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# Facile Synthesis of 2,6-Disubstituted Benzobisthiazoles: Functional Monomers for the Design of Organic Semiconductors

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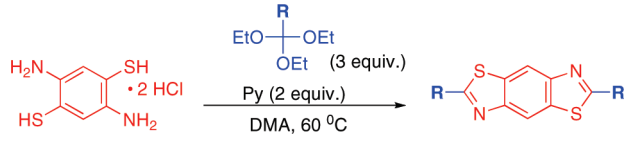
*Received November 7, 2009*




The synthesis of several synthetically useful 2,6-disubstituted benzobisthiazoles is described. The method is based on the Lewis acid-catalyzed ring-closing reaction between substituted orthoesters and diamino benzene dithiol. The resulting benzobisthiazoles are obtained cleanly and in good yields. These materials are of interest for the development of new organic semiconductors.

The design and synthesis of new organic semiconducting materials is of current interest due to the important roles these materials play in the development of plastic electronics.[1] Although many $\pi$-conjugated materials are known, most of them are electron rich and exhibit electron-donating and hole-transporting (p-type) electronic properties. Thus the synthesis of electron-deficient $\pi$-conjugated materials, which can exhibit electron-accepting and electron-transporting properties (n-type), remains an important problem in the field.

The electron-deficient benzo[1,2-*d*;4,5-*d*′]bisthiazole moiety (*trans*-BBZT) is a promising building block for the development of new organic semiconductors because materials containing benzobisthiazoles exhibit high fluorescence,[2] thermal stability,[3,4] electron affinity,[5] and interesting nonlinear optical properties.[2,6,7] Typical synthesis of benzobisthiazoles requires strong acids or oxidants[8] and high temperatures.[9] These harsh reaction conditions restrict the types of substituents that can be incorporated onto these moieties, hindering the exploration of materials containing benzobisthiazoles.

Recently we reported the synthesis of 2,6-disubstituted benzobisoxazoles using substituted orthoesters and rare earth metal triflates as catalysts.[10] These reaction conditions facilitated the synthesis of novel benzobisoxazoles bearing a variety of substituents cleanly and in high yield. Inspired by these promising results, we set out to develop a mild, low-temperature method for the synthesis of the analogous 2,6-disubstituted benzobisthiazoles. Although benzo[1,2-*d*;4,5-*d*′]bisoxazole (*trans*-BBO) and *trans*-BBZT are structurally similar, the sulfur atom is less electronegative than the oxygen atom, and has similar electronegativity to the carbon atom. Thus the electron density is more equally shared between sulfur and carbon in *trans*-BBZT than between oxygen and carbon in *trans*-BBO and the $\pi$-orbitals will be more delocalized. Additionally the empty d orbitals of the sulfur atom can contribute to the molecular $\pi$-orbitals decreasing the energy of the $\pi-\pi^*$ transition.[7,11] These changes can be beneficial for the development of new organic semiconducting materials. Herein, we report the successful synthesis of several new benzobisthiazoles. We also demonstrate that functionality can be increased by a simple reaction following ring formation.

The general synthetic route for the benzobisazoles is shown in Scheme 1. Previously, we found that best reaction conditions for the synthesis of benzobisoxazoles are DMSO as a solvent, pyridine as a cosolvent, and rare metal triflates as catalysts.[10] The use of the pyridine as a cosolvent is beneficial since it scavenges the hydrochloride salts that coordinate with the diamino diol. Removing the acids prevents the decomposition of the substituted orthoesters, which is catalyzed by protic acids.[10] Using the reaction between 2,5-diamino-1,4-benzene dithiol (DABDT) (**1**) and triethylorthoacetate (**2b**) as a model, we explored these conditions. Unfortunately, when DABDT was mixed with pyridine in DMSO, an insoluble green precipitate was formed. This was most likely caused by the formation of disulfide linkages, although the insolubility of the material prevented its characterization (entry 1). We then attempted to perform the

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DOI: 10.1021/jo9023864 Published on Web 12/18/2009

**SCHEME 1. Synthesis of 2,6-Disubstituted Benzobisiazoles**

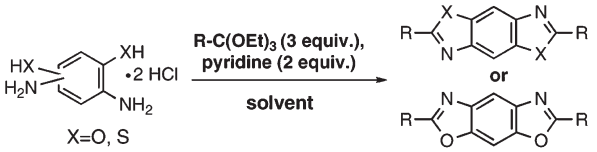
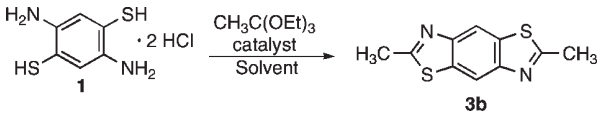



