

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

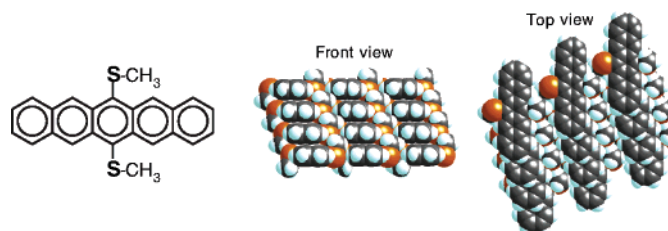
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ABSTRACT



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 π – π 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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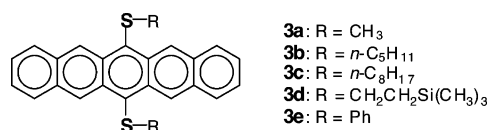
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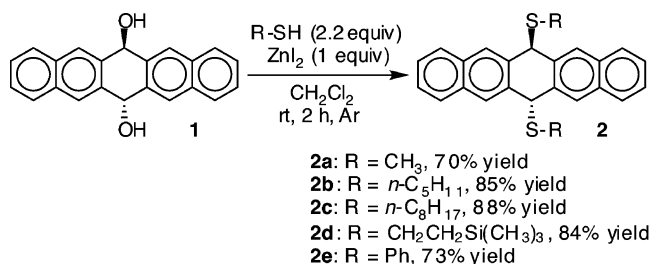
efficiency because this molecular ordering would permit good overlapping of the intermolecular π -orbitals.^{3c,d,6} Thus, control of molecular orientation and arrangement is a very important subject for OFETs. Several groups have reported strategies for molecular design to achieve the cofacial π -stacked packing arrangement of acenes,^{7–9} in which the introduction of aryl,^{7c,d} bulky trialkylsilyl ethynyl,⁸ or halogen groups⁹ 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.



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 ZnI₂-mediated reaction of a benzylic alcohol with alkylthiol to provide a benzylic alkyl sulfide.¹²

The reduction of 6,13-pentacenequinone with NaBH₄ (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 ZnI₂ (1 equiv) in CH₂Cl₂ at room temperature produced *trans*-6,13-bis(alkylthio)-6,13-dihydropentacenes (**2a–d**) or *trans*-6,13-bis(phenylthio)-6,13-dihydropentacene

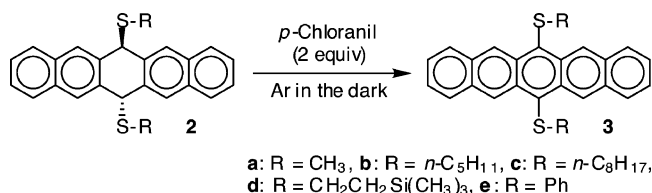
Scheme 1. Formation of **2** by a ZnI₂-Mediated Reaction of **1** with Thiols



(**2e**), respectively, in good yields (Scheme 1). These compounds are freely soluble in CHCl₃. This reaction is applicable to a variety of thiols¹⁴ and scarcely produces any of the *cis* isomer of **2**. In contrast, reaction of the dimesylate of **1** with *n*-C₈H₁₇SnA (4 equiv) in CH₂Cl₂–DMF gave a mixture of **2c** and *cis*-**2c** in a 2:1 ratio (total 57% 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

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



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

establishing the optimum conditions, **2c** (R = *n*-C₈H₁₇) was chosen as a test substrate (entries 3–5). All reactions were

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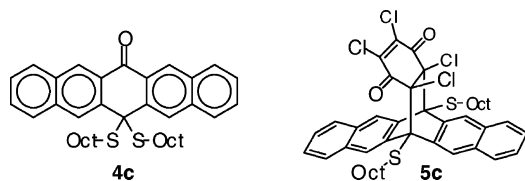
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carried out under an argon atmosphere in the dark. *p*-Chloranil (2 equiv) was the best dehydrogenative aromatization reagent for **2c**.¹⁵ In entry 3, the reaction of **2c** with *p*-chloranil in CHCl₃ at 40 °C for 3 days gave **3c** in 40% yield, along with 6,13-dihydro-13,13-bis(*n*-octylthio)pentacene-6-one (**4c**: 42% yield) as a rearrangement product¹⁶ 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 K₂CO₃ 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 K₂CO₃ (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 = CH₃, 66% yield), **3b** (entry 2: R = *n*-C₅H₁₁, 85% yield), and **3d** (entry 6: R = (CH₂)₂Si(CH₃)₃, 45% yield), respectively. The transformation of **2e** into **3e** (entry 7: R = Ph, 79% yield) was carried out in CHCl₃ because hardly any **4e** and **5e** were produced. Compounds **3a** and **3e** are less soluble in CHCl₃ 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 CH₂Cl₂ showed $\lambda_{\text{max}} = 617$ 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



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.

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(15) The reaction of **2c** with DDQ in CHCl₃ gave **3c** in very low yield, wherein the main product was **4c**.

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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).

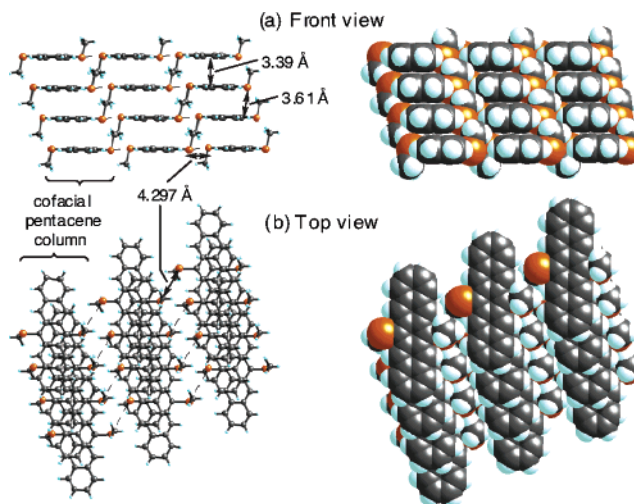


Figure 1. 2-D network sheet of **3a** in the crystal structure: (a) front and (b) top views.

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···C3' = 3.610, S···C4' = 3.611, and S···C5' = 3.652 Å.²⁰ The intermolecular S···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···S' distance is 16% longer

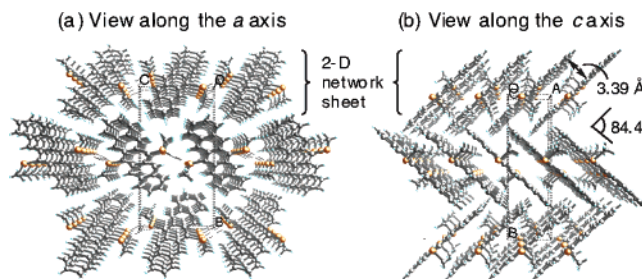


Figure 2. 3-D packing structure of **3a**: perspective views looking down (a) the *a* axis and (b) the *c* axis.

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 $S\cdots S'-C_{\text{pentacene}}$ and $S\cdots S'-C_{\text{Me}}$ are 119.88 and 70.92°, respectively. Thus, the pentacene columns of **3a** formed by slipped-cofacial π -stacking and $S-\pi$ 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 $S-\pi$ 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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