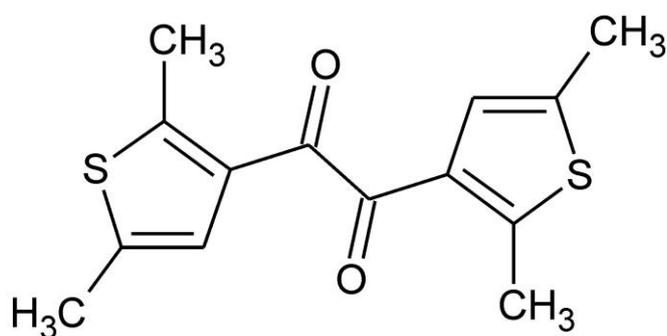
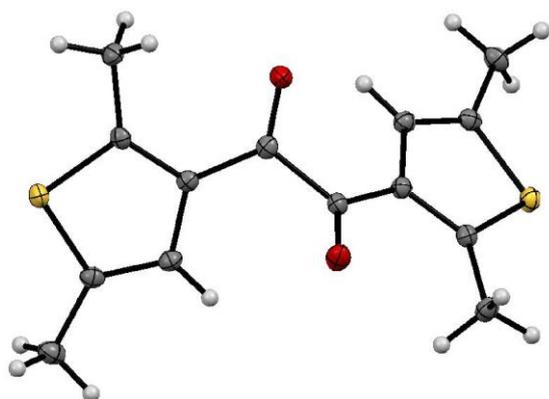




Preparation and crystal structure of 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione

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Introduction

1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione is a convenient starting material for the synthesis of various photoactive organic molecules that belong to the group of diarylethenes (dae).[1] Diarylethenes exhibit a reversible photocyclisation-induced photochromism, photoswitching behavior and memory effects.[1,2] Greater stabilization of the closed-form photocyclisation product, leading in general to improved photochromic properties, can be achieved by the modification of the diarylethene backbone – bis(2,5-dimethylthiophen-3-yl) perfluorocyclopentene is perhaps the most recognizable example of such an approach[3].

The title compound can be obtained in a Friedel-Crafts acylation of 1,2-dimethylthiophene with oxalyl chloride in the presence of metal chlorides such as AlCl_3 or TiCl_4 . [4] Herein, we report the use of ZrCl_4 as the catalyst, leading to slightly higher yield. We also report for the first time the crystal structure of 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione. Crystals suitable for the single-crystal X-ray diffraction (sc-XRD) experiments were obtained by a careful evaporation of a diethyl ether solution of the title compound.

Results and discussion

1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione crystallizes in a monoclinic $C2/c$ space group. The details of the sc-XRD experiment can be found in the cif file deposited with the CSD database (deposition number CCDC 1895209, DOI: 10.5517/ccdc.csd.cc21m3sl). The asymmetric unit consisting of one and a half of 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione molecules is presented in Figure 1. Both molecules exhibit a *trans* geometry with the $\text{O}=\text{C}-\text{C}=\text{O}$ torsion angle of 121° and 124° , respectively. Selected bond lengths are summarized in Table 1 and correspond well with those of thiophene moiety or carbonyl groups.

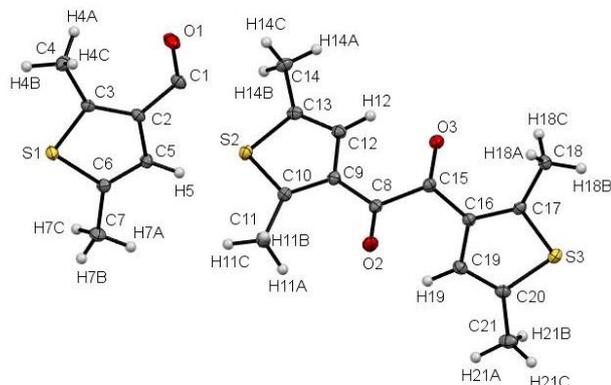


Figure 1. ORTEP representation of the asymmetric unit of 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione with atom labeling scheme

