CRYSTAL STRUCTURE STUDY OF 1-(2-FURYL)-3-(3-METHYL-2-THIENYL)-PROPENONE, C₁₂H₁₀O₂S

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ABSTRACT

This structure is related to synthesis of new polythiophene derivatives. Their most interesting aspects are to be found in their interatomic interactions, of varied type (C—H...O, C—H... π , π ... π) and strength. In the title compound C₁₂H₁₀O₂S there are two independent molecules per asymmetric unit but unlike the former one (where interatomic interactions do not “mix” them), herein both types of independent molecules are interlinked through H-bonding interactions to form broad strips along [010], four molecules in width and displaying a zig-zag pattern. These structures fit into each other along the [100] direction, in a “gear-like” fashion, giving raise to some π — π contacts.

INTRODUCTION

The polythiophene family of compounds has undergone a important progress in the last few years due to their technological applications in different areas as photochemistry and electrochemistry.¹⁻³

It is possible to synthesize conjugated polymers as organic wide-gap semi-conductors, with electronic and optoelectronic applications. In this field, polythiophenes derivatives are among those more studied for their use in organic light-emitting diodes.⁴⁻⁶

In general there is not much structural information available for these families. Theoretical studies show that the conformations of these molecules are the result of the interactions between the electronic coupling of the oxygen in the carbonyl group and the heteroatom in the neighboring ring, indicating a favored conformation.⁷⁻⁹

On the other hand, these compounds can act as ligands in order to coordinate metal ions and give origin to poly-dimensional structures, due to the particular disposition of their donor atoms, O and S.

The precursors employed have been a series of heterocyclic α,β' -unsaturated ketones containing thiophene and/or furane rings (1,2,5) similar to the molecule reported in this work; these molecules have been studied and characterized by electrochemical and *ab-initio* methods.¹⁰⁻¹⁶

Herein we present a structural study of 1-(2-furyl)-3-(3-methyl-2-thienyl)-propenone, C₁₂H₁₀O₂S, see scheme (1). This is the second example of a family that we have synthesized, the recently published (1,5-bis(3-methyl-2-thienyl) penta-1,4-dien-3-one, C₁₅H₁₄OS₂)¹⁷ being the first one, and both structures present analogous intermolecular interactions. In fact, other research groups have studied similar compounds, which have in general very similar structural characteristics.¹⁸

EXPERIMENTAL

SYNTHESIS

Compound C₁₂H₁₀O₂S was obtained following the procedure described by Brovelli et al.¹⁹

3-methyl-2-thiophenecarboxaldehyde (0,1 mol) was dissolved in acetyl furan (0,1mol). The mixture was cooled to 0°C and KOH/ethanol 20% was slowly added. The mixture was stirred for 10 h, and it was filtered and washed with cool ethanol. Pale yellow crystals were obtained from an ethanol/water solution (5:1). The yield was 69%. Elemental Analysis (%) (exp/theo): 64.65/64.69 (C); 3.70/3.95 (H); 15.43/15.67 (O); 16.22/15.70 (S).

IR SPECTRUM

The IR spectrum was carried out in an FTIR-NICOLET MAGNA 550.

STRUCTURE DETERMINATION

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. The Table 1 shows some crystal data.

COMPUTING DETAILS

Data collection: SMART-NT²⁰; cell refinement: SAINT-NT²⁰; data reduction: SAINT-NT; program(s) used to solve structure: SHELXS97²¹; program(s) used to refine structure: SHELXL97²¹; molecular graphics: SHELXTL-NT²²; software used to prepare material for publication: SHELXTL-NT, PLATON.²³

RESULT AND DISCUSSION

Fig. 1 shows an ellipsoid plot of the two independent molecules in C₁₂H₁₀O₂S; both have the same conformation and consist of two terminal rings (thiophene and furane) bridged by a propenone link, which leaves both rings almost coplanar to the whole group and with their substituent atoms in *cis* orientation to each other. The carbonyl oxygen is in turn, *trans* to both heteroatoms. One of this independent propenone groups presents some disorder, accounted for in refinement by some enlarged displacement ellipsoids (see refinement section).

Fig.1: Molecular diagram of $C_{12}H_{10}O_2S$. Anisotropic displacement ellipsoids drawn at 40% level. In hollow bonds, the disordered part, only accounted for by the elongated ADF. H-bonding interactions with neighboring molecules presented in broken lines. Hydrogen atoms shown as arbitrary radii spheres

The IR spectrum agrees with the X-ray structure. It shows the bands typical for the functional groups, but as the molecule is almost planar (there is a small torsion angle between aromatic rings), the conjugation of C=O with C=C bond result in delocalization of π electrons in both unsaturated groups; this causes absorption at lower wave-numbers; then C=O, $\sim 1650\text{cm}^{-1}$; C=C, $\sim 1600\text{cm}^{-1}$.

The planarity of the group is perturbed by a slight twist along the bridge axis. The rotation between rings (10.4(1), 17.8(2)) is larger in the disordered moiety as are the differences between equivalent bonds, probably an artifact of refinement.

