Tetrahedron Letters 57 (2016) 2608–2611

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Single precursor for the synthesis of donor and acceptor units of the low band gap polymers: synthesis of benzodithiophene and thienopyrroledione from maleic anhydride

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ARTICLE INFO

Article history:
Received 10 February 2016
Revised 28 April 2016
Accepted 29 April 2016
Available online 30 April 2016

Keywords:
Maleic anhydride
Dimethyl thiophene-3,4-dicarboxylate
Benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT)
Thieno[3,4-*c*]pyrrole-4,6-dione (TPD)
Donor–acceptor conjugated polymers

ABSTRACT

An efficient route was developed to synthesize dimethyl thiophene-3,4-dicarboxylate from maleic anhydride. Dimethyl thiophene-3,4-dicarboxylate was used as a single precursor for synthesis of benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) and Thieno[3,4-*c*]pyrrole-4,6-dione (TPD) derivatives. BDT and TPD derivatives have been highly exploited as donor and acceptor units, respectively, to synthesize important donor–acceptor (D–A) conjugated polymers. BDT-based polymers were found to be one of the most efficient conjugated polymers for organic photovoltaic application. Synthesis of quinone precursor of the dihydroxybenzothiophene was accomplished by a new and unconventional methodology which includes reaction of 3,4-thiophene dicarboxylate with sodium hydride in THF. Dithienobenzoquinone dicarboxylate and dihydroxybenzodithiophene dicarboxylate were characterized structurally by single-crystal X-ray diffraction. Both compounds show strong π-stacking interaction and arrange in the parallel molecular sheets in the crystals.

Introduction

Conjugated polymers have attracted significant research interest because of their applications in organic electronic devices such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs).[1] Among them organic photovoltaic devices are often seen as inexpensive, greener, and renewable alternate energy sources to that of the conventional ones.[2] The light weight, flexibility and ability to cast them over large area are described as their advantages.[3]

The donor–acceptor concept[4] has been greatly exploited in the conjugated polymers to tune the electronic and structural properties.[5] The thiophene-fused ring systems in the conjugated polymer backbone possess several advantages. Such thiophene-fused conjugated systems exhibit extended π-conjugation along with structural rigidity in the conjugated polymer. These factors improve the intermolecular interaction in the solid films as well as lower the band gap of the polymers. The flat π-systems improve charge transport properties as well as they increase quinoidal character of the conjugated systems which leads to lowering of the bandgap. Benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) are examples of thiophene-fused ring systems which are among the most explored building blocks of conjugated polymers.

BDT-based molecules have emerged as prominent building blocks for conjugated systems in the number of organic electronic applications.[6] Initially, these conjugated systems were used as active materials in OFETs.[7,8] In recent years, these building blocks were used to construct donor conjugated systems for OPV devices.[9,10] The power conversion efficiencies of the OPV devices using conjugated systems comprising BDT unit have exceeded 8%.[11,12] Conjugated systems comprising the symmetric, rigid, and highly planar BDT unit showed better charge mobility due to presence of efficient π-stacking interaction. Alkoxy substituents at the 4,8-positions of BDT improve the solubility of the resulting polymers without steric hindrance in the conjugation. Recently two dimensional conjugations on BDT units have been reported where the BDT has been functionalized through two perpendicular directions.[13] TPD has been considered as an excellent acceptor unit in the synthesis of low band gap polymers.[14] TPD have distinct benefit of lower energy bands resulted from stabilization energy acquired from the formation of a quinoidal thiophene-maleimide species in their excited state. *N*-Substitution of alkyl groups

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http://dx.doi.org/10.1016/j.tetlet.2016.04.114
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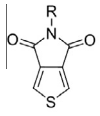
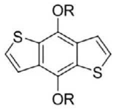
increases in solubility while the rigidity enhances the favorable solid state arrangement.[15]



TPD



BDT

There are only few methods reported in the literature to synthesized BDT and TPD. BDT have been synthesized from *p*-benzoquinonedithiophene, whereas TPD has been synthesized from thiophene-3,4-dicarboxylic acid. Synthetic methods for BDT and TPD are multistep. Here we report the synthesis of BDT (donor unit) and TPD (acceptor unit), two important building blocks for the conjugated polymers, from a single precursor, dimethyl thiophene-3,4-dicarboxylate (**6**). This compound (**6**), in turn, was synthesized from maleic anhydride.