Table 1. Selected bond lengths in 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione

Bond type	Length / Å
C1–C1	1.540
C8–C15	1.542
C1=O1	1.224
C8=O2	1.223
C15=O3	1.227
S1–C3	1.720
S1–C6	1.733
S2–C10	1.721
S2–C13	1.735
S3–C17	1.715
S3–C20	1.734

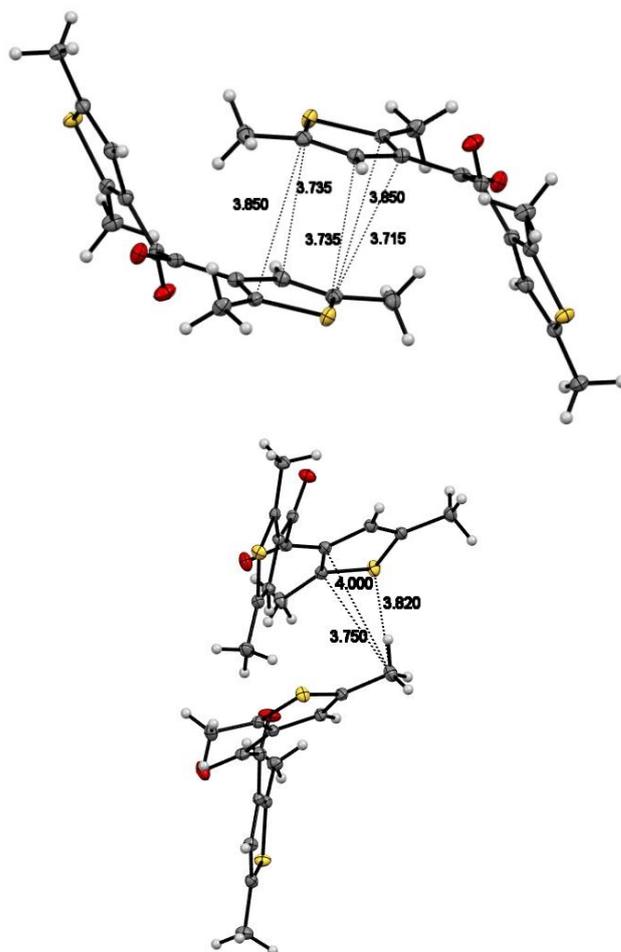


Figure 2. π - π (top) and CH/π (bottom) contacts in the crystal structure of 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione

