ORGANIC
LETTERS

2012
Vol. 14, No. 24
6138–6141

Efficient Synthesis of Benzo[1,2-*b*:6,5-*b*′]dithiophene-4,5-dione (BDTD) and Its Chemical Transformations into Precursors for π-Conjugated Materials

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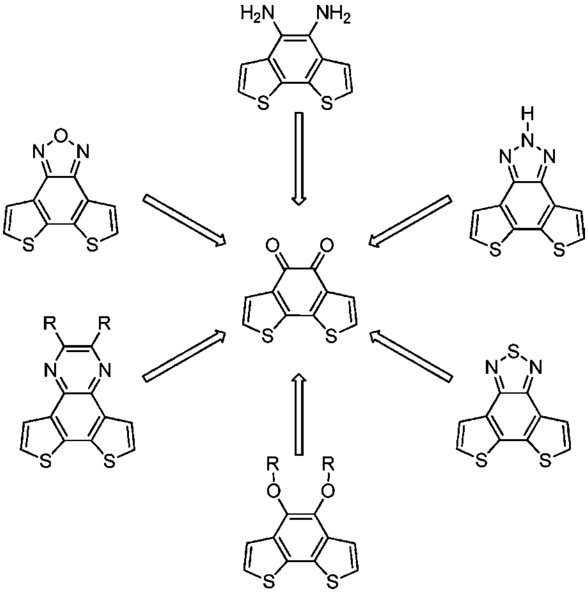
Received September 30, 2012

ABSTRACT



A straightforward synthesis of the fused-aromatic dione benzo[1,2-*b*:6,5-*b*′]dithiophene-4,5-dione (BDTD) has been developed. This fused-aromatic dione was subjected to various chemical transformations to generate diverse molecules with potential use in π-conjugated materials for organic electronics.

The donor–acceptor approach–orbital mixing of alternating donor and acceptor units in a π-conjugated copolymer or oligomer to decrease the electronic band gap has become one of the most powerful strategies for band gap engineering in π-conjugated polymers;[1,2] therefore, access to new donor and acceptor molecules is highly convenient since it can lead to new π-conjugated systems with assorted band gaps and properties. Aromatic diones are versatile starting materials that can generate a wide variety of monomers for the synthesis of π-conjugated materials. The ketone groups in these diones can be easily converted into other organic functionalities leading to new molecules with different properties and characteristics (i.e., electron

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(1) Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.

(2) Van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng., R* **2001**, *32*, 1.

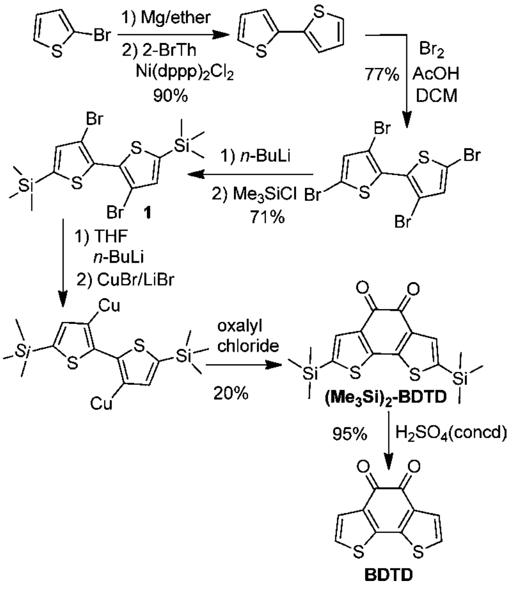
10.1021/ol302704v

donors or electron acceptors), and most of these transformations can be carried out in one or two steps, which demonstrates the usefulness of these intermediates. The research described in this report focuses on the synthesis of the fused-aromatic dione benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (BDTD) and its conversion to new π-conjugated materials precursors by different synthetic approaches. This work is a helpful contribution to the field since it reports not only the synthesis of novel donor and acceptor molecules based on BDTD but also a creative synthetic approach to new molecules. This approach can be adapted to other aromatic diones, giving access to novel donor and acceptor molecules, which is key to generating new π-conjugated materials with improved physical and electronic properties.

