Revista Mexicana de Física
ISSN: 0035-001X
rmf@ciencias.unam.mx
Sociedad Mexicana de Física A.C.
México

Estévez-Hernández, O.; Rodríguez-Hernández, J.; Yee-Madeira, H.; Duque, J.
1-(2-furoyl)-3,3-(diphenyl)thiourea: spectroscopic characterization and structural study from x-ray powder diffraction using simulated annealing
Revista Mexicana de Física, vol. 61, núm. 1, enero-febrero, 2015, pp. 64-68
Sociedad Mexicana de Física A.C.
Distrito Federal, México

RESEARCH Revista Mexicana de Física **61** (2015) 64–68 JANUARY-FEBRUARY 2015

1-(2-furoyl)-3,3-(diphenyl)thiourea: spectroscopic characterization and structural study from x-ray powder diffraction using simulated annealing

O. Estévez-Hernández[a,*], J. Rodríguez-Hernández[b], H. Yee-Madeira[c] and J. Duque[a]
[a] *Instituto de Ciencia y Tecnología de Materiales,*
Universidad de La Habana, Cuba,
e-mail: oestevezh@yahoo.com
[b] *Instituto de Investigaciones en Materiales,*
Universidad Nacional Autónoma de México, DF, México.
[c] *Escuela Superior de Física y Matemática,*
Instituto Politécnico Nacional, México.

Received 24 October 2014; accepted 6 January 2015

1-Furoyl-3,3-diphenylthiourea (FDFT) was synthesized, and characterized by FTIR, ^{1}H and ^{13}C NMR and *ab initio* X-ray powder structure analysis. FDFT crystallizes in the monoclinic space group P2$_1$ with $a = 12.691(1)$, $b = 6.026(2)$, $c = 11.861(1)$ Å, $\beta = 117.95(2)$ and $V = 801.5(3)$ Å^3. The crystal structure has been determined from laboratory X-ray powder diffraction data using direct space global optimization strategy (simulated annealing) followed by the Rietveld refinement. The thiourea group makes a dihedral angle of 73.8(6)° with the furoyl group. In the crystal structure, molecules are linked by van der Waals interactions, forming one-dimensional chains along the a axis.

Keywords: Furoylthioureas; X-ray powder diffraction; crystal structure; simulated annealing; FTIR.

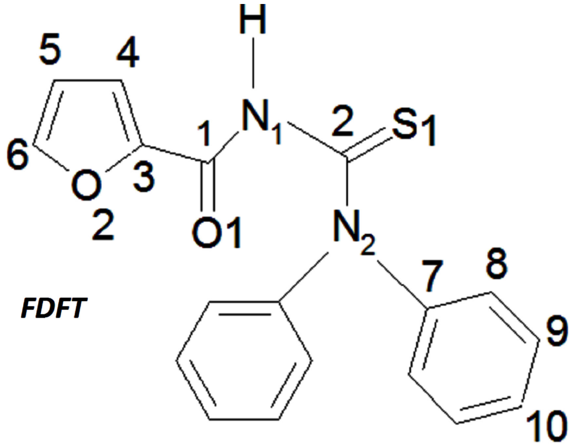
PACS: 61.05.cp; 32.10.-f; 33.15.-e

1. Introduction

Thiourea derivatives have been largely studied due to the application to the fields such as molecular recognition, coordination chemistry of heavy metals, molecular electronics and bioactivities [1,2]. Over the past few years electrochemical sensors based in aroylthioureas as ionophores have been successfully developed and some basic approach to describe the interaction mechanism of the ionophore with the heavy metal ion have been investigated [3-6]. Particularly, structural studies of this type of molecules have attracted much attention [7-9]. Knowledge of crystal structure of these versatile compounds is important to understand the behavior of these ligands as ionophores [10] and also the complex formation.

