

SYNTHESIS AND STRUCTURAL DETERMINATION OF A NEW CHALCONE 1,5-BIS(3-METHYL-2-THIENYL)PENTA-1,4-DIEN-3-ONE, C₁₅H₁₄OS₂

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ABSTRACT

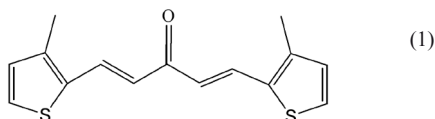
This is a structure in a family concerning new polythiophene derivatives. This kind of compounds, a chalcones, has interesting aspects about its intermolecular interactions, of varied type (C-H···O, C-H···π, π···π) and strength. In the case of the title compound, C₁₅H₁₄OS₂, interactions of all three types generate a rather compact, evenly connected 3D structure.

INTRODUCTION

The electronic and optoelectronic applications of conjugated polymers as organic wide-gap semi-conductors have attracted considerable interest in the last decade. In this field, polythiophenes derivatives are among the most studied because of their potential use in organic light-emitting diodes.¹⁻³

These polymers (used to prepare electroluminescent devices) are obtained through monomer polymerization via electrochemical deposition on indium tin oxide.^{4,5} The polymeric films obtained show photoluminescent emission between 660 and 720 nm and exhibit a turn-on voltage at about 2-4 V. The I-V curves of device have been interpreted by mean tunneling process described by the Fowler—Nordheim theory.^{5,6} The polymeric precursors employed have been a series of heterocyclic α, β⁻unsaturated ketones containing thiophene rings^{4,5,7,8} similar to the molecule reported in this work and it has been studied and characterized by electrochemical and *ab-initio* methods.^{9,10}

Computational studies proved that the conformation of these molecules are the result of the interaction between the electronic pair of the oxygen in the carbonyl group and the heteroatom in the neighboring ring, indicating a favored conformation.¹¹⁻¹³ Electrochemical studies showed the existence of irreversible and asymmetrical peaks. This behavior was explained by the simultaneous oxidation of the heterocyclic rings and the functional groups acting as bridges.¹⁴⁻¹⁶ The reduction of the species involves only the carbonyl groups through a free radical.¹⁷ This process is very close to the reduction mechanism of chalcones proposed in Cassidy & Whitcher¹⁸ and in Tirouflet & Corvaisier.¹⁹



Following our interest in this kind of compounds, mainly directed to their use as potential ligand in further complex development we have synthesized and structurally characterized a new compound in this populous family: 1,5-bis(3-Methyl-2-thienyl)penta-1,4-dien-3-one, C₁₅H₁₄OS₂ (see scheme 1)

EXPERIMENTAL

SYNTHESIS

The compound was synthesized according to Miller & Nord.²⁰

3-methyl-2-thiophenecarboxaldehyde (0.0219 mol) was mixed with acetone (0.0267 mol). The mixture was cooled to 0°C and KOH/Ethanol 20% was slowly added.

The mixture was further stirred by 7 h, it was filtered and washed with ethanol. Pale yellow crystals were obtained from an ethanol/water solution (5:1). The yield was 70%. Elemental Analysis (%) (exp/theo): 65.65/65.66 (C); 5.08/5.14 (H); 5.73/5.83 (O); 23.12/23.37 (S).

The IR spectrum shows the characteristic bands of the functional groups of the compound, but slightly displaced. The molecule is nearly planar and the

conjugation of C=O with a C=C bond result in delocalization of the π electrons in both unsaturated groups, causing absorption at lower wave-numbers; then C=O, 1651cm⁻¹; C=C, 1600cm⁻¹.

STRUCTURE DETERMINATION

The present structure posed no problems for data collection. Hydrogen atoms were placed at calculated positions (C-H: 0.93-0.97 Å) and allowed to ride; methyl groups were allowed to rotate as well. Displacement factors were taken as U(H)isot = x.U(host), x: 1.2-1.5

COMPUTING DETAILS

Data collection: *SMART-NT*;²¹ cell refinement: *SAINT-NT*;²¹ data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97*;²² program(s) used to refine structure: *SHELXL97*;²² molecular graphics: *SHELXTL-NT*;²³ software used to prepare material for publication: *SHELXTL-NT*, *PLATON*.²⁴

RESULT AND DISCUSSION

Figure 1 shows an ellipsoid plot of C₁₅H₁₄OS₂; the molecule consists of two terminal thiophene rings bridged by a penta-1,4-diene-3-one link, in such a way as to have both sulfur atoms in the rings at the same side of the bridge, the carbonyl oxygen being trans to both. **Table 1** shows some crystal data.