Molecules such as BDTD (shown in Scheme 1) offer various features that make them attractive for π-conjugated materials. These molecules inherit the wide range of electronic properties offered by thiophene-based materials[3a] and also offer the possibility for postderivatization on the thiophene rings (i.e., halogenation, borylation, stannylation, etc.) and on the carbonyl groups. Due to these features, various syntheses and uses for BDTD have been reported.[3b−e]

Initially, to make BDTD, we used the synthetic route shown in Scheme 1. This synthetic route employs the readily available 2-bromothiophene as the starting material and was based on previously reported literature procedures[4] to generate the intermediate **1**. Unfortunately, this route contains a considerable number of synthetic steps (> 6), with a low overall yield (~9%), and in some cases requires column purification, which makes the synthesis expensive and unsuitable for a large-scale synthesis of BDTD. It is worthy to note that, as shown in the final step in Scheme 1, the deprotection of the silyl compound $(Me_3Si)_2$-BDTD was only achieved by dissolving the $(Me_3Si)_2$-BDTD in concentrated sulfuric acid and immediate quenching with water. This approach was necessary since the removal of the TMS groups could not be accomplished by the standard deprotection methods such as using fluoride sources or dilute acids.

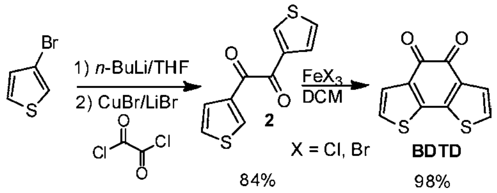
Scheme 1. Multi-step Route toward BDTD



We report here an alternative synthetic route toward BDTD, and this approach is presented in Scheme 2. This synthetic path uses the inexpensive and readily available 3-bromothiophene as starting material, and it is highly convenient, since the reaction can be carried out in only two steps, in high yields, from inexpensive starting materials, and requiring no column purification, which allows a multigram synthesis.

The synthesis of the diketone **2**, which is the key intermediate, was carried out using a modified literature procedure for analogous systems.[5] After **2** was isolated, it was subjected to oxidative ring closing using iron trichloride or iron tribromide in dichloromethane (DCM).

Scheme 2. Short Synthesis of BDTD



Various experiments were carried out to optimize the oxidative ring-closing conditions in DCM, i.e. different concentrations, reaction times, and temperatures (20, 35, and 40 °C). Monitoring of the reaction by TLC for several hours (1−24 h) lead to the conclusion that the reaction must be carried out at room temperature, for at least 2 h, and using 3 equiv or more of $FeCl_3$ or $FeBr_3$ to achieve high conversion. If less than 2.5 equiv of iron chloride were employed full reaction conversion was not observed, even if the reaction was run for more than 24 h.

We carried out various chemical transformations on BDTD (Table 1). Most of these chemical transformations are straightforward and can be done in one or two steps,

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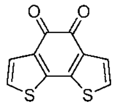
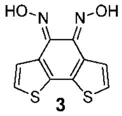
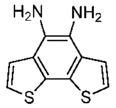
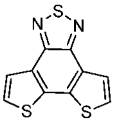
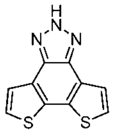
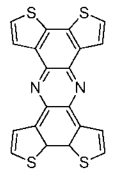
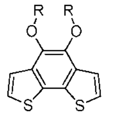
(3) (a) Skotheim, T. A., Reynolds, J. R., Eds. *Conjugated Polymers: Theory, Synthesis, Properties, and Characterization (Handbook of Conducting Polymers)*, 3rd ed.; CRC Press LLC.: Boca Raton, FL, 2007. (b) Wynberg, H.; Sinnige, H. J. M. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1244. (c) Letizia, J. A.; Cronin, S.; Ortiz, R. P.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *Chem.—Eur. J.* **2010**, *16*, 1911. (d) Mondal, R.; Becerril, H. A.; Verploegen, E.; Kim, D.; Norton, J. E.; Ko, S.; Miyaki, N.; Lee, S.; Toney, M. F.; Bredas, J.-L.; McGehee, M. D.; Bao, Z. *J. Mater. Chem.* **2010**, *20*, 5823. (e) Getmanenko, Y. A.; Risko, C.; Tongwa, P.; Kim, E.-G.; Li, H.; Sandhu, B.; Timofeeva, T.; Bredas, J.-L.; Marder, S. R. *J. Org. Chem.* **2010**, *76*, 2660.