Usually, single crystal X-ray diffractometry is the preferred method for crystal structure determination of small molecules. However, for several materials it could be complicated to grow single crystals of suitable size and quality that make them appropriated to structure analysis. This fact is especially true for the title compound. With recent advances and readiness of software that apply Monte-Carlo/simulated annealing or molecular search methods to powder diffraction data [11-13], crystal structure resolution of molecular solids can nowadays be achieved from experimental X-ray diffraction data [14-18].

Following with our interest about ion-recognition properties of 1-furoylthiourea derivatives 3,3-disubstituted, we report in this paper the spectroscopic characterization and crystal structure analysis from X-ray powder diffraction data of the 1-Furoyl-3,3-diphenylthiourea (FDFT) (Scheme 1).



SCHEME 1. Chemical diagram of FDFT.

2. Experimental

2.1. Materials and methods

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purification. The melting point was determined with a Reichert-Jung rheostat coupled to a Reichert-Thermovar binoculars and a RS-3.722 digital thermometer. The FTIR spectrum was recorded as KBr pellets on a Perkin Elmer Spectrum One FT-IR spectrometer in transmission mode with 10 scans at a resolution of 2 cm^{-1}. 1H and ^{13}C NMR spectra were obtained on a Bruker AC-250F spectrometer equipped with a computer ASPECT 3000 at frequencies of 250 MHz

(^{1}H) and 62.89 MHz (13C) at 25°C. Sample (30 mmol/L) was dissolved in DMSO-$d6$ (Aldrich). X-ray powder diffraction data was collected with a Bruker D8 Advanced diffractometer, equipped with a Lynxeye detector and CuKα1 radiation (1.54056 Å) at 25 °C.

2.2. Synthesis of FDFT

FDFT was synthesized as previously reported [3], by converting furoyl chloride into furoyl isothiocyanate and then condensing with the diphenylamine. Yield: 93 %. The precipitated FDFT was recrystallized from ethanol. The formation of FDFT was established by the similarity of melting point reported in the literature [19]. Some of the spectroscopic data for product FDFT were previously published [20,21]. Melting point (°C): 140-141.

IR spectrum [KBr] (cm^{-1}): $\nu_{\max}/\text{cm}^{-1}$ 3250 (N-H), 3121-3033 (aromatic C-H), 1698 (C=O), 1590-1562 (aromatic C=C), 1489 (Thioamide band I, ν(C-N) + ν(NH)), 1369 (Thioamide band II, ν(C-N) + ν(C=S)), 1155 (Thioamide band III, ν(C-N) + ν(C=S)) and 702 (Thioamide band IV, ν(C=S)).

^{1}H NMR (DMSO-$d6$) δ 11.04 (1H, s, NH), 7.82 (1H, d, H_6), 7.15-7-40 (11H, m, furan H_4, 10H of phenyl groups) and 6.56 (1H, dd, H_5); ^{13}C NMR (DMSO-$d6$) δ 182.8 (CS), 153.1 (CO), 146.6 (C_6), 145.5 (C_3), 145.3 (C_7), 128.9, 126.8, 126.5 (C_{10}, C_9, C_8), 116.3 (C_4), 111.8 (C_5).

2.3. X-ray data collection and structure analysis of FDFT

The sample was ground using agate pestle and mortar, and mounted in a top-loaded sample holder. X-ray powder diffraction data was recorded by a linear position-sensitive Lynxeye detector with a step size of 0.01° (2θ) and a counting time of 2 s per step over an angular range of $5.0° < 2\theta < 60.0°$ using the Bragg-Brentano para-focussing geometry. Indexing of the X-ray powder pattern of FDFT carried out using the program N-TREOR09 [22] indicated a monoclinic unit cell with a = 12.691(1), b = 6.026(2), c = 11.861(1) Å and $\beta = 117.95$ (2)°. The figure of merits were M(20) = 20 and F(20) = 36, respectively. P2$_1$ space group was determined on the basis of systematic absences. The full pattern decomposition was performed with EXPO2009 [23] following the Le Bail algorithm [24] and using a split type pseudo-Voigt peak profile function [25].

