STRUCTURAL STUDY OF A NEW 1-(2-THIENYL)-3-(3-METHYL-2-THIENYL)-PROPENONE, IN-SITU RADIATION-INDUCED DIMERIZATION PRODUCTS

Y. MORENO^{1*}, D. CONTRERAS¹, A. BULJAN², F. BROVELLI³, R. BAGGIO⁴

¹ Depto. de Quím. Analítica e Inorgánica, Fac. Cs. Químicas, Universidad de Concepción, Chile.

² Depto. de Físicoquímica (Lab. QTC), Fac. Cs. Químicas, Universidad de Concepción, Chile.

³ Depto. de Cs. Básicas, Campus Los Ángeles, Universidad de Concepción, Chile.

⁴ Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina.

(Received: September 1, 2010 - Accepted: December 28, 2010)

ABSTRACT

The new conjugated system ("chalcone kind") reported herein, 1-(2-thienyl)-3-(3-methyl-2-thienyl)-propenone, C₁₂H₁₀OS₂, presents a monomeric molecular structure, and its most interesting aspects are to be found in its intermolecular interactions, of varied type (C—H...O, C—H...π, π...π) and strength. Some anomalies detected in the refinement process, however, provided evidence that an unexpected in-situ, radiation-induced dimerization reaction had taken place during data collection, with the starting and final products coexisting in a topotactic fashion. This effect is depended of structural packing; that is not all this kind of conjugated system presents this effect. The main factor is the distance between the double bonds of neighboring monomers (about 3 Å)

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 precursors employed have been a series of heterocyclic α, β-unsaturated ketones containing thiophene rings,^{2,4,5} similar to the molecule reported in this work and they have been studied and characterized by electrochemical and ab-initio methods.^{4,6,9}

In general there is not much structural information about this class of compounds. The structural information available is related to conformational studies and crystal structure as electronic interactions between oxygen of carbonyl group and the heteroatom^{5,7,9} and interatomic interactions of type C—H...O, C—H...π, π...π^{10,11}

Following our interest in this kind of compounds, mainly directed to their use as potential ligands in further complex development we have synthesized and characterized a new compound in this populous family, viz: 1-(2-thienyl)-3-(3-methyl-2-thienyl)-propenone, C₁₂H₁₀OS₂. See **scheme 1**.

In this work, we report the crystal structure of 1-(2-thienyl)-3-(3-methyl-2-thienyl)-propenone. The structure was solved by single crystal X-ray diffraction.

EXPERIMENTAL

SYNTHESIS

Compound C₁₂H₁₀OS₂ was synthesized following methods reported in literature.^{4, 10, 11} 3-methyl-2-thiophenecarboxaldehyde (0.1 mol) was mixed with 2-acetylthiophene (0.1 mol). The mixture was cooled at 0°C and KOH/ethanol 20% solution was slowly added. The mixture was stirred during 12 h. Then the mixture was filtered and washed with cool ethanol. The product was recrystallized from an ethanol/water solution (5:1) and pale yellow crystals were obtained. The yield was 70%. The elemental analysis gives the following results: (%) (exp/theo): 61.47/61.50 (C); 4.27/4.30 (H); 6.78/6.83 (O); 27.18/27.37 (S).

IR SPECTRUM

Spectra of 1-(2-thienyl)-3-(3-methyl-2-thienyl)-propenone in KBr pellets were recorded on a FTIR-NICOLET MAGNA 550 spectrometer.

X-RAY DIFFRACTION

Diffraction spectra were recorded in a Bruker SMART AXS CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Semi-empirical absorption correction based on symmetry equivalent reflections was applied. A total of 8994 reflections were collected, of which 3877 reflections were unique (Rint = 0.057). The structure was resolved by direct methods and refined by the full-matrix least-squares method based on F². Structure solution, refinement, and generation of publication materials were performed with the use of the SHELXTL crystallographic software package¹²⁻¹⁵. The final refinement includes anisotropic displacement parameters for the non-hydrogen atoms. The crystal data and structure refinement of Compound C₁₂H₁₀OS₂ were summarized in **Table 1**.

REFINEMENT

Table 1-3 shows the crystal data and refinement details. The principal problems in this compound was the coexistence of symmetry related monomeric units and their cyclization dimerization products resulting from irradiation. The transformations were clearly topotactic, but resented the crystal and (accordingly) the refinement quality. The amount of dimerized material was directly related to the more or less favorable position in the original packing for such a reaction (see comment section for a detailed discussion). 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

Table 1. Crystal data.

