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Structural and spectral studies of thiosemicarbazones derived from 3-furaldehyde and 3-(2-furyl)prop-2-enal

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Abstract

3-Furaldehyde thiosemicarbazone (3FTSC) and 3-(2-furyl)prop-2-enal thiosemicarbazone (FATSC) have been prepared, their structures solved and IR, ¹H NMR spectra recorded. The thiosemicarbazone moiety in both compounds shows an *E* configuration about C1–N2 and C2–N3. Intramolecular and intermolecular hydrogen bondings occur in both the molecules. The angles between the mean planes of the furanic ring and thiosemicarbazone moiety present a significant difference in the two compounds. Moreover, the ¹H NMR and IR spectral studies of two compounds are quite similar. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thiosemicarbazone; Crystal structure; 3-Furaldehyde; 3-(2-Furyl)prop-2-enal

1. Introduction

Thiosemicarbazone derivatives and their metallic complexes have extensive biological properties such as antitumoral [1–5], fungicidal [6,7], bactericidal [8] and antiviral [3] activity. As part of our continued research work on synthesis and biological activity, specially with thiosemicarbazones and semicarbazones of furaldehyde and their metal complexes, we report here the crystal structure of two new thiosemicarbazones derived from 3-furaldehyde (3FTSC) and 3-(2-furyl)prop-2-enal (FATSC). The chemical structures are shown in Fig. 1.

2. Experimental

2.1. Synthesis

The 3FTSC was synthesized by refluxing 3-furaldehyde and thiosemicarbazide (1:1 molar ratio) in absolute ethanol in the presence of acetic acid (5 cm³). The mixture was refluxed for 1 h and then cooled, filtered and recrystallized from a mixture of ethanol (75%) and water. Yellow microcrystalline products are obtained. (Analysis results for C₆H₇N₃OS: Found: C, 42.90; H, 4.19; N, 24.70. Calculated: C, 42.59; H, 4.17; N, 24.83.) Mp 154–155°C.

FATSC was obtained after a 24 h contact of 3-(2-furyl)prop-2-enal with thiosemicarbazide in a mixture of 20 cm³ of methanol and 30 cm³ of ethanol at room temperature. A yellow precipitate is formed, which is filtered, washed with ethanol and recrystallized in

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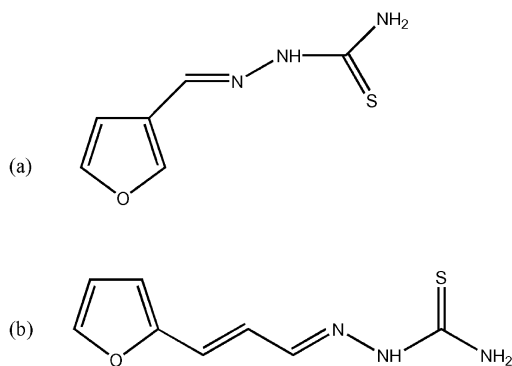


Fig. 1. Chemical structures of 3FTSC (a) and FATSC (b).

ethanol solution with some water drops. Yellow microcrystalline products are obtained. (Analysis results for $C_8H_9N_3OS$: Found: C, 49.29; H, 4.48; N, 21.46. Calculated: C, 49.21; H, 4.65; N, 21.52.) Mp 157–158°C.

Table 1

Crystal data and structure refinement for 3-furaldehyde and 3-(2-furyl)acrolein thiosemicarbazone, 3FTSC and FATSC, respectively