(4) (a) Khor, E.; Ng, S. C.; Li, H. C.; Chai, S. *Heterocycles* **1991**, *32*, 1805. (b) Nicolas, Y.; Blanchard, P.; Roncali, J.; Allain, M.; Mercier, N.; Deman, A.-L.; Tardy, J. *Org. Lett.* **2005**, *7*, 3513. (c) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034. (d) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144.

(5) Babudri, F.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron Lett.* **1995**, *36*, 7305.

and without requiring laborious purifications, hence demonstrating the versatility of the aromatic dione BDTD.

Table 1. Various Chemical Transformations for BDTD

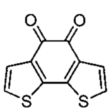
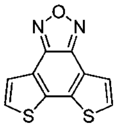
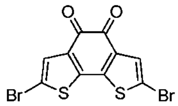
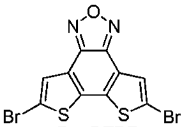
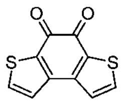
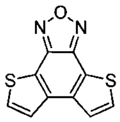
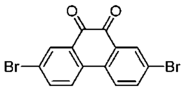
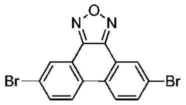
	dione	reaction conditions	product
1	 **BDTD**	i) $NH_2OH\cdot HCl$ EtOH, reflux, 36 h 74%	 **3**
2	**BDTD**	(i), then ii) Pd/C, N_2H_4 *one pot* 70%	 **BDTDA**
3	**BDTD**	(i) and (ii), then iii) S_2Cl_2, DMF, 2 h 82%	 **DT-BTD**
4	**BDTD**	(i) and (ii), then iii) $NaNO_2$(aq), AcOH 75%	 **DTBT**
5	**BDTD**	BDTDA, EtOH, AcOH 88%	 **TTPA**
6	**BDTD**	iv) Zn, Ac_2O, Et_3N, DCM v) Cs_2CO_3, R-Br, ACN 87% R = Octyl 70% R = (2-Ethyl)hexyl	 **BDT(OR)$_2$**

Treatment of **BDTD** with hydroxylamine–hydrochloride yielded dioxime **3**; use of other reagents, including methanolic or aqueous hydroxylamine solutions and hydroxylamine hydrochloride–base did not yield **3**. Compound **3** was treated with palladium on carbon and hydrazine to produce benzo[1,2-*b*:6,5-*b*′]dithiophene-4,5-diamine, BDTDA, and as shown in Table 1 (entries 3–5), this is an interesting derivative that can be further derivatized to generate new molecules such as dithieno[3′,2′:3,4;2″,3″:5,6]benzo[1,2-*c*][1,2,5]thiadiazole (DT-BTD), 2*H*-dithieno[3′,2′:3,4;2″,3″:5,6]benzo[1,2-*d*][1,2,3]triazole (DTBT) and tetrathieno[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (TTPA). It is noteworthy that DT-BTD can also be synthesized by reacting the dioxime **3** and sulfur monochloride in DMF,[6] but this reaction condition leads to a mixture of two products, the thiadiazole and the oxadiazole derivatives.

During the synthesis of the dioxime **3**, the formation of an additional product was observed, and in a further investigation of this reaction, we found that this product corresponded to the dithieno[3′,2′:3,4;2″,3″:5,6]benzo[1,2-*c*]furazan (DTBF). Acceptable yields for the formation of DTBF can be achieved if the reaction is carried out for 10 days under refluxing conditions or in 3 days when run in a pressure vessel at 140 °C (Table 2, entry 1). Table 2 summarizes the results of this reaction and its application to analogue molecules.

Electrochemical experiments on DTBF showed HOMO and LUMO energy values of −6.36 and −3.13 eV respectively, and in the case of *iso*-DTBF these values were HOMO = −6.65 eV and LUMO = −3.25 eV. Thus, based on this and other preliminary data (see UV–vis and electrochemistry in the Supporting Information), we propose that these molecules will perform as acceptor moieties in π-conjugated materials. Therefore, the furazan derivatives, along with those shown in Table 1, will be investigated as donor and acceptor building blocks for π-conjugated oligomers and polymers.

