

## NOTE

### Solvent Evaporation Method and Crystal Structure of Thiophene-2,3-dicarboxylate

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Received: 20 February 2014;

Accepted: 21 May 2014;

Published online: 10 January 2015;

AJC-16665

One new thiophene compound *i.e.*, thiophene-2,3-dicarboxylate with 2,3-dibromo thiophene, butyllithium and anhydrous ether has been successfully synthesized. The compound has been characterized by X-ray single-crystal diffraction. The new synthesized compound shows a one-dimensional framework. The 3D supramolecular structure is formed *via* hydrogen bonding connection.

**Keywords:** Solvent evaporation, Crystal structure; Thiophene-2,3-dicarboxylate.

Thiophenes and their derivatives have been of interest for use in next generation electronic materials owing to their ease of production, synthetic versatility and low cost compared to traditional inorganic materials<sup>1</sup>. Until now, there are a few examples of thiophenes derivatives which have been synthesized and characterized<sup>2,3</sup>. As part of our work, we report the synthesis and crystal structure of the title compound.

All reagent and solvents employed were commercially available and used as received without further purification.

To a stirred suspension of ethereal butyllithium (0.4 mol) at 203 K was added 2,3-dibromo thiophene (30.5 g, 0.126 mol) over 5 min. The mixture was stirred at 203 K for 0.5 h and then poured slowly into a slurry of dry ice in anhydrous ether. After 3 h, water (200 mL) was added to the ethereal suspension. The aqueous layer was separated and the ether layer was extracted several times with water. The combined aqueous phase was washed with ether and then warmed to remove dissolved ether. After cooling to 298 K, a small amount of a solid was filtered off. The filtrate was acidified to pH 1 with concentrated HCl and immersed in an ice-water bath. After several hours the solid was filtered off. Colourless crystals of the compound formed (Fig. 1).

**Detection method:** Diffraction intensity data of the single crystal of the compound was collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using a  $\omega$ -scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  using the program SHELXL 97<sup>4</sup>. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrical calculations and their positions and thermal parameters

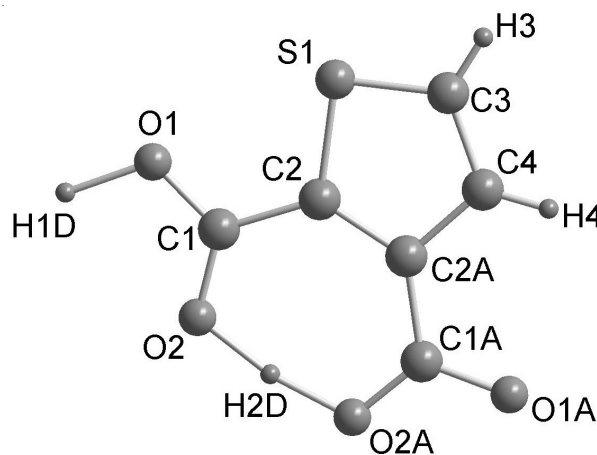


Fig. 1. Molecular structure of the title compound at 30 % probability displacement ellipsoids

were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table-1. Selected bond and angle parameters are listed in Table-2.

X-ray diffraction analysis revealed that the fundamental building unit consists of the title compound, C-6-H-3-O-4-S-1-, crystallizes in a orthorhombic Pbcn space group, with four molecules in the unit cell. The asymmetric unit of the crystal structure is build up of one molecule. On the thiophene ring, the hydrogen atoms were assigned with  $U_{iso}(H) = 1.2 \text{ Ueq}(C)$  and included in the final refinement by using geometrical restraints, with  $d(C-H) = 0.93 \text{ \AA}$ . The C(1)-O(1) and C(1)-O(2) bond lengths are nearly identical at  $1.269(4) \text{ \AA}$ ,  $1.265(4) \text{ \AA}$ , respectively. The C-C bonds within the thiophene are

TABLE-1  
CRYSTALLOGRAPHIC DATA AND STRUCTURE  
REFINEMENT SUMMARY FOR COMPLEX

Empirical formula	C <sub>6</sub> H <sub>3</sub> O <sub>4</sub> S
Formula weight	171.14
Crystal system space group	Orthorhombic, Pbcn
Unit cell dimensions	a = 6.056(7) Å; b = 14.510(17) Å c = 8.023(9) Å
Volume (Å <sup>3</sup> )	705.0(14)
θ range for data collection	2.81-25.47
Final R indices [I>2σ(I)]	R <sub>1</sub> = 0.0604; wR <sub>2</sub> = 0.1446
Z, calculated density (mg/m <sup>3</sup> )	4, 1.612
Absorption coefficient (mm <sup>-1</sup> )	0.416
F(000)	348
Limiting indices	-6 ≤ h ≤ 7; -17 ≤ k ≤ 17; -9 ≤ l ≤ 7
Largest diff. peak and hole (e/Å <sup>3</sup> )	0.206 and -0.275
Goodness-of-fit on F <sup>2</sup>	1.016
R indices (all data)	R <sub>1</sub> = 0.0793, wR <sub>2</sub> = 0.1537

TABLE-2  
SELECTED BOND LENGTHS (Å)  
AND ANGLES (°) FOR COMPLEX

S(1)-C(3)	1.554(3)	C(1)-O(1)	1.269(4)
S(1)-C(2)	1.687(3)	C(1)-O(2)	1.265(4)
C(4)-C(3)	1.398(6)	C(4)-C(2)	1.435(6)
C(3)-S(1)-C(2)	93.5(2)	C(4)-C(2)-C(1)	124.8(3)
C(3)-C(4)-C(2)	113.0(5)	C(4)-C(3)-S(1)	11.5(3)
O(1)-C(1)-O(2)	120.9(3)	C(4)-C(2)-S(1)	8.0(3)
O(2)-C(1)-C(2)	122.7(3)	C(1)-C(2)-S(1)	116.7(2)

significantly shorter compared to other C-C bonds. The thiophene ring (P1) is almost planar with the maximum deviation of 0.0032 Å for C1. The chains are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 3D framework (Fig. 2).

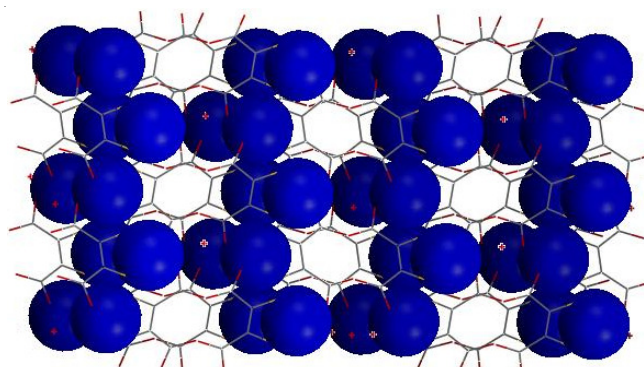


Fig. 2. 3D structure formed via hydrogen bonding interactions

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