Compound	3FTSC	FATSC
Empirical formula	$C_8H_7N_3OS$	$C_8H_9N_3OS$
Color, habit	Yellow, switch needle	Yellow, plate
Crystal size (mm)	$1.40 \times 0.14 \times 0.11$	$0.34 \times 0.29 \times 0.11$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	10.792(5)	13.305(3)
<i>b</i> (Å)	5.705(4)	9.485(4)
<i>c</i> (Å)	13.821(7)	7.501(3)
β (°)	109.29(2)	88.66(5)
Volume (Å ³)	803(1)	946(1)
<i>Z</i>	4	4
Formula weight	169.21	195.24
Density calculated (g/cm ³)	1.40	1.37
Diffractometer	Enraf Nonius MACH3	Enraf Nonius MACH3
Radiation (λ , Å)	Mo K α (0.71073)	Mo K α (0.71073)
Abs. coeff. (mm ⁻¹)	0.347	0.304
<i>F</i> (000)	352	408
θ range for data collected (°)	11–16	10–11.9
Index ranges	$0 \leq h \leq 12$ $0 \leq k \leq 6$ $-16 \leq l \leq 15$	$-8 \leq h \leq 0$ $0 \leq k \leq 10$ $-15 \leq l \leq 15$
Total reflections	1651	1725
Unique reflections	1566	1559
Observed reflections, [<i>I</i> > 3 σ (<i>I</i>)]	1108	508
Final <i>R</i> indices	$R_1 = 0.040$; $wR = 0.053$	$R_1 = 0.057$; $wR = 0.073$
<i>R</i> indices (all data)	$R_1 = 0.057$; $wR = 0.056$	$R_1 = 0.266$; $wR = 0.201$
Goodness-of-fit	1.141	1.311
Large diff. peak (e ⁺ Å ⁻³)	0.305	0.267

2.2. Physical measurements

Elemental analysis were carried out by the Service Central d'Analyses (CNRS, Vernaison, France). Melting points were determined with a digital melting point apparatus using capillary technique. IR spectra were recorded with a Shimadzu FTIR-8010M spectrometer between 400 and 4600 cm^{-1} (KBr disks). The ¹H NMR spectra were recorded on a Bruker Advance DRX500 in DMSO-*d*₆ operating at 500 MHz. The chemical shifts, δ , are given in parts per million (relative to TMS) and coupling constants in hertz.

2.3. X-ray data collection, structure solution and refinement

Yellow crystals of 3FTSC and FATSC were mounted on glass fibres and used for data collection.

Table 2
Selected bond distances (Å) and angles (°) for 3FTSC and FATSC

	3FTSC	FATSC
<i>Bond distance</i>		
S–C1	1.690(2)	1.675(9)
O–C5	1.363(3)	1.41(1)
O–C6	1.366(3)	–
O–C8	–	1.33(1)
N1–C1	1.322(2)	1.33(1)
N2–N3	1.386(2)	1.37(1)
N2–C1	1.338(2)	1.33(1)
N3–C2	1.271(2)	1.27(1)
C2–C3	1.446(3)	1.42(1)
C3–C4	–	1.34(1)
C4–C5	–	1.41(1)
<i>Bond angle</i>		
N3–N2–C1	120.4(1)	121.4(7)
N2–N3–C2	115.2(2)	117.8(7)
S–C1–N1	123.6(1)	122.0(7)
S–C1–N2	119.0(1)	121.8(6)
N1–C1–N2	117.4(2)	116.2(8)
N3–C2–C3	121.3(2)	121.2(8)
C2–C3–C4	129.4(2)	124.4(8)
C2–C3–C6	124.9(2)	–
C3–C4–C5	–	126.5(8)

X-ray diffraction data were collected at 293 K on an Enraf Nonius MACH3 four-circle diffractometer ($\lambda\text{Mo K}\alpha = 0.71073 \text{ \AA}$) equipped with a graphite monochromator (IMMO, UMR 6501 CNRS). Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffrac-

tion data from 25 reflections. The two structures were solved by direct methods (SIR) using MolEN package programs [9] and F was refined by a full-matrix least-squares technique using anisotropic displacement parameters, except for C atoms in FATSC, which were refined using isotropic displacement parameters. The reason for this is that the small size of crystal is not sufficient in this case to obtain enough data (Table 1).

All hydrogen atoms in 3FTSC and those attached to nitrogen atoms in FATSC were located from Fourier difference synthesis and refined isotropically. The remaining hydrogen atoms in FATSC were located from the HYDRO program [9].

3. Results and discussion

Table 1 gives the crystal data collection, data reduction and structure refinement for 3FTSC and FATSC. The selected bond distances and angles are listed in Table 2. Intramolecular and intermolecular hydrogen bonding parameters are presented and the mean plane data are compiled in Table 3.

