O-benzyl-N-(2-furoyl)thiocarbamate

Luis Alberto Montiel-Ortega,⁽¹⁾* Susana Rojas-Lima,⁽¹⁾ Elena Otazo-Sanchez,⁽²⁾ and Roberto Villagómez-Ibarra⁽¹⁾

Received February 5, 2003

The *O*-benzyl-*N*-(2-furoyl)thiocarbamate (1) was obtained by direct reaction between furoyl isothiocyanate and benzyl alcohol. The X-ray diffraction analysis of 1 showed an orthorhombic system, with a = 7.811(4) Å, b = 9.685(4) Å, c = 33.562(15) Å, and space group $P2_12_12_1$. This compound showed two different arrays of structure, corresponding to two conformers in the same crystal unit. In one conformer the carbonyl and thiocarbonyl groups are in a syn arrangement while in the other the groups are anti. Both structures present a non-restricted conformation and show NH–OC hydrogen bonding between them.

KEY WORDS: O-benzyl-N-(2-furoyl)thiocarbamate; conformation; thiocarbamic acid O-ester.

Introduction

Materials that can recognize ions or molecules have wide applications and are subjects of intense study. For example, *O*-alkyl-*N*aroylthiocarbamates are useful as selective extractants of heavy metal ions in water solutions.¹ These compounds are also employed in studies of liquid–liquid extraction of Ag(I).²

The structure of O-alkyl-N-furoylthiocarbamates is similar to that reported for furoylthioureas,³ which show good ion recognition properties in electrochemical sensors. However, 3-monosubstituted 1-furoylthioureas show an intramolecular hydrogen bond that forces the compound to adopt a rigid structure (Fig. 1), which diminishes the chelating ability of the carbonyl and thiocarbonyl groups towards metallic ions. The *O*-alkyl-*N*-furoylthiocarbamates present other structural alternatives because of free bond rotation within the CO–NH–CS–O moiety and they represent a new family of potential ionophores. Their flexible structure could, in principle, be useful to selectively complex a metallic ion with high affinity. These ionophores could also have improved liposolubility into the sensor membrane compared to thioureas.

To obtain more information about the structure of thiocarbamate compounds, we synthesized the O-benzyl-N-(2-furoyl)thiocarbamate (1), searching for different types of ionrecognition materials.

Experimental section

O-benzyl-N-(2-furoyl)thiocarbamate (1). Furoyl chloride (30 mmol, 3.12 mL) was added to a solution of KSCN (30 mmol, 2.91 g) in dry acetone (15 mL) with magnetic stirring, at room temperature. After 10 min, a precipitate of

⁽¹⁾ Centro de Investigaciones Químicas (CIQ), Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo km 4.5, Ciudad Universitaria, 42074 Pachuca, México.

⁽²⁾ Instituto Tecnológico de Toluca (ITT). Av. Instituto Tecnologico s/n Metepec. 52140 Toluca, México.

^{*} To whom correspondence should be addressed; e-mail: luisalberto_montiel@chemist.com.



Fig. 1. Hydrogen bonded structure reported for 3-monosubstituted furoylthioureas. The anti conformer is fixed.

KCl was filtrated and benzyl alcohol (30 mmol, 3.06 mL) in dry acetone (20 mL) was added to the mixture which was stirred overnight. The mixture was poured slowly into 200 mL of ice-water with magnetic stirring. The furoyl thiocarbamate separated as an oily product which was extracted with diethyl ether, dried over Na₂SO₄ and purified by flash chromatography (using SiO₂ with a gradient of hexane-ethyl acetate 10:0, 9:1, 8:2, etc.). The product was collected using the 7:3 hexane-ethyl acetate mixture, the combined fractions were evaporated and the product crystallized as pale vellow needles (m.p. 378 K). Spectroscopic analysis—IR (KBr, cm⁻¹)v: 3354 (NH), 3132 (CH_{ar}), 3032 (CH_{as}), 2944 (CH_s), 1581 and 1469 (C=C), 1664 (C=O), 1286 (COC), 1013 (furan), 1507 (thioureide I), 1196 (thioureide II), 768 (thioureide IV). IR (CHCl₃, cm⁻¹) ν : 3413 (NH), 3065 (CHar), 2977 (CHas), 2894 (CH_s), 1603 and 1476 (C=C), 1683 (C=O), 1286 (COC), 1011 (furan), 1509 (thioureide I), 1196 (thioureide II), 771 (thioureide IV). ¹H NMR (CDCl₃ 400 MHz) δ: 9.58 (N–H), 7.1–7.6 (H(1), H(51) and H(3), H(53)), 6.51 (H(2), H(52); dd, $J_{2-1,52-51} = 1.8$ Hz, $J_{2-3,52-53} = 3.3$ Hz), 4.5 (CH₂O), 7.1–7.6 (5H). ¹³C NMR (CDCl₃ 100 MHz) δ: 187.8 (C=S), 160.5 (C=O), 152.6, 147.2 (C(4), C(54)), 118.2, 115.2 (C(3), C(53)), 112.9, 112.2 (C(2), C(52)), 145.7, 144.0 (C(1), C(51)), 73.9, 64.9 (CH₂O), 134.4 (1CH), 128.5 (2CH), 127.9 (2CH), 141.0 (1C). ¹H NMR (DMSO-*d*₆,400 MHz) δ: 12.07 (N-H), 8.10, 7.9 (H(1), H(51), s), 7.75, 7.27 (H(3), H(53); d, $J_{3-2,53-52} = 3.4$), 6.80, 6.70 (H(2), H(52); dd, $J_{2-1, 52-51} = 1.9$ Hz, $J_{2-3,52-53} = 3.4$ Hz), 5.71, 4.69 (CH₂O), 7.2–7.6 (5H arom.). ¹³C NMR (DMSO- d_6 100 MHz) δ : 188.8 (C=S), 159.8, 154.8 (C=O), 148.3, 146.1

