentacene column. Instead, there are weak intermolecular S–π interactions between the sulfur atom and the neighboring pentacene ring in the pentacene column, with the interatomic distances of $S\cdots C3' = 3.610$, $S\cdots C4' = 3.611$, and $S\cdots C5' = 3.652$ Å.[20] The intermolecular $S\cdots S'$ closest distance between the neighboring pentacene columns in **3a** is 4.297 Å (the second closest distance is 4.563 Å). Although this intermolecular $S\cdots S'$ distance is 16% longer

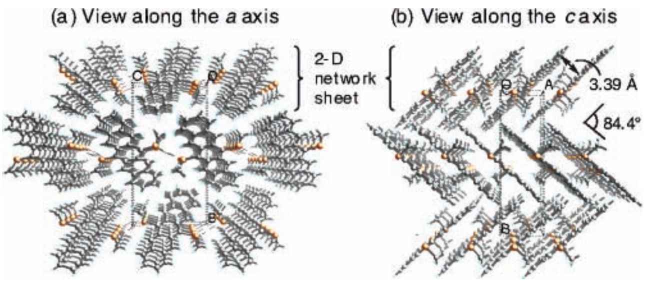


Figure 2. 3-D packing structure of **3a**: perspective views looking down (a) the *a* axis and (b) the *c* axis.

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[13] The reduction of 6,13-pentacenequinone with $NaBH_4$ in refluxing THF gives the trans and cis isomers of **1** in a 65:35 ratio. Vets, N.; Smet, M.; Dehaen, W. *Tetrahedron Lett.* **2004**, *45*, 7287–7289.

[14] For the synthesis of **2a**, a 1:1 mixture of CH_3SNa and acetic acid in CH_2Cl_2 was used as CH_3SH without any purification.

[15] The reaction of **2c** with DDQ in $CHCl_3$ gave **3c** in very low yield, wherein the main product was **4c**.

[16] For an anthracene analogue of **4c**, see: Koyama, E.; Kobayashi, K.; Horn, E.; Furukawa, N. *Tetrahedron Lett.* **1999**, *40*, 8833–8836.

[17] A 1:1 mixture of **3c** with tetrachlorohydroquinone in C_6D_6 at 60 °C for 2 days remained intact. The isomerization of **2c** to *cis*-**2c** could occur at the back reaction of a 6,13-bis(*n*-octylthio)-6-hydropentacene radical with a phenoxy radical of tetrachlorohydroquinone as intermediates in the reaction of **2c** with *p*-chloranil. K_2CO_3 as an additive would be effective in trapping of the hydroquinone or its phenoxy radical.

than the van der Waals distance,[20] this value is still sufficiently in the range of van der Waals interactions.[11,21] The contact angles of S···S′−$C_{pentacene}$ and S···S′−C_{Me} are 119.88 and 70.92°, respectively. Thus, the pentacene columns of **3a** formed by slipped-cofacial π-stacking and S−π interactions are parallel to each other and are linked by the S−S interactions to self-assemble into a 2-D network sheet (Figure 1). Figure 2 shows the 3-D packing structure of **3a**. The **3a** molecules in one 2-D network sheet and in the neighboring 2-D network sheets are packed relative to each other with a large tilt angle of 84.4°, in what is called the γ-motif.[4a]

In summary, we have developed a general method for the synthesis of 6,13-bis(alkylthio)pentacenes (**3**) and demonstrated that the intermolecular S−S and S−π interactions assist the cofacial π-stacked packing arrangement of the pentacene rings of **3a**. It is noted that the introduction of a small methylthio group into pentacene at the 6,13-positions changes the packing structure from a herringbone to a cofacial π-stacking motif. Studies on the preparation of thin films and OFET properties of **3** are currently in progress.

Supporting Information Available: Synthetic procedures and spectral data for **1**−**3**, **4c**, and **5c** and ORTEP drawing and CIF file of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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