**TABLE 1. Optimization Reactions with DABDT 1 and Triethyl Orthoacetate 2b[a]**




| entry | solvent | catalyst | temp (°C) | time (h) | yield[b] (%) |
|---|---|---|---|---|---|
| 1 | DMSO | $Y(OTf)_3$ | 50 | n/a | 0 |
| 2 | none | none[c] | 90 | 6 | 51 |
| 3 | none | $H_2SO_4$[c] | 90 | 3 | 45 |
| 4 | DMAc | $Eu(OTf)_3$ | 50 | 1.5 | 77 |
| 5 | DMAc | $La(OTf)_3$ | 50 | 1.5 | 72 |
| 6 | DMAc | $Sc(OTf)_3$ | 50 | 1.5 | 75 |
| 7 | DMAc | $Y(OTf)_3$ | 50 | 1.5 | 69 |
| | DMAc | $Yb(OTf)_3$ | 50 | 1.5 | 77 |

[a]Standard reaction conditions: substrate 1 M in solvent, 3 equiv of ortho ester, 5 mol % of catalyst, and 2 equiv of pyridine. [b]Isolated yields. [c]10 equiv of orthoester used without pyridine.

reaction without any additional solvents, using 10 equiv of the triethylorthoformate and the coordinated hydrochloride salts as an acid catalyst (entry 2). These conditions produced 2,6-dimethylbenzobisthiazole **3b** in a 51% yield. With use of the same reaction conditions and sulfuric acid as a catalyst, similar results were obtained (entry 3). In both cases the resulting products were formed along with some dark impurities, which could be removed after careful recrystallization.

To reduce the amount of orthoester required for these reactions, we performed a solubility test with DABDT to find a cosolvent. We investigated the use of DMA as a solvent, since DABDT dissolves in DMA at room temperature, and this solvent was not prone to the side reactions experienced previously. The reaction of DABDT and triethylorthoformate occurrs rapidly, when performed slightly above room temperature. The solid that forms is easily isolated by precipitation into water and filtration. We then explored the use of several different rare earth metal triflates to catalyze the reaction. The results are summarized in Table 1. On the basis of the model reactions, we found that most triflates gave similar results. Since all of these catalysts are commercially available, our bias toward the use of $Eu(OTf)_3$, $La(OTf)_3$, or $Y(OTf)_3$ was due to their lower cost relative to the other rare earth metal triflates.

Upon determining the optimum reaction conditions, we evaluated the scope of this reaction with respect to the orthoester. To accomplish this we utilized the commercially available triethyl orthoformate (**2a**) in addition to triethyl orthochloroacetate (**2c**), triethyl orthopropiolate (**2d**), and ethyl triethoxyacetate (**2e**), which were prepared in our laboratories. In all cases the orthoesters reacted with DABDT cleanly and in moderate yields. As a follow-up to our previous work, we also explored the use of DMA as a solvent

**SCHEME 2. Synthesis of Monomer 3f**

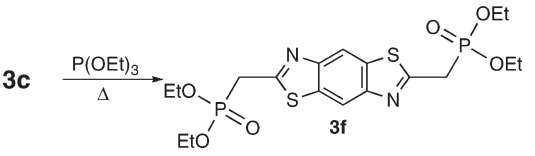
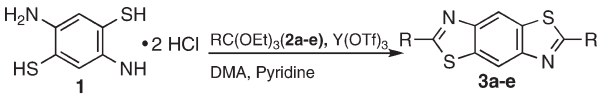
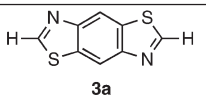
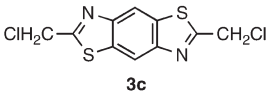
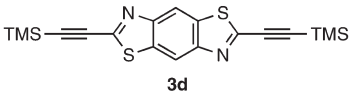
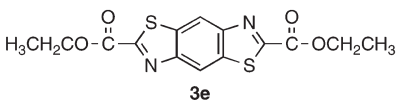



**TABLE 2. Reaction of 1 with Various Orthoesters 2a and 2c−e[b]**




**a:** R=H, **b:** R=$CH_3$, **c:** R=$CH_2Cl$, **d:** R=$C_2Si(CH_3)_3$, **e:** R= COOEt

| ortho ester | benzobisthiazole | % yield[a] |
|---|---|---|
| **2a** |  **3a** | 68 |
| **2c** |  **3c** | 59 |
| **2d** |  **3d** | 38 |
| **2e** |  **3e** | 53[c] |