3.1. Structural characterization

The numbering scheme and a displacement ellipsoid plot of 3FTSC and FATSC are shown in Figs. 2 and 3, respectively. In the two compounds, the sulfur atom and the hydrazone nitrogen N3 are in *trans* position with respect to the C1–N2 bond,

Table 3
Intramolecular and intermolecular hydrogen bonding parameters, the mean planes, deviations from mean planes, and angles between mean planes for 3FTSC and FATSC

Compound	D–H...A	$d(\text{D–H})$	$d(\text{H...A})$	$d(\text{D...A})$	$\angle(\text{DHA})$
3FTSC	N1–H2...N3	0.902	2.203(7)	2.648(2)	104(2)
	N1–H1...S	0.772	2.66(2)	3.432(2)	173.83(7)
	N2–H3...S	0.897	2.51(2)	3.394(2)	167.97(7)
FATSC	N1–H2...N3	0.879	2.28(2)	2.64(1)	112.3(5)
	N1–H1...S	0.915	2.649(3)	3.464(8)	115.0(1)
	Plane	Mean deviation	Largest deviation	Angle with previous plane	
3FTSC	C3–C2–C5–O–C6	0.0043	0.0079		
	C2–N3–N2–C1–N1–S	0.0715	0.1203	7.94(1)	
FATSC	C5–C6–C7–C8–O	0.0241	0.0357		
	C2–N3–N2–C1–N1–S	0.1513	0.2720	22.6(1)	

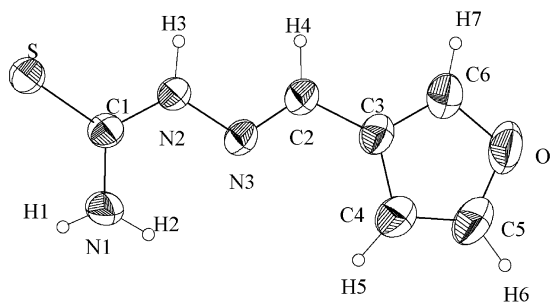


Fig. 2. Perspective view with atom numbering scheme and displacement ellipsoids at 50% probability level of 3FTSC.

and the molecular configuration is determined by the presence of the intramolecular hydrogen bond N1–H2···N3 (Table 3).

The two molecules also show a difference in planarity (Table 3). In FTSC, the thiosemicarbazone moiety (CSNN) and the furanic ring present a slight dihedral angle of $7.94(1)^\circ$, which gives a remarkable planarity to the whole molecule. This is not the case with FATSC because of the length of the side chain and the angle between the mean planes is $22.6(1)^\circ$.

The bond distances shown in Table 2 indicate that the C–S bond length of 1.690(2) and 1.675(9) Å in 3FTSC and FATSC, respectively, agree with similar bond in related compounds [10,11]. This distance is intermediate between that of single C–S bond distance of 1.82 Å and that of double C–S bond 1.56 Å [12]. Consequently, the C–S bond in these thiosemicarbazones possesses only partial double-bond character. This hypothesis is supported by the bond distances around C(1), which is 1.322(2) and 1.338(3) Å for N(1) and N(2), respectively, in

3FTSC. As regards FATSC, the corresponding distances are 1.33(1) Å for both of them. These values are indicative of partial double-bond character.

A comparison of the N(2)–N(3) distance of 1.386(2) Å for 3FTSC and 1.37(1) Å for FATSC with the corresponding N–N distance of 1.411(2) Å for unsubstituted [13], 1.395(2) and 1.431(6) Å for 1-phenyl [14] and 4-phenyl [15] thiosemicarbazide, respectively, suggests that the N–N bond also has some double-bond character. A similar shortening of the N–N bond, with an average value of 1.37 Å, was observed in thiosemicarbazones having an extensively delocalized group on the nitrogen N(3) [16,17]. This delocalization is shown by the furanic ring in the case of 3FTSC whereas in FATSC it is the conjugation of the π bond in the side chain, which leads to the same phenomenon.