The Monte-Carlo structure determination method implemented in the program EXPO2009 [22] was used for solving the crystal structure of FDFT. The molecular geometry used as input for structure solution was constructed using standard bond lengths and angles. The furan and benzene rings were maintained as rigid fragments. In the generation of trial structure during Monte-Carlo simulations, the structural fragment translation and rotation within the unit cell were carried out simultaneously with the intramolecular rotations. The molecular structure starting with a typical two-dimensional drawing and transform it into a tri-dimensional structure. The initial position, orientation and intramolecular geometry of the structural fragment were chosen arbitrarily, and the random movement of the molecule in each Monte-Carlo move constrained such that the maximum displacement in any of the x, y, z coordinates (in orthogonal reference frame) was 0.5 Å and the maximum rotation of the molecule about three mutually perpendicular axes was ± 45. The scale factor functioning analogous to temperature in conventional Monte-Carlo simulations was fixed giving a 40.9 % acceptance of

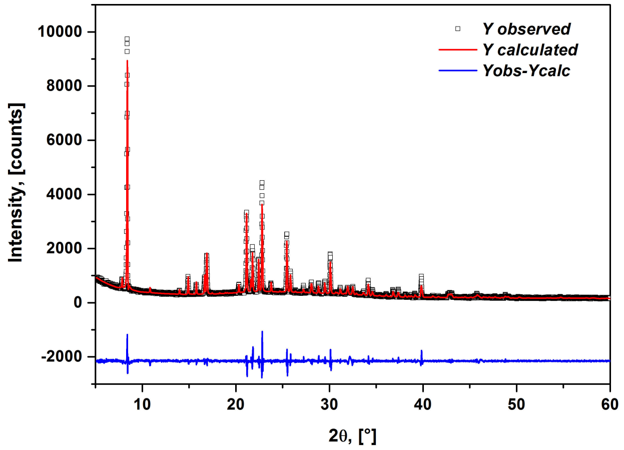


FIGURE 1. Final Rietveld plot of FDFT. Observed pattern (crosses); calculated pattern (full line) and difference profiles (lower trace).

TABLE I. Crystal data and Rietveld refinement parameters of FDFT.

Chemical formula	$C_{18}H_{14}N_2$ O_2S
Formula weight (M_r)	322.4
Crystal system, space group	Monoclinic, P2$_1$
Temperature (°K)	294 K
Unit cell dimensions	
a, b, c (Å)	12.691 (1), 6.026 (2), 11.861 (1)
β(°)	117.95 (2)
V (Å^3)	801.5 (3)
Z	2
Wavelength (Å)	1.54056
D_{calc} (gcm^{-3})	1.330
2 θ interval (°)	5.0-60.0
Step size (°), time (s)	0.01, 2
No. of reflections	270
R_p	7.71
Rwp	11.40
$R[F^2 > 2\sigma(F^2)]$	7.31
S	2.17

TABLE II. Selected bond lengths (Å) and bond angles (°) of FDFT.

C1-C3	1.47 (5)	C7-N2	1.43 (2)
C1-O1	1.21 (2)	C8-C9	1.39(3)
C1-N1	1.383 (19)	C9-C10	1.393(8)
C2-N1	1.39 (3)	C10-C11	1.397(13)
C2-N2	1.40(3)	C11-C12	1.400(17)
C2-S	1.61 (4)	C13-C14	1.394(8)
C3-C4	1.38 (6)	C13-C18	1.394(10)
C3-O2	1.24 (3)	C13-N2	1.432(14)
C4-C5	1.37 (3)	C14-C15	1.391 (8)
C5-C6	1.406 (18)	C15-C16	1.391 (8)
C6-O2	1.294 (12)	C16-C17	1.387 (7)
C7-C8	1.39 (3)	C17-C18	1.386 (8)

