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Dithienothiophenes

Turan Ozturk,[a,*] Erdal Ertas[b] and Olcay Mert[c]

[a]*Organic Chemistry, Chemistry Department, Science Faculty, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey*
[b]*Tubitak, Marmara Research Centre, FSTRI, 41470 Gebze-Kocaeli, Turkey*
[c]*Organic Chemistry, Department of Chemistry, Middle East Technical University, Ankara, Turkey*

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Abbreviations: CA, chloranil; CV, cyclic voltammetry; DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; DMeDTT, dimethyldithienothiophene; DMF, *N*,*N*-dimethylformamide; ESR, electron spin resonance; LDA, lithium diisopropylamide; LED, light-emitting devices; LR, Lawesson's reagent; *m*CPBA, 3-chloroperoxybenzoic acid; NBS, *N*-bromosuccinimide; NMP, *N*-methylpyrrolidine; pDTDP, poly(dithienothiophene–dithienopyrrole); pDTT, polydithienothiophene; PPA, polyphosphoric acid; pT, polythiophene; pTT, polythienothiophene; TCNEO, tetracyanoethylene oxide; TCNQ, 7,7,8,8-tetracyano-*p*-quinodimethane; TFA, trifluoroacetic acid; TFT, thin-film transistor; TMS, trimethylsilyl; TTF, tetrathiafulvalene.

* Corresponding author. Tel.: +90 212 285 69 94; fax: +90 212 285 63 86; e-mail: ozturktur@itu.edu.tr

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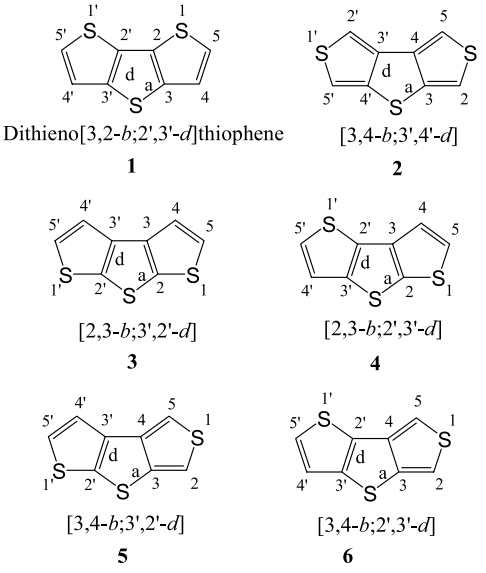
1. Introduction

Dithienothiophenes (DTT) possess three fused thiophene rings, the orientations of which vary depending on the locations of the sulfur atoms of the peripheral thiophenes. Six isomers, dithieno[3,2-*b*;2′,3′-*d*]thiophene **1**, dithieno[3,4-*b*;3′,4′-*d*]thiophene **2**, dithieno[2,3-*b*;3′,2′-*d*]thiophene **3**, dithieno[2,3-*b*;2′,3′-*d*]thiophene **4**, dithieno[3,4-*b*;3′,2′-*d*]thiophene **5**, and dithieno[3,4-*b*;2′,3′-*d*]thiophene **6** can be depicted and all have appeared in the literature.

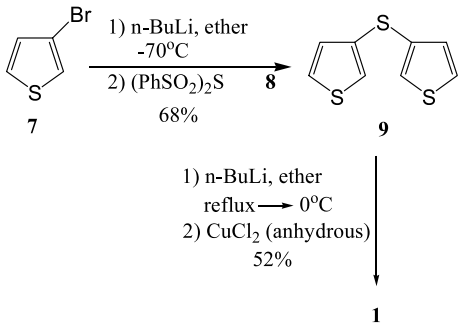
Due to their interesting electrochemical and optical properties, dithienothiophenes have been receiving increasing attention. As these compounds are rich in sulfur, with three S atoms, they are electron rich species, which makes them good electron donors and important building blocks of a wide variety of materials for electronic and optical applications such as electroluminescence, two-photon absorption, excited fluorescence, photochromism, nonlinear optical chromophores, transistors with high mobilities of on/off ratios, conducting polymers and charge-transfer complexes. Easy oxidation of the thiophene sulfur of the middle ring gives the molecules property of fluorescence, which makes them good candidates for labelling, particularly important for biological systems.