Table 2. Synthesis of Furazan-Based Acceptors

	diketone	reaction conditions	product
1	 **BDTD**	i) $NH_2OH\cdot HCl$ EtOH, reflux, 10 days or 140 °C, 72 h[a] 60%	 **DTBF**
2	 **Br$_2$-BDTD**	(i) 140 °C, 72 h[a] 62%	 **Br$_2$-DTBF**
3	 ***iso*-BDTD**	(i) 140°C, 48 h[a] 48%	 ***iso*-DTBF**
4		(i) 120 °C, 72 h[a] 81%	 **Br$_2$-PF**

[a] Reaction was carried out in a glass pressure vessel.

A plausible mechanism for the formation of DTBF is presented in Scheme 3. As was mentioned before, the dioxime **3** only formed when hydroxylamine hydrochloride was employed. As such, the acid plays an important role in the mechanism, not only in the formation of the dioxime but also in its tautomerization and further dehydration to form DTBF. It can be assumed that the tautomerization is favored due to aromatization of the central phenyl ring.

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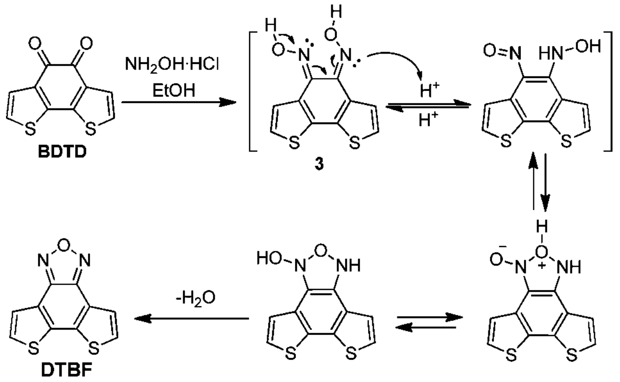
(6) Weinstock, L. M.; Davis, P.; Handelsman, B.; Tull, R. J. *J. Org. Chem.* **1967**, *32*, 2823.

Scheme 3. Proposed Mechanism for Formation of DTBF

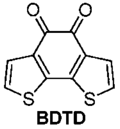
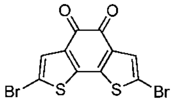
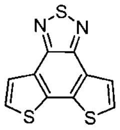
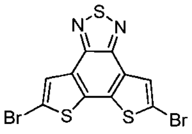
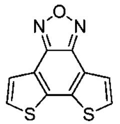
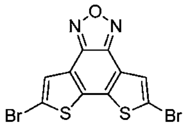


The bromination conditions for various molecules presented in Table 1 are summarized in Table 3. The bromination of BDTD can be carried out in high yield by employing NBS in DMF at 65 °C, and brominations for DT-BDTD and DTBF were carried out in high yield using bromine and chloroform.

Currently, we are pursuing the synthesis of a BDTD analogue containing solubilizing alkyl chains, and also applying the transformations presented in this communication to other fused-aromatic diones. In addition, we are including these moieties in π-conjugated oligomers and polymers.

In summary, we have shown a straightforward synthetic path toward BDTD and how this aromatic dione can be derivatized to produce various acceptor and donor molecules by relatively simple synthetic methodologies. This scientific contribution can help the continuous development of the π-conjugated polymer field given that access to novel donor and acceptor molecules is vital to generate new π-conjugated materials with improved physical and electronic properties.

Table 3. Bromination of BDTD, DT-BTD, and DTBF

	substrate	brominating conditions yield	Product
1	 **BDTD**	DMF, NBS, 65 °C 96%	 **Br_2-BDTD**
2	 **DT-BDTD**	chloroform/Br_2 reflux 91%	 **Br_2-DT-BTD**
3	 **DTBF**	chloroform/Br_2 reflux 89%	 **Br_2-DTBF**

Acknowledgment. We gratefully acknowledge the DOE (DE-FG-02-96ER14617) for the funding for this project. Dr. Dan Patel and Dr. Chad Amb are also acknowledged for their helpful scientific discussions.

Supporting Information Available. Experimental procedures and spectral data for relevant compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.