[a]Standard reaction conditions: substrate 1 M in solvent, 3 equiv of orthoester, 5 mol % of catalyst, and 2 equiv of pyridine, 1.5 h. [b]Isolated yields. [c]Reaction time was 18 h.

for the synthesis of benzobisoxazoles. Interestingly, significantly lower yields were observed with DMSO as solvent.[10] These lower yields were most likely due to the poor solubility of diaminohydroquinone and diaminoresorcinol in this solvent. We did not investigate the synthesis of benzo[1,2-*d*;5,4-*d*′]bisthiazole (*cis*-BBZT) derivatives because of the inability to synthesize 4,6-diamino-1,3-benzene dithiol. Although the synthesis of this compound has been reported previously,[12] we, like those before us, have struggled to obtain pure material due to its instability.[4]

To increase the functionality of these BBZT derivatives, we synthesized the diphosphonate ester **3f** via the Arbuzov reaction of **3c** with triethylphosphite (Scheme 2). This reaction occurred cleanly to produce the **3f** in an 80% yield (Table 2). Monomers of this type have been useful for the synthesis of vinylene polymers via the Horner−Wadsworth−Emmons reaction.

We were able to obtain X-ray quality crystals of **3a**, **3b**, **3c**, and **3f** suitable for analyses to be performed by recrystallization. Detailed crystallographic data can be found in the Supporting Information, and a representative example is shown in Figure 1. In addition to confirming the identity of these new compounds, the X-ray analyses show that these

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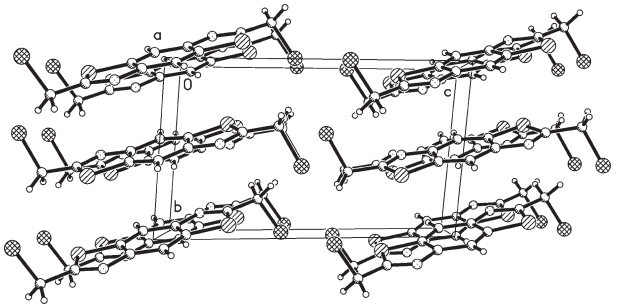


**FIGURE 1.** Crystal structure of **3c** along the *a*-crystallographic axis.

monomers are all planar with a mean deviation from planarity of 0.0114 Å. The flat nature of the benzobisthiazoles is beneficial to promoting efficient $\pi$-stacking and improving the charge transport of materials derived from them.

In summary, we have developed a new method for the synthesis of novel 2,6-disubstituted benzobisthiazoles. The benefits of this approach include the mild reaction conditions and ease of purification without column chromatography. Currently we are developing new organic semiconductors using these compounds.

## Experimental Section

**Typical Procedure for the Synthesis of Benzobisthiazoles (3a−e). Benzo[1,2-*d*;4,5-*d*′]bisthiazole (3a).** In a round-bottomed flask 2,5-diamino-1,4-benzene dithiol **1** (1.23 g, 5.0 mmol) and pyridine (791 mg, 10.0 mmol) were dissolved in DMA (10 mL). The resulting solution is added via a syringe to a mixture of triethylorthoformate **2a** (2.22 g, 15.0 mmol) and $Y(OTf)_3$ (134 mg, 0.255 mmol) in a round-bottomed flask. The reaction is stirred at 55 °C for 1 h and then cooled. The reaction is diluted with water and the crude product collected by filtration. Recrystallization of the crude with dichloromethane/heptanes gave white needles (0.65 g, 68% yield). Melting point >260 °C. $^1$H NMR (400 MHz; DMSO-$d_6$) $\delta$ 8.92 (2H, s), 9.49 (2H, s); $^{13}$C NMR (100 MHz; DMSO-$d_6$) $\delta$ 116.3, 132.7, 151.2, 157.9. HRMS (EI) 191.98189, $C_8H_4N_2S_2$ requires 191.98159, deviation 1.6 ppm.

**2,6-Dimethylbenzo[1,2-*d*;4,5-*d*′]bisthiazole (3b).** Compound **3b** was synthesized following the same protocol as for compound **3a** with **4** and triethylorthoacetate **2b**. The product was obtained after recrystallization from dichloromethane/heptanes as white needles (0.85 g, 77% yield). Melting point 232−233 °C. $^1$H NMR (400 MHz; $CDCl_3$) $\delta$ 2.86 (6H, s), 8.34 (2H, s); $^{13}$C NMR (100 MHz; $CDCl_3$) $\delta$ 20.5, 114.4, 134.5, 151.0, 167.9. HRMS (EI) 220.01289, $C_{10}H_8N_2S_2$ requires 220.01330, deviation 1.9 ppm.