C3-C1-O1	119.6 (19)	C7-C8-C9	120.5 (12)
C3-C1-N1	120.4 (16)	C8-C9-C10	120.2 (17)
O1-C1-N1	119.9 (19)	C9-C10-C11	118.7 (14)
N1-C2-N2	124.3 (19)	C10-C11-C12	118.0 (11)
N1-C2-S	118 (3)	C7-C12-C11	120.3 (16)
N2-C2-S	118 (2)	C14-C13-C18	118.5 (11)
C1-C3-C4	124 (2)	C14-C13-N2	120.4 (12)
C1-C3-O2	123 (4)	C18-C13-N2	121.1 (11)
C4-C3-O2	111 (4)	C13-C14-C15	120.8 (1)
C6-O2-C3	107(3)	C14-C15-C16	119.5 (10)
C3-C4-C5	102 (2)	C15-C16-C17	120.0 (11)
C4-C5-C6	104.6 (13)	C16-C17-C18	119.9 (10)

trial structure close to the optimum 40.0 %. Finally, after 437000 trials, a structural model with $R_{wp} = 21.88$ was obtained.

The atomic coordinates obtained in the Monte-Carlo calculation were used as the starting model for the Rietveld refinement using the EXPO2009 [22] program package. In the final refinement all non-hydrogen atomic positions in the furan and benzene rings were restrained to the average values reported for analogous structures (1.380 Å). Removal of these restrains resulted in less satisfactory distances and angles without any improvement in the profile fit. For this reason, they were retained in refinements. The position of all N, O and S isotropic atomic displacement parameters were refined. Hydrogen atoms were placed in the calculated positions using N-H =0.96 Å and C-H =0.96 Å (aromatic), but without effect on the refinement. Final Rietveld refinement converged to $Rp = 7.71$ and $R_{wp} = 11.40$ for 270 reflections with a good agreement between the observed and calculated profiles (Fig. 1). Relevant crystallographic data are summarized in Table I. Atomic coordinates and equivalent isotropic displacement parameters are listed in supplementary information file. Selected bond lengths and bond angles of FDFT are given in Table II.

3. Results and discussion

3.1. X-ray crystallography

A view of the asymmetric unit of FDFT comprising of one molecule is shown in Fig. 2. The main bond lengths and angles are given in Table II, and they are between the ranges obtained for similar compounds from single-crystal data [25,26]. Generally for the compound refinement from powder data the distances are longer that those obtained from refinement with data collected using single-crystal. The C2-S1 and C1-O1 bonds show typical double-bond character. Particularly, the C2-S1 distance of 1.600 (2) Å is shorter than those reported for related compounds from single-crystal dat. However, the C-N bond lengths, C1-N1, C2-N1 and C2-N2 are shorter than the normal C-N single bond length of about 1.48 Å. These results can be explained by the existence of resonance in this part of the molecule. The central thiourea fragment (N1-C2-S1-N2) makes dihedral angle of 73.8 (6)° with the furan carbonyl (O1-O2-C1-C3) group, whereas the C7-C12 and C13-C18 benzene rings are inclined by 54.5 (6)° and 63.7 (1)°, respectively. In addition, the conformation with respect to the carbonyl and thiocarbonyl moieties is twisted, as reflected by the torsion angles O1-C1-N1-C2 and C1-N1-C2-S1 of -45.8 (3)° and 85.5 (3)°. In this conformation the sulfur and oxygen atoms are pointing approximately in opposite directions. Although from electronic consideration, planarity should be favored by resonance interactions [27], steric effects play an important role in determining the molecular structure. In the crystal structure (Fig. 3) only van der Waals interactions are observed. For other structures related has been reported intermolecular N-H· · · O hydrogen bonding and weaker C-H· · · O hydrogen interactions [5,25,26].