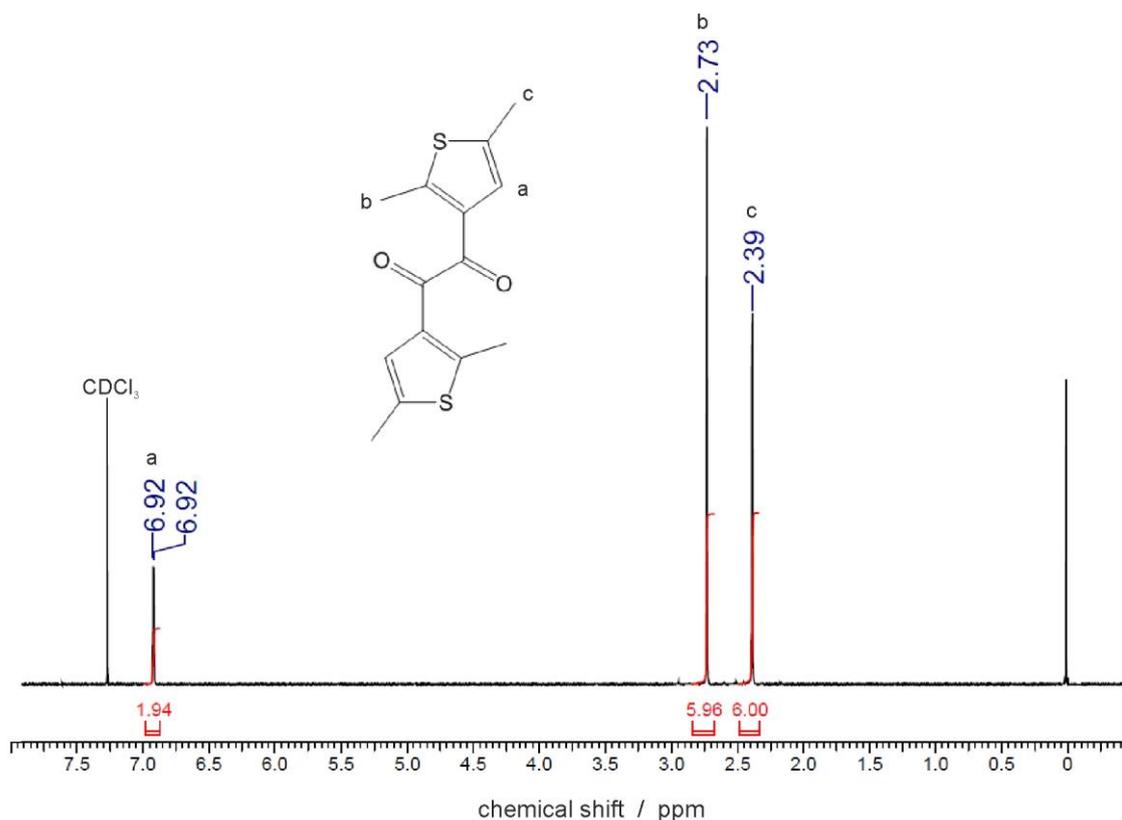


Figure 3. ^1H NMR spectrum of 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione in CDCl_3 at room temperature

Crystal packing of the title compound is defined by weak π - π and CH/π intermolecular contacts. Each molecule forms two π - π contacts with two adjacent molecules. These contacts involve the thiophene rings and the average C-C distance is ca. 3.8 Å. Each two molecules form also two CH/π interactions between the thiophene ring carbon atoms and the methyl group carbon atom of the other molecule with the C-C distance of ca. 3.9 Å (Figure 2). Both interactions must be quite weak if we consider the shortest CH/π distances to be around 2.8-3.1 Å and the shortest π/π contacts around 2.6-2.8 Å.[5]

Experimental

2,5-dimethylthiophene (0.85 ml, 7.50 mmol, Aldrich) was dissolved in 15 ml of dichloromethane (DCM) and chilled to -20°C . A solution of oxalyl chloride (0.225 ml, 2.85 mmol, Aldrich) in 15 ml of DCM was added and the reaction flask was flushed with argon. Zirconium(IV) chloride (1.00 g, 4.27 mmol) was then added in one portion and the flask was flushed with argon again. The reaction was carried out at -20 to 0°C for 75 minutes. It was poured on 20 ml of ice and the organic phase was separated. The aqueous phase was extracted with three 50 ml portions of chloroform. The combined organic extracts were washed with 20 ml of water, saturated sodium carbonate solution and water again, dried over anhydrous magnesium sulfate and evaporated to a red oil. The crude product was purified by column chromatography (SiO_2 , petroleum ether 60:90/ethyl acetate/chloroform 20:2:1) to afford the title compound as a bright yellow oil (358 mg) in nearly 50% yield. The purity and identity of the compound was confirmed by ^1H NMR in

CDCl_3 : δ [ppm] 6.92 (m, 2H) 2.73 (s, 6H) 2.39 (m, 6H) (Figure 3).

If the oil is dissolved in ca. 10 ml of diethyl ether and slowly evaporated, yellow prism crystals suitable for single-crystal X-ray diffraction are obtained.

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