The overall group is almost planar, with a slight twist along the bridge axis, leading to a small rotation (16.1(1)%) between the terminal rings. G. Liang et al. has found a similar rotation (5.16(9)°) in a similar but more rigid compound.⁸

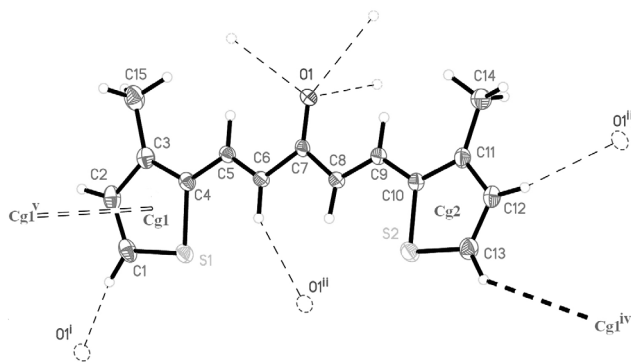


Fig. 1: Molecular diagram of C₁₅H₁₄OS₂. Anisotropic displacement ellipsoids draw at a 40% level. H-bonding interactions with neighboring molecules presented in simple broken, C-H···π bonds in heavy broken, and π-π bonds in double broken lines Symmetry codes, as in **Tables 2 and 3**.

Table 1. Crystal data.

$C_{15}H_{14}OS_2$	$V = 2835.7 (2) \text{ \AA}^3$
$Mr = 274.38$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$
$a = 15.8094 (3) \text{ \AA}$	$\mu = 0.36 \text{ mm}^{-1}$
$b = 7.7683 (6) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 23.0896 (8) \text{ \AA}$	$0.40 \times 0.18 \times 0.15 \text{ mm}$
Data collection	
APEXII, Bruker-AXS diffractometer	2487 independent reflections
Absorption correction: multi-scan SADABS (Sheldrick, 2002 ²⁵)	2119 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.92$, $T_{\max} = 0.95$	$R_{\text{int}} = 0.038$
12351 measured reflections	
Refinement	
$R[F^2 > 2\sigma(F^2)] = 0.040$	165 parameters
$wR(F^2) = 0.100$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$
2487 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Bonds along the bridge are almost theoretical, with differences between equivalent ones being smaller than their respective s.u.'s; slightly larger, though still non significant, differences appear in the thiophene rings.

In fact, in several of similar studied compounds the molecules can be considered featureless and their most appealing details should be looked at their intermolecular interactions, of varied type and strength, leading to different packing schemes. In the present case, oxygen O1 lies in a rather unscreened position (**Fig 1**), favoring its role as a triple H-bond acceptor (**Fig 2**) of three non-conventional C-H...O bonds (**Table 2**, three uppermost entries). These interactions are completed by a C-H... π H-bond (**Table 2**, last entry) as well as π - π contacts (**Table 3**) which connect evenly neighboring molecules to generate a rather compact 3D structure. Other important distances are in **Table 4**.

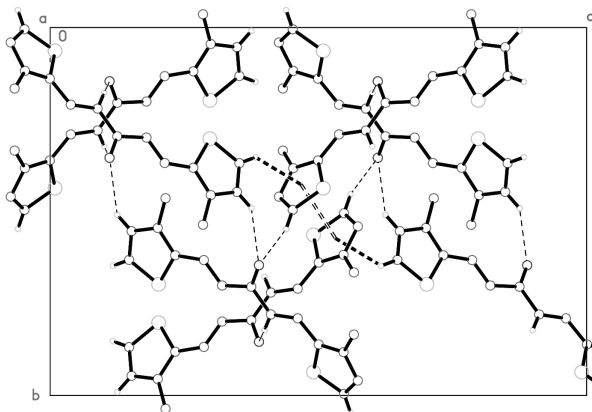


Fig. 2: Packing diagram of the H-bonded 3D structure of $C_{15}H_{14}OS_2$. The interaction codes are the same as in Fig. 1

Table 2. Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1...O1i	0.93	2.35	3.248 (3)	162
C6—H6...O1ii	0.93	2.42	3.213 (3)	143
C12—H12...O1iii	0.93	2.56	3.374 (3)	147
C13—H13...Cg1iv	0.93	2.90	3.683 (3)	141

Symmetry codes: (i) $x+1/2, -y+1/2, -z$; (ii) $-x+1/2, y+1/2, z$; (iii) $-x, y+1/2, -z+1/2$; (iv) $-x+1/2, -y+1, z+1/2$.