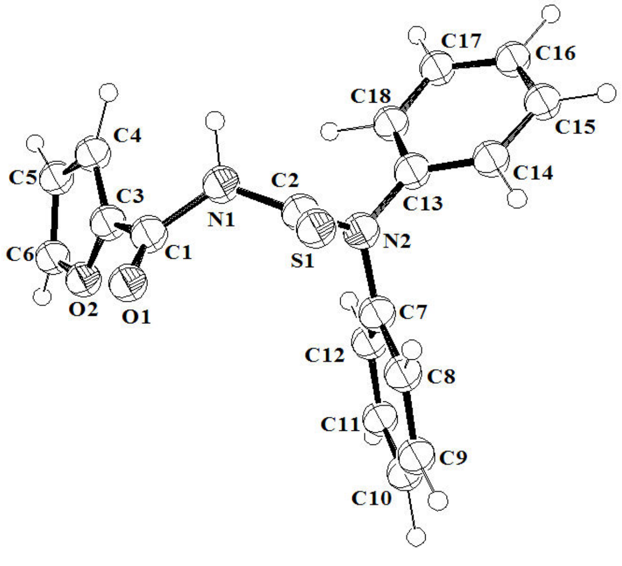


FIGURE 2. View of the asymmetric unit of FDFT with atom numbering scheme (50% probability displacement ellipsoids).

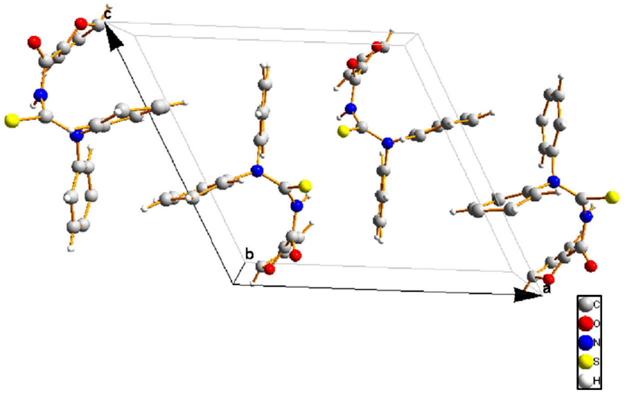


FIGURE 3. View of the crystal packing of the FDFT molecules along the a axis.

3.2. FTIR spectroscopy

The FTIR spectrum of FDFT showed a sharp peak at 3250 cm^{-1} due to NH vibration. The peaks at 3121-3033 cm^{-1} region are due to aromatic CH stretching of furan and phenyl rings. The strong peak observed at 1698 cm^{-1} correspond to C=O stretching. The aromatic C=C stretching frequency bands appear 1564-1590-1562 cm^{-1}, while the most intense peaks at 1489, 1369 and 1155 cm^{-1} can be assigned to Thioamide bands I [ν(C-N) + δ(NH)], II [ν(C N) + ν(C=S)] and III [ν(C-N) + ν(C=S)], respectively. A weak peak at 702 cm^{-1} can be ascribed to Thioamide band IV [mainly ν(C=S)]. This band is difficult to assign in the FTIR spectra of thiourea derivatives.

3.3. ^{1}H and ^{13}C NMR spectroscopy

The ^{1}H NMR spectrum of FDFT shows a broad signal at 11.04 ppm in DMSO-d_6, which disappears with addition of D_2O. It was assigned to the acidic NH proton (aroylthiourea). The furan protons 7.82-6.56 ppm show the typical spin system of a carbonyl substituted furan. The ^{13}C NMR spectrum show the C=S and C=O signals at 182.8 and 153.1 ppm respectively.

4. Conclusion

We have synthesized and spectroscopic characterized a furoylthiourea derivative 3,3-disusbtituted. The crystal structure of FDFT was determined using X-ray powder diffraction method and Monte-Carlo Simulated Annealing technique. Non H-bonding interactions are present in the crystal packing unlike of that observed for related structures.

Supporting information

Crystallographic data for the structure $C_{18}H_{14}N_2O_2S$ reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 911822. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

The authors thank financial support of CONACyT project IO110/127/08 by México-Cuba cooperation project CONACyT-CITMA JO10.600. JD acknowledge the financial support from Consejo Nacional de Ciencia y Tecnología (CONACyT), México. “Programa de Estancias Posdoctorales y Sabáticas al Extranjero para la Consolidación de Grupos de Investigación”, N° de Propuesta: 203824.