**2,6-Bis(chloromethyl)benzo[1,2-*d*;4,5-*d*′]bisthiazole (3c).** Compound **3c** was synthesized following the same protocol as for compound **3a** with **4** and triethyl orthochloroacetate **2c**. The product was obtained after recrystallization from heptanes as pale yellow needles. The reaction was run on 15 mmol scale with a 2.54 g yield (59%). Melting point 219−220 °C. $^1$H NMR (400 MHz; DMSO-$d_6$) $\delta$ 5.28 (4H, s), 8.82 (2H, s); $^{13}$C NMR (100 MHz; DMSO-$d_6$) $\delta$ 42.1, 116.5, 134.7, 150.5, 168.8. HRMS (EI) 287.93549, $C_{10}H_6Cl_2N_2S_2$ requires 287.93495, deviation 1.9 ppm.

**2,6-Bis(trimethylsilylethynyl)benzo[1,2-*d*;4,5-*d*′]bisthiazole (3d).** Compound **3d** was synthesized following the same protocol as for compound **3a** with **4** and triethyl orthopropiolate **2d**. The product was obtained after recrystallization from pentane as pale yellow needles (38% yield). Melting point >260 °C (pentane). $^1$H NMR (400 MHz; $CDCl_3$) $\delta$ 0.331 (18H, s), 8.478 (2H, s); $^{13}$C NMR (100 MHz; $CDCl_3$) $\delta$ −0.4, 96.8, 104.9, 115.9, 135.1, 150.0, 151.7. HRMS (EI) 384.06158, for $C_{18}H_{20}N_2S_2Si_2$, requires 384.06064, deviation 2.4 ppm.

**Benzo[1,2-*d*;4,5-*d*′]bisthiazole Diethyl Ester (3e).** Compound **3e** was synthesized following the same protocol as for compound **3a** with **4** and ethyl triethoxyacetate **2e**. The product was obtained after recrystallization from pentane as pale yellow needles (53% yield). Melting point 241−242 °C (chloroform/ethanol). $^1$H NMR (400 MHz; $CDCl_3$) $\delta$ 1.52 (6H, t, $J$ = 5.4 Hz), 4.59 (4H, q, $J$ = 5.4 Hz), 8.83 (2H, s); $^{13}$C NMR (100 MHz; $CDCl_3$) $\delta$ 14.5, 63.7, 118.9, 136.5, 152.6, 160.4, 161.3. HRMS (EI), found 336.02464, $C_{14}H_{12}N_2O_4S_2$ requires 336.02385, deviation 2.3 ppm.

**2,6-Dimethylbenzo[1,2-*d*;4,5-*d*′]bisthiazolediethylphosphonate Ester (3f).** Triethylphosphite (1.12 g, 7.75 mmol) and 2,6-(bischloromethyl)benzo[1,2-*d*;4,5-*d*′]benzobisthiazole **3c** (650 mg, 2.25 mmol) were heated to 150 °C for 4 h. The reaction was cooled to yield crude **3f**. Recrystallization from chloroform/heptanes afforded the product as a white solid (885 mg, 80%). Melting point 203−204 °C. $^1$H NMR (400 MHz; $CDCl_3$) $\delta$ 1.32 (12H, t, $J$ = 6.0 Hz), 3.75 (4H, d, $J$ = 15 Hz), 4.18 (8H, m), 8.44 (2H, s). $^{13}$C NMR (100 MHz; $CDCl_3$) $\delta$ 16.6 (d, $J$ = 6.0 Hz), 33.1, 34.5, 63.1 (d, $J$ = 6.0 Hz), 115.3, 135.2, 148.8, 151.1, 162.6, 162.7. HRMS (EI) 492.07227, $C_{18}H_{26}N_2O_6P_2S_2$ requires 492.07075, deviation 3.0 ppm.

**Acknowledgment.** We are grateful to the 3M Foundation and the National Science Foundation (DMR-0846607) for their generous support of this work. We thank Dr. Kamel Harrata and the Mass Spectroscopy Laboratory of Iowa State University (ISU) for analysis of our compounds. We also thank Brian Tlach for help with the synthesis of **2e** and Dr. Jessie Waldo (ISU) for helpful discussions of this research.

**Supporting Information Available:** Crystallographic information files (CIF) for **3a**−**c** and **3e**, experimental details for the synthetic intermediates, and NMR spectra ($^1$H and $^{13}$C) for **3a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.