Table 3. π - π contacts (\AA , $^\circ$) for $C_{15}H_{14}OS_2$

Compound	Group 1	Group 2	ccd(\AA)	da($^\circ$)	ipd(\AA)
$C_{15}H_{14}OS_2$	Cg1	Cg1v	3.542 (2)	0.00	3.43 (2)

Symmetry codes: (v) $-x, -y, 1 - z$; Cg1: defined in Fig. 1 cc (center-to-center distance): distance between ring centroids; da: (dihedral angle) angle between planar groups; ipd (interplanar distance): mean distance from one plane to the neighbouring centroid. (For details, see Janiak 2000²⁶)

Table 4. Some important distances (\AA) and angles ($^\circ$)

C4-C5: 1,446	C7-O1: 1,241	C1-S1-C4: 91,35
C5-C6: 1,341	C4-S1: 1,749	C10-S2-C13: 91,69
C6-C7: 1,473	C1-S1: 1,715	C6-C7-C8: 117,16
C7-C8: 1,473	C10-S2: 1,743	C6-C7-O1: 121,50
C8-C9: 1,344	C13-S2: 1,718	C8-C7-O1: 121,34
C9-C10: 1,439		

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REFERENCES

- Lee, C., Kim, K. J. & Rhee, S. B. *Synth. Met.* **69**, 295-296 (1995).
- Diaz, F. R., del Valle, M. A. & Brovelli, F. *J. Applied Polymer Science*, **89**, 1614-1621(2003).
- Nguyen, T. P., Molinie, P. & Destruel, P. (2000). Handbook of Advanced Electronic and Photonic Materials and Devices; Nalwa, H.S., Ed; Academia: San Diego
- Brovelli, F., Del Valle, M. A., Diaz, F. R. & Bernede, J. C. *Bol. Soc. Chil. Quim.* **46**, 319 (2001a)
- Brovelli, F., Bernede, J. C., Marsillac, S., D az, F. R., del Valle, M. A. & Beaudouin, C. *J. Applied Polymer Sci.* **86**, 1128-1137 (2002).
- Fowler, R. H. & Nordheim, L. *Proc. R Soc Lond A*, **119**, 173-181 (1928).
- Diaz, F. R., del Valle, M. A. & Brovelli, F. *J. Applied Polymer Science*, **89**, 1614-1621(2003).
- G. Liang, S. Yang, X. Wang, Y. Li, X. Li. *Acta. Cryst.*, **E63**, o4118-o4121 (2007).
- Brovelli, F., Rivas, B. L. & Basaez, L. *J. Chil. Chem. Soc.*, **48**, 135-140 (2003).
- Y. Moreno, F. Brovelli, A. Buljan, J. Belmar. *J. CHIL. CHEM. SOC.*, **53**, 1689-1693 (2008).
- Distefano, G., Jones, D., Guerra, M., Favaretto, I., Modelli, A. & Mengoli, G. *J. Phys. Chem.*, **95**, 9746-9753 (1991).
- Cheng, C. L., John, I. G., Ritchie, G. L. D., Gore, P. H. & Farell, L. *J. Chem. Soc. Perkin Trans 2*, 744 (1975).
- Benassi, R., Folli, U., Iarossi, D., Mussatti, A., Nardelli, M., Schenetti, L. & Taddei, F. *J. Chem. Soc. Perkin. Trans 2*, 1851 (1987).
- Brovelli, F., Diaz, F. R., del Valle, M. A., Bernede, J. C. & Molinie, P. *Synth. Met* **122**, 123-126 (2001b).
- Onoda, M., Morita, S., Iwasa, T., Nakayama, H. & Yoshino, K. *J. Chem. Phys.* **95**, (11) 8584-8584 (1991).

- 16) Randazzo, M., Toppare, L. & Fernandez, J. *Macromolecules*, **27**, 5102-5106 (1994).
- 17) Mann, C. & Barnes, K. (1970). *Electrochemical Reaction in Nonaqueous System*, Marcel Dekker, New York
- 18) Cassidy, J. E. & Whitcher, W. J. *J. Phys. Chem* **63**, 1824-1826 (1959).
- 19) Tiroufflet, J. & Corvaisier, A. *Bull. Soc. Chim. France* **99**, 535 (1962).
- 20) Miller, R. & Nord, F. *J. Org. Chem.* **16**, 1720 (1951).
- 21) Bruker (2006). *SMART, SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- 22) Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Gottingen, Germany.
- 23) Bruker (2001). *SHELXTL-NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- 24) Spek, A. L. *J. Appl. Cryst.* **36**, 7--13 (2003)..
- 25) Sheldrick, G. M. (2002). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- 26) Janiak, C. *J. Chem. Soc., Dalton Trans.*, 3885-3898 (2000).
- 27) Allen, F. H. *Acta Cryst.* **B58**, 380-388 (2002).