JOC*Note*

Efficient Isomer-Pure Synthesis of a Benzo[*b*]thiophene Analogue of Pentacene[†,‡]

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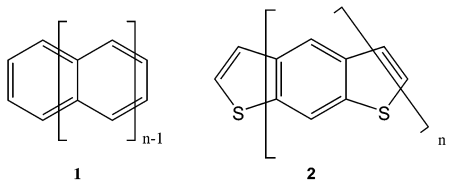
Abstract: Isomer-pure thieno[3,2-*f*:4,5-*f*′]bis[1]benzothiophene (**2**, $n = 2$) has been synthesized in an efficient four step approach without column chromatography.

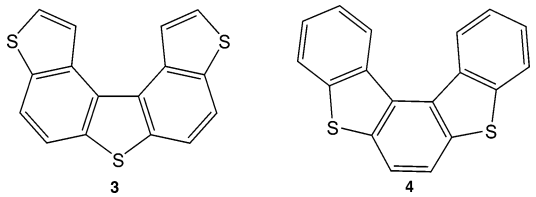
Thiophene and other fused sulfur containing compounds make up to 10−30% of the aromatic fraction of crude oil.[1] The unique reactivity and electronic properties of thiophene derivatives have led to many applications, particularly as oligomers and polymers.[2] Polyacenes (**1**) have recently gained attention as charge-transport materials in both theoretical and experimental studies.[3] Current synthetic procedures, however, are limited. Heptacene (**1**, $n = 7$) is the largest reported, having been last synthesized in 1952.[4] Despite interesting electronic properties, polyacenes have major drawbacks. For all practical purposes, hexacene (**1**, $n = 6$) is the largest stable polyacene, since oxidative stability[5] and solubility in common organic solvents decrease with increasing length of the polyacene.

Our approach to the problem involves the development of analogues of polyacenes having a benzo[*b*]thiophene repeat unit (Figure 1). In this paper, we demonstrate an efficient synthetic approach for **2** ($n = 2$),[6] one of the isomeric thiophene analogues of pentacene. In future work, we will demonstrate that this unit provides a synthon for target polyacenes.



1 2

FIGURE 1. General structure of polyacene (**1**) and polybenzo[*b*]thiacene (**2**).



3 4

FIGURE 2. Structures of [5]heterohelicenes **3** and **4**.

Benzo[1,2-*b*:5,4-*b*′]dithiophene (**2**, $n = 1$) has been synthesized.[7] Both benzodithiophene isomers were obtained using a series of organolithium reactions to generate dithienylmethane, followed by a formylation and acid-catalyzed cyclization to generate the central arene moiety. The electronic properties of only the *syn*−*anti* isomer, benzo[1,2-*b*:4,5-*b*′]dithiophene,[8] and derivatives thereof have been extensively studied.[9] An improvement of the overall yield of this synthetic scheme resulted when hydrobromic acid (HBr) was replaced with polyphosphoric acid (PPA) as the acid catalyst in the cyclization reaction.[10] The main drawbacks of PPA remain the high viscosity, the poor solubility,[11] and the subsequent neutralization step.

Previously prepared [5]heterohelicenes **3**[12] and **4** (Figure 2) exhibit nonlinear optical properties and optical activity.[13] These compounds were prepared by oxidative photolysis of the 1,2-dithienylethenes.[14]

Laquindanum et al.[15] reported substituted anthradithiophenes (ADT). These compounds showed signifi-

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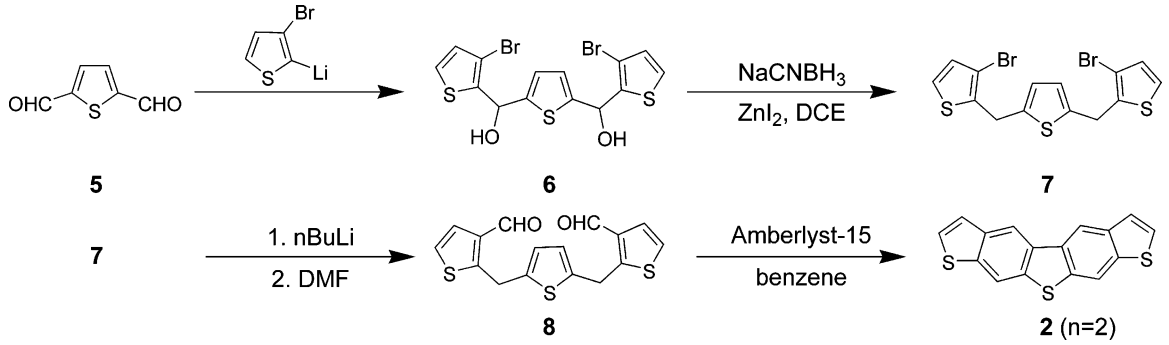
SCHEME 1. Synthesis of Thieno[3,2-*f*:4,5-*f*′]bis[1]benzothiophene (2, *n* = 2)