Results and discussion

Synthesis of compound **6** was accomplished in six steps from maleic anhydride as shown in Scheme 1. The maleic anhydride was converted to 2,3-dimethyl maleic anhydride (**1**) following the reported procedure.[16] Compound **1** was further converted into 2,3-dimethyl dimethyl maleate (**2**).[17] The bromination of compound **2** was carried out by NBS and benzoyl peroxide as initiator.[18] Dibromo compound **3** was cyclized to dimethyl 2,5-dihydrothiophene-3,4-dicarboxylate (**4**) using sodium sulfide in THF as solvent at room temperature. Aromatization of compound **4** was accomplished by oxidation and followed by dehydration. Compound **4** was oxidized using *m*-CPBA to afford sulfoxide **5** and further dehydrated using acetic anhydride to afford compound **6**. This synthetic pathway to synthesize compound **6** is simple with an overall good yield of 32%.

The traditional route to synthesize thiophene-3,4-dicarboxylic acid includes the Rosenmund–von Braun Reaction.[19] The overall five step reaction strategy of the synthesis of thiophene-3,4-dicarboxylic acid mainly involves reaction of 3,4-dibromothiophene with toxic cuprous cyanide affording expected compound in moderate yields. The Gewald reaction was used as the another strategy to synthesize 3,4-thiophene dicarboxylate derivatives.[20] Recently, Leclerc and coworkers have synthesized 3,4-thiophene dicarboxylate using the Gewald reaction followed by the Sandmeyer reaction to extrude the amino group.[21] This procedure has been regarded as a cheap and efficient method to synthesize 3,4-thiophene dicarboxylate.

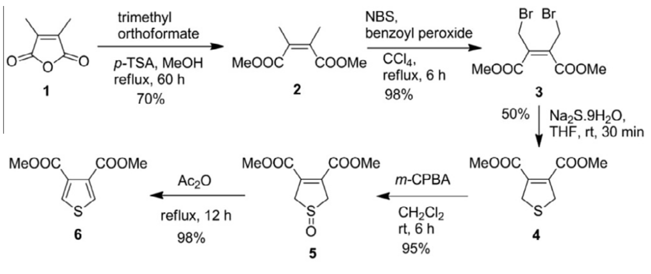
Synthesis of 3,7-dimethyl-4,8-dihydrobenzo[1,2-*b*:4,5-*b*′]dithiophen-4,8-dione-dicarboxylate (**7**), a precursor to dihydoxy benzodithiophene **9**, was accomplished by new and unconventional approach. Compound **7** was obtained by treating compound **6** with an excess of sodium hydride under refluxing condition in dry THF for 15 h in 89% yield. The plausible mechanism of the formation of compound **7** may include the abstraction of α-H of compound **6** to form carbanion which reacts with carboxylate group of another molecule of compound **6** to cyclize into the *p*-benzoquinone moiety. Most common route to synthesize *p*-benzoquinonedithiophene comprises 3-thiophene carboxylic acid as starting material.[22] After functionalization of thiophene carboxylic acid into amide, *p*-benzoquinonedithiophene was obtained by treating resulting amide with *n*-BuLi at low temperature. In the synthesis of compound **7**, NaH effectively works as base due to presence of two electron-withdrawing carboxylate groups in compound **6**, which, in turn, increase the acidity of α-H of compound **6**. Compound **7** can be used as precursor to obtain many benzodithiophene derivatives. Additionally, the carboxylate groups may play an important role in controlling conformation by nonbonding interactions in the resulting conjugated systems.[23] The electron-withdrawing carboxylate substituents as the side chains are known to lower the HOMO level of the conjugated systems with minor effect on the optical bandgaps.[24]

The diester **7** was hydrolyzed with aqueous NaOH to afford dicarboxylic acid **8**, which subsequently aromatize and decarboxylated by heating with Cu/quinolone to afford dihydroxy benzodithiophene **9**. When compound **7** was treated with aqueous NaOH solution in presence of Zn powder, it afforded dihydroxy benzodithiophene dicarboxylic acid (**10**). Interestingly, when compound **7** was stirred with excess of NaH in ethyl acetate, aromatization with trans-esterification occurred to afford dicarboxylate (**11**) (Scheme 2).