$C_{12}H_{10}O_2S_2$	$V = 1112.2 (4) \text{ \AA}^3$
$Mr = 234.32$	$Z = 4$
Triclinic, $P\bar{1}$	$D_x = 1.399 \text{ Mg m}^{-3}$
$a = 9.671 (2) \text{ \AA}$	Mo $K\alpha$
$b = 9.689 (2) \text{ \AA}$	$\mu = 0.45 \text{ mm}^{-1}$
$c = 13.772 (3) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 74.381 (7)^\circ$	Prism, yellow
$\beta = 74.854 (7)^\circ$	$0.19 \times 0.11 \times 0.08 \text{ mm}$
$\gamma = 65.242 (6)^\circ$	

SMART Bruker-AXS diffractometer	3877 independent reflections
CCD rotation images, thin slices scans	2943 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan SADABS ¹⁵	$R_{int} = 0.057$
$T_{min} = 0.93$, $T_{max} = 0.97$	$\theta_{max} = 25.0^\circ$
8994 measured reflections	

Table 3: Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 2.9P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.143$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.97 \text{ e \AA}^{-3}$
3877 reflections	$\Delta\rho_{min} = -0.70 \text{ e \AA}^{-3}$
287 parameters	Extinction correction: none

RESULT AND DISCUSSION

STRUCTURAL STUDY

Compounds $C_{12}H_{10}O_2S_2$ present two independent molecules in the asymmetric unit (**Table 1-3** shows the crystal data and refinement details). We shall describe in what follows the monomeric part, drawn in shaded full thermal ellipsoids and full lines in **Figures 1**. The dimerization products (drawn in open ellipsoids and bonds, Fig. 1b) will be treated afterwards.

Fig.1: Molecular diagram of $C_{12}H_{10}O_2S_2$. Anisotropic displacement ellipsoids drawn at a 40% level. a) The unprimed, non-dimerized molecule. b) The primed moiety, showing in hollow bonds, the dimerized part. The doubly primed indicates the displacement of the electronic density owing to the radiation. Symm. op.: ii) $2-x, 1-y, -z$ iii) $-x, -y, -z$

The two independent molecules present the same conformation; that is two terminal thiophene rings bridged by a propa-1-en-3-one link, with both rings almost coplanar to the whole group and with the sulfur atoms in *trans* conformation. The oxygen in the carbonyl group is *cis* to the nearest sulfur atom and *trans* to the other one

The planarity of the group is perturbed by a slight twist along the bridge axis, difficult to quantify due to the disordered nature of the groups. In general, the spatial arrangement is governed by a number of intermolecular interactions, of varied type and strength.

The intermolecular interactions (mainly of the C-H...O type, **Table 4**) do not “mix” unrelated molecules (“primed” and “unprimed” ones in **Fig. 1**); they generate, instead, two distinct families of non intersecting 1D structures parallel to $[100]$ and $[010]$ as shown in **Fig 2**

Tables 5 and 6 show some distances and angles respectively

Fig.2: Packing diagram of $C_{12}H_{10}O_2S_2$, showing in bold lines the unprimed molecules (forming chains coming out of the figure) and primed ones, in thin lines (as vertical chains).

Table 4: Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C1'-H1'\cdots O1^{vi}$	0.95	2.33	3.279 (6)	167
$C1-H1\cdots O1^{ii}$	0.95	2.29	3.220 (6)	165

Symmetry codes: (i) $x+1, y, z$; (ii) $x, y+1, z$.**Table 5:** Some important distances (Å) of C12H10O2S.

bond	distance/ Å
C4-C5	1.43(1)
C5-C6	1.359(9)
C6-C7	1.467(9)
C5-C6 ⁱⁱ	3.803(7)
C7-O1	1.233(6)
C4'-C5'	1.43(1)
C5'-C6'	1.36(2)
C6'-C7'	1.46(1)
C5'-C6' ⁱⁱⁱ	3.21(2)
C7'-O1'	1.225(6)

Symmetry codes: (ii) $2-x, 1-y, -z$; (iii) $1-x, -y, 1-z$.**Table 6:** Some important angles (°) of C₁₂H₁₀O₂S.