5 **6** **7**

7 **8** **2** (n=2)

cantly better solubility and solution stability, when compared to the analogous hydrocarbon pentacene. This synthetic approach was based on the double condensation of thiophenedicarboxaldehyde with 1,4-cyclohexanedione under basic conditions,[16] followed by the reduction of the generated dione. While it was an efficient strategy, no attempt was made to determine or separate the *syn* and *anti* isomers. Isomeric purity is of importance in achieving high charge-transport mobilities, as Sirringhaus et al.[17] reported recently. Dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]bis-[1]benzothiophene (DBTBT) was synthesized via the intramolecular acid-induced coupling reaction of aromatic methyl sulfoxides. Similar to the approach for ADT, this material could only be synthesized as a mixture of isomers.[17]

Previously, we reported the photochemical cycloaddition of benzodithiophene to acetylenes and diynes.[18] In this Note, we report an efficient approach to the synthesis of **2** ($n = 2$) (Scheme 1). This synthetic approach gives high yields, eliminates PPA for acid-catalyzed cyclization, and produces an isomer-free final product. Current investigations are ongoing to prepare the isomer, thieno-[2,3-*f*:5,4-*f*′]bis[1]benzothiophene. X-ray structure analysis and mobility measurements of **2** ($n = 2$) are currently underway.

Thiophenedicarboxaldehyde (**5**)[19] was added dropwise to a solution of 3-bromo-2-lithiothiophene, generated from 2,3-dibromothiophene. The resulting 2,5-bis(3-bromo[2]-hydroxythienylmethyl)thiophene (**6**) was used without further purification, since ^{1}H NMR confirmed the reaction to yield **6** in synthetic purity.[20] Traditional reducing agents of dithienylcarbinols such as $LiAlH_4/AlCl_3$,[5] $NaBH_4$/TFA,[21] and even TMSCl/NaI[22] did not produce the desired product **7** in satisfactory yields. A mild and effective reducting agent is $NaCNBH_3/ZnI_2$,[23] by means of which the reaction mixture yields synthetically pure **7**. Dialdehyde **8** is prepared in nearly quantitative yield if the conditions are carefully timed and the solution is carefully cooled during the procedure. Reprecipitation from $CHCl_3$/hexanes yields pure product. Efficient cyclization occurs when **8** is refluxed in benzene in the presence of Amberlyst 15[24] using a Dean−Stark trap. The final product **2** ($n = 2$) was isolated by sublimation and recrystallized from ethanol.

In summary, we have developed an effective, column chromatography-free, synthetic approach for the synthesis of thieno[3,2-*f*:4,5-*f*′]bis[1]benzothiophene (**2**, $n = 2$) with an overall yield of 34%. This approach eliminates the generation of multiple isomers.

Experimental Section

General Experimental Procedues. Ethyl ether and tetrahydrofuran were distilled freshly from sodium/benzophenone ketyl radical prior to use. ^{n}BuLi was titrated prior to each use using *N*-pivaloyl-*o*-toluidine.[25] DMF was kept over BaO overnight and distilled from alumina prior to use. All organolithium reactions were carried out under inert atmosphere (Ar) and on a bath of diethyl ether and dry ice as cooling agent. ^{1}H NMR spectra were obtained at 300 and 400 MHz, as indicated. ^{1}H chemical shifts (δ) were reported in ppm with $CHCl_3$ (δ 7.26 ppm) or TMS (δ 0.00 ppm) as internal standard. ^{13}C NMR (75, 100 MHz) spectra were obtained using $CDCl_3$ (δ 77 ppm) as internal standard. Melting points are uncorrected.