---

1. A.A. Aly, E.K. Ahmed, K.M. El-Mokadem, M.E.F Hegazy, *J Sulfur Chem* **28** (2007) 73.
2. A. Saeed, U. Flörke, M.F. Erben, *J Sulfur Chem* **35** (2014) 318.
3. E. Otazo-Sánchez, L. Pérez-Marín, O. Estévez-Hernández, S. Rojas-Lima, J. Alonso-Chamorro, *J Chem Soc Perkin Trans II* (2001) 2211.
4. D. Wilson, M.A. Arada, S. Alegret, M. Del Valle, *J Hazard Mater* **181** (2010) 140.
5. A.R. Lazo Fraga, G. Li Destri, G. Forte, A. Rescifina, F. Punzo, *J Mol Struct* **929** (2009) 174.
6. A.R. Lazo Fraga, G. Li Destri, G. Forte, A. Rescifina, F. Punzo, *J Mol Struct* **981** (2010) 86.
7. A. Saeed, M.F. Erben, U. Flörke, *J Mol Struct* **982** (2010) 91.
8. C.K. Özer, H. Arslan, D. VanDerveer, N. Külcü, *Molecules* **14** (2009) 655.
9. Y. Wen, Z. Weiqun, Z. Zhengjiang, *J Mol Struct* **828** (2007) 46.
10. O. Estévez-Hernández, J. Duque, E. Reguera, *J Sulfur Chem* **32** (2011) 213.
11. V.F. Nicolin, R. Cern, *J Appl Crystallogr* **35** (2002) 734.
12. K.D.M. Harris *et al.*, (Evolutionary Algorithm Generalized for Energy and R-factor, University of Birmingham, Birmingham, UK, 2001).
13. W.I.F David, K. Shankland, J. Cole, S. Maginn, W.D.H. Motherwell, R. Taylor, *DASH User Manual* (Cambridge Crystallographic Data Center, Cambridge, UK, 2001).
14. Bruker AXS, TOPAS (Bruker AXS, Karlsruhe, Germany, 2006)
15. K. Fujii *et al.*, *Chem Commun* **46** (2010) 7572.
16. R.M. Ibberson, A.J. Fowkes, M.J. Rosseinsky, W.I.F. David, P.P. Edwards, *Angew Chem Int Ed* **48** (2009) 1435.
17. U. Das, B. Chattopadhyay, M. Mukherjee, A.K. Mukherjee, *Cryst Growth Des* **12** (2012) 466.

18. B. Chattopadhyay, S. Ghosh, S. Mondal, M. Mukherjee, A.K. Mukherjee, *CrystEngComm* **14** (2012) 837.

19. B. Douglas, F.D. Dains, *J Am Chem Soc* **56** (1934) 719.

20. O. Estévez-Hernández, E. Otazo-Sánchez, J.L. Hidalgo-Hidalgo de Cisneros, I. Naranjo-Rodríguez, E. Reguera, *Spectrochimica Acta Part A* **62** (2005) 964.

21. E. Otazo-Sánchez *et al*., *Spectrochimica Acta Part A* **58** (2002) 2281.

22. A. Altomare, M. Camalli, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, *J Appl Crystallogr.* **43** (2009) 798.

23. A. Le Bail, H. Duroy, J.L. Fourquet, *Mater Res Bull* **23** (1988) 447.

24. M.M Hall, V.G. Veeraraghavan, H. Rubin, P.G. Winchell, *J Appl Crystallogr* **10** (1977) 66.

25. H. Pérez, Y. Mascarenhas, O. Estévez-Hernández, S. Santos Jr, J. Duque, *Acta Cryst E* **64** (2008) o513.

26. O. Estévez-Hernández, R.S. Corrêa, J. Ellena, J. Duque, *Acta Cryst E* **65** (2009) o648.

27. S. Torrico-Vallejos, M.F. Erben, O.E. Piro, E.E. Castellano, C.O. Della-Védova, *Polyhedron* **28** (2009) 937.