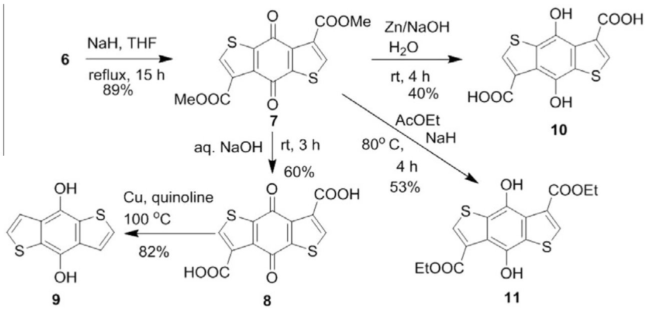
Absorption spectra of **7**, **8**, **10,** and **11** showed three distinct absorption peaks. Compound **7**, **8**, **10,** and **11** showed π–π* absorption peaks at 332, 368, 403, 407 nm, respectively (Figs. S8–S12). Electrochemical experiments were conducted on compound **8** and compound **11** by cyclic voltammetry (CV). Both the compounds **8** and **11** showed oxidation peaks at 0.87 and 0.91 V versus Ag/Ag$^+$, respectively (Figs. S13 and S14). Compound **8** showed reduction peak at 0.5 V versus Ag/Ag$^+$.

TPD was synthesized from compound **6** in three steps, which mainly includes hydrolysis of dimethyl thiophene-3,4-dicarboxylate in aqueous NaOH solution followed by its reaction with oxalyl chloride to form diacid dichloride and its subsequent reaction with alkyl amine (Scheme S1, ESI). Similar methodology can be employed to synthesis of 5-alkyl-thieno[3,4-*f*]-isoindole-5,7-dione (TID).[25] Thieno[3,4-*c*]pyrrole-4-6-dione (TPD) has been synthesized in literature from 3,4-thiophenedicarboxylic acid and amine condensation reaction.[26]

Crystals of compound **7** and **11** suitable for single crystal X-ray diffraction were obtained by slow evaporation of saturated solution in hexane. The compound **7** was crystallizing with triclinic crystal packing system with space group P-1. Molecular structure of compound **7** possess center of symmetry. The unit cell of



Scheme 1. Synthesis of thiophene-3,4-dicarboxylate.



Scheme 2. Synthesis of benzodithiophene derivatives.

compound **7** contains two non symmetric equivalent molecules (Fig. 1a). These two molecules differ in the dihedral angle between the plane of benzodithiophene plane and carboxylate group. Compound **7** shows π-stacking (C4···C10, 3.346 (3) Å) and intermolecular CH···O interaction (H4···O5, 2.479; H4···O6, 2.610 Å). These interactions resulted in the formation of 1-dimensional molecular sheets along *a*-axis.