atoms	angle
C5C6C7	120.7(5)
C4C5C6C7	179.9(6)
C1S1C4C5	178.3(5)
C11S2C8C7	179.7(5)
C5'C6'C7'	119.3(8)
C4'C5'C6'C7'	168.5(8)
C1'S1'C4'C5'	176.5(7)
C11'S'2C8'C7'	179.3(5)

During the refinement of the structure, evidence of an unexpected *in situ*, radiation-induced dimerization reaction was apparent, with the starting and final products coexisting in a topotactic fashion. This kind of reaction have been studied by different research group in similar compound as the cinnamic acid derivatives.¹⁶ In this reaction kinds, the spatial disposition (parallel) of the molecules and the distance between them, is fundamental for the dimerization phenomenon.¹⁷ The **scheme 2** shows the dimerization reaction. The X-ray radiation would undergo interactions with the matter and generate ultraviolet photons. This radiation would cause the dimerization phenomenon.

We have done the infra-red spectrum with the hope of observed any change on the structure of the compounds due to ultra-violet radiation. In general the frequencies of the bands in these conjugated compounds are smaller than simple systems. This is due to minor bond order. The infra-red spectrum before the UV radiation is similar to infra-red spectrum after radiation.

This phenomenon is a $[2 + 2]$ photodimerization homogenous and return thermally to a pure crystal of the monomers. It is the reason why is not possible to detect the structure changes by infra-red analysis.

CONCLUSIONS

A new heterocyclic system was synthesized, 1-(2-thienyl)-3-(3-methyl-2-thienyl)-propenone, (C₁₂H₁₀OS₂) and their crystal structure was established. The structure presents intermolecular interactions of varied type (C—H $\cdots$ O, C—H $\cdots$ π , $\pi\cdots\pi$) and strength. The anomalies detected in the refinement process, however, provided evidence that an unexpected *in-situ*, radiation-induced dimerization reaction had taken place during data collection, with the starting and final products coexisting in a topotactic fashion.

ACKNOWLEDGEMENTS

We acknowledge funding by project DIUC 208.021.026-1.0 and 209.021.028-1.0; Chilean-French *Laboratoire International Associé* (LIA MIF 836). Dr. Thierry Roisnel of Centre de Diffractométrie X of Université de Rennes 1 "Sciences Chimiques de Rennes" by diffraction experiences. We also acknowledge the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system.¹⁸

REFERENCES

- Lee, C., Kim, K. J. & Rhee, S. B. *Synth. Met.* **69**, 295-296, (1995).
- Díaz, F. R., del Valle, M. A. & Brovelli, F. J. *Applied Polymer Science*. **89**, 1614-1621, (2003).
- Nguyen, T. P., Molinie, Handbook of Advanced Electronic and Photonic. P. & Destruel, P. (2000).
- Brovelli, F., Del Valle, M. A., Díaz, F. R. & Bernede, J. C. *Bol. Soc. Chil. Quim.* **46**, 319, (2001).
- Brovelli, F., Bernede, J. C., Marsillac, S., Díaz, F. R., del Valle, M. A. & Beaudouin, C. J. *Applied Polymer Sci.* **86**, 1128-1137, (2002).
- Brovelli, F., Rivas, B. L. & Basaez, L. J. *Chil. Chem. Soc.* **48**, 135-140, (2003).
- 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. & Farrell, 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).
- D. Contreras, Y. Moreno, C. Soto, M. Saavedra, F. Brovelli, R. Baggio. *J. Chil. Chem. Soc.* **54**, 289-291 (2009)
- Y. Moreno, F. Brovelli, M. Dahrouch, R. Baggio, L. Moreno, *J. Chil. Chem. Soc.* **55**, 331-333, (2010).
- Bruker (2001). SHELXTL-NT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2006). SMART, SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Sheldrick, G. M. (2002). SADABS Bruker AXS Inc., Madison, Wisconsin, USA.
- Murthy, G.S., Ramamurthy, V. Venkatesan K., *Acta Crystallographica Section C-Crystal Structure Communications*, **44**, 307-311, (1988).
- Ramamurthy, V., Venkatesan, K. *Chem. Rev.*, **87**, 433-481, (1987).
- Allen, F. H. *Acta Cryst.* **B58**, 380-388, (2002).