In both compounds, the three hydrogens attached to N1 and N2 atoms have the potential to form donor hydrogen bonds. In 3FTSC, the intermolecular hydrogen bonds link the molecules together in the solid state and they are N2–H3···S ($0.5 - x, -0.5 + y, 0.5 - z$) and N1–H1···S ($1.5 - x, 0.5 + y, 1.5 - z$) hydrogen bonds. On the other hand, the molecules of FATSC form a zig-zag chain parallel to the *b*-axis in the most common setting. The packing is governed by interaction-type hydrogen bonds, viz., N1–H1···S ($0.5 - x, 1 + y, 1 + z$). Separations of all these hydrogen bonds (Table 3) agrees well with that in most thiosemicarbazones [18,19].

3.2. Spectral studies

The ^1H NMR spectrum of compound 3FTSC shows

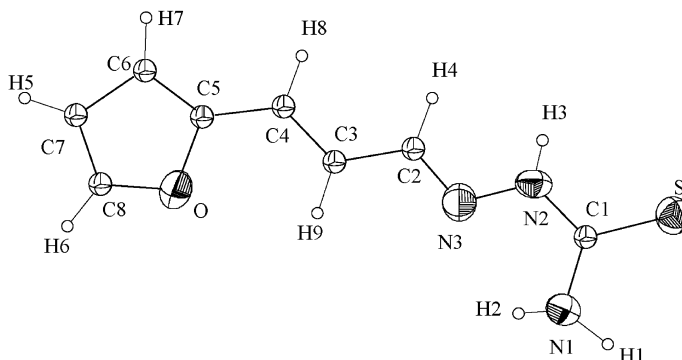


Fig. 3. Perspective view with atom numbering scheme and displacement ellipsoids at 50% probability level of FATSC.

Table 4

Main IR spectral vibrations (cm^{-1}) for 3FTSC and FATSC, a: anti-symmetric, s: symmetric, (s): strong, (m): medium, (w): weak

	3FTSC	FATSC
$\nu(\text{NH}_2)$	3434a (s) 3252s (m)	3421a (s) 3262s (w)
$\nu(\text{NH})$	3309 (m)	3148 (m)
$\nu(\text{C}=\text{S})$	1362 (w) 765 (m)	1352 (w) 748 (m)
$\nu(\text{C}=\text{N})$	1584 (s)	1597 (m)
$\delta(\text{C}-\text{O}-\text{C})$	1290 (m)	1272 (m)
$\nu(\text{C}-\text{N})$	1153 (w)	1096 (w)
$\nu(\text{N}-\text{N})$	936 (m)	923 (m)
Ring breathing	1070 (s)	968 (s)

a singular peak at 13.37 ppm relative to the H3 while the signal of the proton on the H4 double bond appears at 8.10 ppm. It is interesting to note the presence of two broad singlets for H1 and H2 protons at 8.16 and 7.99 ppm, which means that the free rotation around the C–N bond is blocked because of its partial double-bond character [17]. As regards FATSC, ^1H NMR analysis shows that it has a signal identical with 3FTSC, in the same range with a massive between 6.91 and 6.54 ppm, which corresponds to the chemical shift of H5, H7 and H9 protons.

The main IR data are given in Table 4 and it can be seen that the infrared spectra of the two compounds are quite similar. The spectroscopical data agree with the structural results.

The bands appearing around 1355 and 752 cm^{-1} are assigned to $\nu(\text{C}=\text{S})$ vibration [11,20]. The bands in the region 3270–3440 cm^{-1} are attributed to symmetrical and asymmetrical stretching modes $\nu(\text{NH}_2)$ [21]. On the other hand, the strong band observed at 1600 cm^{-1} is assigned to $\nu(\text{C}=\text{N})$ frequencies [11,21].

4. Supplementary material

Crystallographic data for $\text{C}_6\text{H}_7\text{N}_3\text{OS}$ (3FTSC), CCDC #157882 and $\text{C}_9\text{H}_8\text{N}_3\text{OS}$ (FATSC), CCDC #157883 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/m. Copies of available material can be obtained, free of charge, on applica-

tion to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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