Other interesting aspects are to be found in the hydrogen atoms and their interatomic interactions of varied type (C-H $\cdots$ O, C-H $\cdots\pi$, $\pi\cdots\pi$) and strength.

Fig.2: Packing view of (3) a) Lateral view of a strip, in the form of a broad 1D structure, four molecules wide, running along [010] (at the center, in bold lines), ribbed by unprimed molecules (in thin lines). b) View at right angle of a), showing the "zig-zag" strip cross section.

The two independent molecules *per* asymmetric unit, are interlinked through some C-H $\cdots$ O interactions having the carbonyl oxygen as acceptor (structural data are given in Table 1) to form broad strips along [010], four molecules in width (Fig. 2a) and displaying a lateral zig-zag pattern (Fig. 2b). These structures fit into each other along [100] and [001] directions, in a "gear-like" fashion, and are further connected through C-H $\cdots\pi$ and $\pi\cdots\pi$ contacts described in Tables 2 and 3 respectively. Some important distances ($\text{\AA}$) and angles ($^\circ$) are given in Table 4. More information like coordinated and thermal factors of agitation can be found in the Cambridge Database (see annexed materials)

Table 1. Crystal data

$C_{12}H_{10}O_2S$	$V = 4178.0 (10) \text{ \AA}^3$
$Mr = 218.26$	$Z = 16$
Monoclinic, $C2/c$	Mo $K\alpha$
$a = 36.688 (5) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$b = 7.5889 (10) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 15.209 (2) \text{ \AA}$	
$\beta = 99.375 (4)^\circ$	$0.11 \times 0.06 \times 0.03 \text{ mm.}$
Data collection	
APEXII, Bruker-AXS Diffractometer	3662 independent reflections
Absorption correction: multi-scan SADABS (Sheldrick, 2002 ²⁴)	2550 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.96$, $T_{\max} = 0.99$	$R_{\text{int}} = 0.097$
12263 measured reflections	
Refinement	
$R[F^2 > 2\sigma(F^2)] = 0.078$	4 restraints
$wR(F^2) = 0.156$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\max} = 0.67 \text{ e \AA}^{-3}$
3662 reflections	$\Delta\rho_{\min} = -0.78 \text{ e \AA}^{-3}$
273 parameters	

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

D—H $\cdots$ A	D—H	H $\cdots$ A	D $\cdots$ A	D—H $\cdots$ A
C2—H2 $\cdots$ O2 ⁱ	0.95	2.57	3.385 (5)	144
C9—H9 $\cdots$ O2 ^r	0.95	2.58	3.315 (7)	134
C11 ^r —H11 ^r $\cdots$ O2 ^{vi}	0.95	2.36	3.262 (7)	159
C10—H10 $\cdots$ Cg3 ⁱⁱⁱ	0.95	2.79	3.582 (5)	141
C12—H12A $\cdots$ Cg1 ^{iv}	0.98	2.92	3.764 (5)	144

Symmetry codes: (i) $-x+3/2, y+1/2, -z+3/2$; (ii) $x, y-1, z$; (iii) $-x+1, y, -z+1/2$; (iv) $-x+3/2, y-1/2, -z+3/2$.

Table 3. $\pi\cdots\pi$ contacts ($\text{\AA}$, $^\circ$) for $C_{12}H_{10}O_2S$

Group 1	Group 2	ccd($\text{\AA}$)	da($^\circ$)	ipd($\text{\AA}$)
Cg1	Cg2 ^v	3.650 (3)	10.4	3.59 (1)
Cg3	Cg4 ^{vi}	3.728 (3)	17.8	3.56 (4)

Symmetry codes: (v) $3/2 - x, 1/2 - y, 1 - z$; (vi) $1 - x, y, 1 - z$ For the group codes, see 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 2000²⁵)

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

O1—C8 1.389	C4—S1 1.746	C9—O2' 3.315
C7—C8 1.464	C6—C7—C8 117.30	C9'—C10 3.825
C2—O7 1.216	C5—C6—C7 120.70	
C6—C7 1.469	S1—C4—C5 121.73	
C5—C6 1.365	O1C8—C4S1 8.29	
C4—C5 1.441	O1'C8'—C4'S1' 10.48	

Crystals of $C_{12}H_{10}O_2S$, were very small and weakly diffracting, providing rather poor data sets. This was confirmed by the structure solution and the refinement of the models: atoms C5' and C6' in the central bridge of one of

the two independent moieties appeared severely disordered, and the attempts to model this part with split wouldn't refine properly. A metrically constrained refinement of an un-split model was thus performed, which converged smoothly at the cost of accepting large anisotropic displacement ellipsoids, elongated along the normal to the planar bridge in order to account for the disordered electron density in the region. This problematic zone has been represented in Fig.1 by hollow bonds.

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 $U(H)_{\text{isot}} = x.U(\text{host})$, x : 1.2-1.5

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ANNEXED MATERIAL

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 759088

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