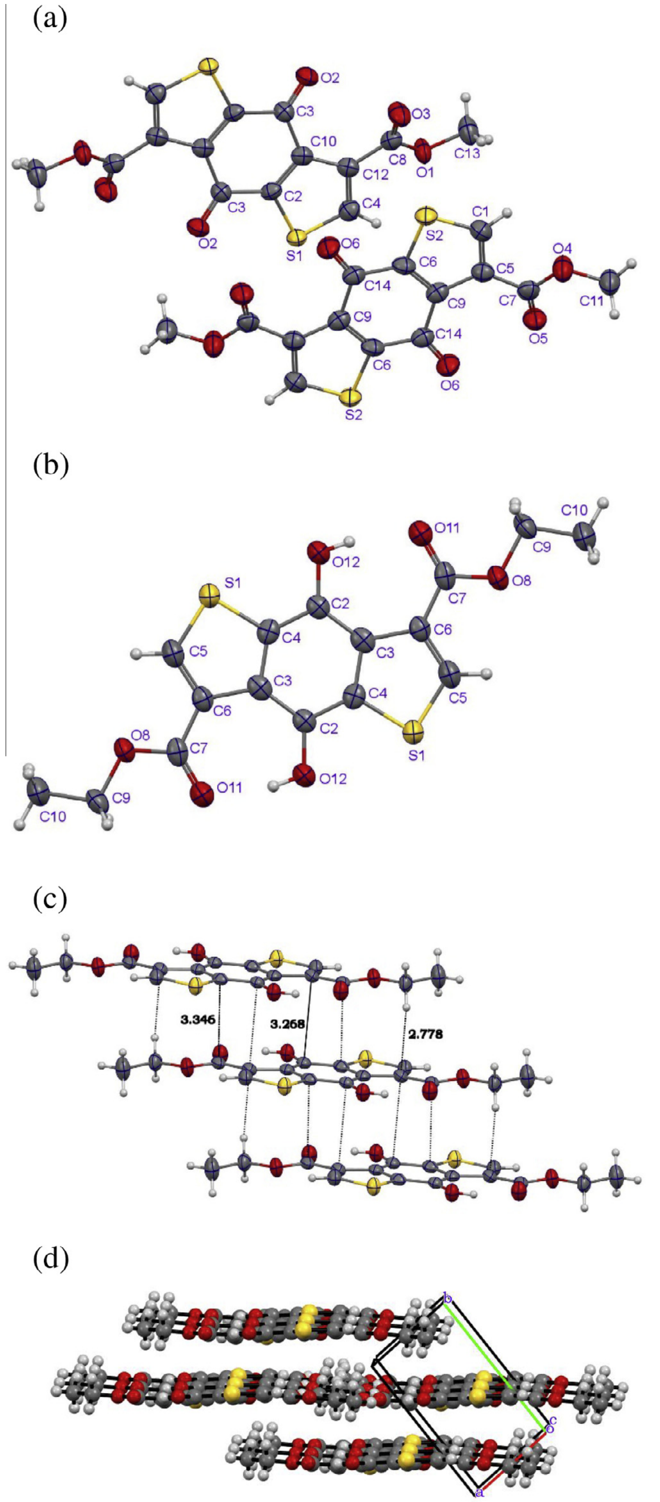


Figure 1. ORTEP diagram of compound (a) **7** and (b) **11** (ellipsoids are drawn at the 50% probability level). Packing diagram of **11** (c) showing π-stacking and CH···π interactions and (d) formation of parallel 1-D molecular sheets.

Compound **11** crystallizes in P-1 space group. In the structure of **11**, molecules possess center of symmetry (Fig. 1b). Because of intramolecular hydrogen bonding between phenolic OH and C=O of carboxylate group (O11–H12, 1.80 Å; O12–H12···O11, 166.4°) compound **11** adopts nearly planar geometry (except H of COOEt groups). Compound 11 exhibits strong π-stacking (C2–C6′, 3.268 (3) Å; C4–C7′, 3.346 (3) Å), CH···π (H9B···C6, 2.778 Å) and intermolecular CH···O (H9A···O12, 2.642 Å) interactions to form π-stacked molecular chain along *a*-axis (Fig. 1c and d). Molecules form one dimensional sheet along *c*-axis with interlayer distance of 3.326 Å (Figs. S1–S7, ESI).

Conclusion

In summary, dimethyl thiophene dicarboxylate, which is very important precursor for conjugated polymers, was synthesized from maleic anhydride in simple six-step synthetic pathway involving mild reagents and in moderate yields. Thiophene-3,4-dicarboxylate is one of the important precursors for many important thiophene derivatives for the conjugated polymers. Dimethyl thiophene dicarboxylate diester obtained was successfully converted into TPD and BDT which were useful building blocks for π-conjugated polymer. 3,7-Dimethyl-4,8-dihydrobenzo[1,2-*b*:4,5-*b*′]dithiophen-4,8-dione-dicarboxylate (**7**), a derivative of BDT was synthesized directly from dimethyl thiophene dicarboxylate in one step. This procedure was further use to synthesize more variant of BDT.

Acknowledgments

V.S.K. acknowledges DST-PURSE program for fellowship. A.L.P. acknowledges GUJCOST for financial support. S.S.Z. acknowledges CSIR, India for funding.

Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra, FT-IR spectra of compounds **2**–**11**; crystal data of compounds **7** and **11**. UV absorption spectra of compounds **4**, **7**, **11**, **8** and **10**. CV curves of compounds **8** and **11**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.04.114.

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