2,5-Bis(3-bromo[2]hydroxythienylmethyl)thiophene (6). 2,3-Dibromothiophene (8.12 g, 33.6 mmol) was added to a 300 mL solution of 5:1 ether/THF and cooled to −78 °C. ^{n}BuLi (14.8 mL, 36.9 mmol) was added dropwise while maintaining the temperature below −60 °C. After 15 min, **5** (2.35 g, 16.7 mmol) dissolved in 150 mL of THF was added slowly and the mixture stirred for 1 h. Aqueous workup and drying over $MgSO_4$ yielded a yellow oil, which was used without further purification. ^{1}H NMR (THF-d_8, 400 MHz): δ 3.05 (2H, s), 6.31 (2H, s), 6.86 (2H, d, $J = 2.8$ Hz), 6.93 (2H, dd, $J = 5.2$ Hz, $J = 0.4$ Hz), 7.27 (2H, d, $J = 5.2$ Hz). MS (EI, 70 eV) *m*/*z* (%): 468 (12) [M + 2], 466 (21) [M$^+$], 464 (12) [M − 2], 448 (18) [M − H_2O], 432 (50), 369 (20), 272 (48), 227 (42), 191 (100), 178 (34), 134 (29), 111 (48).

2,5-Bis(3-bromo[2]thienylmethyl)thiophene (7). To a solution of **6** (7.82 g, 16.7 mmol) in dichloroethane were added ZnI_2 (16.11 g, 53.37 mmol) and $NaCNBH_3$ (14.72 g, 234.9 mmol). The reaction mixture was stirred at room temperature overnight and filtered through Celite. The filtrate was washed with saturated NH_4Cl and water. After drying over $MgSO_4$ and removal of solvent under reduced pressure, the resulting orange oil was

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passed through a short-bed of silica using hexanes as eluent. This yielded 13.46 g of a yellow oil (80% over two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.22 (4H, s), 6.71 (2H, s), 6.92 (2H, d, J = 5.2 Hz), 7.15 (2H, d, J = 5.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.5, 137.6, 129.9, 125.4, 124.2, 109.3, 29.7. GC-MS (EI, 70 eV) m/z (%): 434 (66) [M^+], 355 (51) [M − Br], 259 (100), 177 (69), 137 (54), 45 (68). Anal. Calcd for $C_{14}H_{10}Br_2S_3$: C, 38.72; H, 2.32; Br, 36.80; S, 22.15. Found: C, 38.88; H, 2.34; Br, 36.97; S, 22.00.

2,5-Bis(3-formyl[2]thienylmethyl)thiophene (8). ^{n}BuLi (2.5 M, 2.6 mL, 6.5 mmol) was cooled to −78 °C in 90 mL of ether. **7** (1.30 g, 2.99 mmol) dissolved in 15 mL of ether was added dropwise and the mixture stirred for 10 min. DMF (0.5 mL, 6.23 mmol) was added and the reaction mixture stirred for 1 h. Quenching with water and workup with water and brine yielded 0.939 g (94%) of **8**. Crystallization from CH_2Cl_2/hexanes gave pale pink needles, mp 89−91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.64 (4H, s), 6.73 (2H, s), 7.14 (2H, d, J = 5.6 Hz), 7.40 (2H, d, J = 5.6 Hz), 10.05 (2H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 184.6, 154.1, 140.8, 136.5, 127.9, 125.8, 123.9, 28.5. MS (EI, 70 eV) m/z (%): 332 (45) [M], 303 (13) [M − CHO], 207 (100), 179 (34), 124 (32), 97 (33). Anal. Calcd for $C_{16}H_{12}O_2S_3$: C, 57.80; H, 3.64; O, 9.62; S, 28.93. Found: C, 57.47; H, 3.53; O, 9.85; S, 29.01.

Thieno[3,2-*f*:4,5-*f*′]bis[1]benzothiophene (2, *n* = 2). Dialdehyde **8** (0.919 g, 2.77 mmol) was dissolved in 50 mL of benzene, Amberlyst 15 (1.3 g) was added, and the reaction was refluxed overnight using a Dean−Stark trap. The color changed from pink to pale beige, and the product started to precipitate as a white solid. The solid was dissolved in dichloromethane, the Amberlyst 15 was removed by filtration, and the reaction mixture was washed with water. Drying over $MgSO_4$ and removal of the solvent yielded 0.717 g (88%) of a beige solid. After sublimation (190 °C, 2.0×10^{-2} Torr) and recrystallization from ethanol, 0.412 g of white crystals were obtained in 46% yield, mp 272−273 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (4H, s), 8.28 (2H, s), 8.64 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.4, 137.4, 136.7, 133.3, 126.2, 123.8, 116.0, 115.7. MS (EI, 70 eV) m/z (%): 298 (15) [M + 2], 296 (100) [M], 148 (24). Anal. Calcd for $C_{16}H_8S_3$: C, 64.83; H, 2.72; S, 32.45. Found: C, 64.92; H, 2.81; S, 32.45.

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Supporting Information Available: Spectroscopic data for **5** and copies of NMR data of compounds **2**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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