2. Dithieno[3,2-*b*; 2′,3′-*d*]thiophene 1

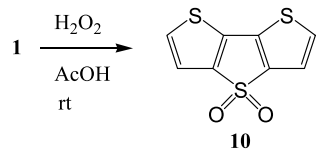
2.1. Methods for synthesizing the ring system

Although the first synthesis of **1** was claimed earlier, no spectroscopic data were reported.[1] In 1971, Jong and Janssen published its first synthesis with spectroscopic data.[2] The crystal structures of **1** and its charge-transfer complex with TCNQ were reported in 1983.[3] Jong and Janssen's synthesis started with lithiation of 3-bromothiophene **7** with *n*-BuLi at −70 °C, which was followed by addition of bis(phenylsulfonyl)sulfide **8** to afford 3,3′-dithienyl sulfide **9**. This was then dilithiated with *n*-BuLi and subjected to oxidative ring closure using $CuCl_2$ to afford **1**, (Scheme 1).



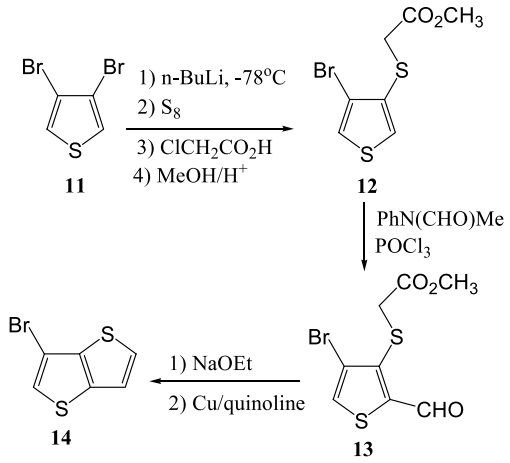
Scheme 1. First synthesis of dithienothiophene **1**.

Conversion of the dithienothiophene **1** into the corresponding dioxide **10** was performed by oxidation of the sulfur of the central thiophene to the sulfone with hydrogen peroxide, which yielded **10** in good yield (Scheme 2).



Scheme 2. Oxidation of **1**.

The second method of synthesis appeared in 1989 with the preparation of two higher homologues **17** and **19**, which contain four and five linearly condensed thiophenes.[4,5] The key intermediate bromothienothiophene **14** was synthesized starting from 3,4-dibromothiophene **11**, which was converted into **12** in a one-pot four-step reaction: (i) lithiation with *n*-BuLi; (ii) addition of sulfur; (iii) reaction with α-chloroacetic acid and (iv) esterification with methanol (Scheme 3). It was then formylated using methylphenylformamide/phosphorus oxychloride, which gave 2-formylthiophene **13**. Treatment of **13** with sodium ethoxide formed bromothienothiophenecarboxylic acid, and the carboxylic acid was removed by using Cu to afford the key intermediate bromothienothiophene **14**.



Scheme 3. Synthesis of higher homologues of **1**.

The thienothiophene **14** was initially treated with *n*-BuLi and then with the dithienyl disulfide **15** to obtain **16**, which was converted into the tetrafused thiophene **17** by oxidative ring closure, using *n*-BuLi and then $CuCl_2$. The X-ray crystal structure of **17** has also been reported (Scheme 4).[6] The fused pentathiophene **19** was obtained in a similar fashion using bis(phenylsulfonyl)sulfide **8** in place of the dithienyl disulfide **15** to provide a sulfur bridge between two thienothiophenes and, after an oxidative coupling of **18**, the fused pentathiophene **19** was obtained in 15–20% yield.