(C(4)–C(54)), 118.4, 113.95 (C(3)–C(53)), 112.7, 112.0 (C(2)–C(52)), 148.1, 145.2 (C(1)–C(51)), 72.76, 63.25 (CH₂O), 142.74, 135.3 (1C), 128.7, 128.5, 128.3, 126.9, 126.7 (5CH). The ¹H NMR and ¹³C NMR spectra were determined on a Jeol eclipse +400 spectrometer at 400 and 100 MHz, respectively, using DMSO- d_6 and/or CDCl₃. The FTIR spectra (KBr pellet or film) were recorded in a spectrophotometer Perkin-Elmer System 2000.

Table 1 shows crystal data and the structure refinement parameters corresponding to the X-ray diffraction analysis. The structure of **1** was solved using the SHELXTL-NT program,⁴ data reduction was carried out using the SAINT-NT⁵

 Table 1. Crystal Data and Structure Refinement for O-benzyl-N-(2-furoyl)thiocarbamate

Compound	O-benzyl-N-(2-furoyl)thiocarbamate
Systematic chemical name	(Furan-2-carbonyl)-thiocarbamic acid O-benzyl ester
CCDC deposit no.	200827
Empirical formula	$C_{13}H_{11}NO_3S$
Formula weight	261.29
Crystal color and habit	Pale yellow/square prism
Crystal system	Orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
Unit cell dimension	a = 7.811(4) Å
(15730 reflections	b = 9.685(4) Å
in full θ range)	c = 33.562(15) Å
Volume, Å ³	2539(2)
Z	8
Density (calculated), Mg/mm ³	1.367
Absorption coefficient, mm ⁻¹	0.254
F(000)	1088
Diffractometer used	Bruker SMART/CCD area-detector
Radiation and wavelength	Mo K α with $\lambda = 0.71073$ Å
Scan type	ϕ and ω scans
Temperature, K	293(2)
θ range for data collection, deg	1.21 to 25.05°
Reflections collected	15730
Independent reflections	4489
Data/restraints/parameters	4489/0/329
Data-to-parameter ratio	13.6:1
Absolute structure parameter ³	0.08(10)
Goodness-of-fit on F^2	0.739
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0568, wR_2 = 0.0536$
R indices (all data)	$R_1 = 0.1826, w R_2 = 0.0744$

Number o	f plane		Plane determining atoms					
1		O(1), C(1), C(2), C(3), C(4) (furanic ring)						
2		O(51), C(O(51), C(51), C(52), C(53), C(54) (furanic ring)					
3		C(8), C(9)	C(8), C(9), C(10), C(11), C(12), C(13) (bencenic ring)					
4	C(58), C(59), C(60), C(61), C			C(62), C(63) (t	encenic ring)			
8		S(1), O(3), N(1), C(6), C(7)						
10		S(2), O(53), N(51), C(55), C(56), C(57)						
		a(_), a(a)	5), 11(51), 0(55), 0(50), 0(57)				
Planes	Angle (deg)	Planes	Angle (deg)	Planes	Angle (deg)			
Planes	Angle (deg)	Planes	Angle (deg)	Planes	Angle (deg)			
Planes 1–2	Angle (deg) 55.3(4)	Planes	Angle (deg) 21.6(3)	Planes 1–4	Angle (deg) 12.2(3)			
Planes 1–2 1–8	Angle (deg) 55.3(4) 30.3(3)	Planes 1–3 1–10	Angle (deg) 21.6(3) 70.3(3)	Planes 1–4 2–3	Angle (deg) 12.2(3) 74.7(4)			
Planes 1–2 1–8 2–4	Angle (deg) 55.3(4) 30.3(3) 45.2(4)	Planes 1–3 1–10 2–8	Angle (deg) 21.6(3) 70.3(3) 76.8(3)	Planes 1-4 2-3 2-10	Angle (deg) 12.2(3) 74.7(4) 16.6(3)			
Planes 1–2 1–8 2–4 3–4	Angle (deg) 55.3(4) 30.3(3) 45.2(4) 29.4(3)	Planes 1–3 1–10 2–8 3–8	Angle (deg) 21.6(3) 70.3(3) 76.8(3) 12.7(3)	Planes 1-4 2-3 2-10 3-10	Angle (deg) 12.2(3) 74.7(4) 16.6(3) 88.0(3)			

Table 2. More Significant Planes and Angles Between Them Obtained Through PLATON Software With Deviation <0.1 Å

program, and the refinement of the structure performed using the SHELXTL-NT software.⁴ The ORTEP-3 software⁶ was used to produce molecular graphics.

Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a "riding-model." H(71) was found by Fourier difference and one overall isotropic thermal parameter was refined. Atomic coordinates and equivalent isotropic displacement parameters are given in the supplementary material. The planes, and the angles between them, are given in Table 2, and were calculated using the PLATON software.⁷

Results and discussion

O-benzyl-*N*-(2-furoyl)thiocarbamate showed two different structures in the same crystal sample. The structures of syn (I) and anti (II) conformers present an almost planar conformation throughout the furoylthiocarbamoyl moiety. Both conformers are hydrogen bonded to each other and contained in the same asymmetric unit. The asymmetric unit is shown in Fig. 2. Torsional angles are listed in Table 3.

The intermolecular hydrogen bonding between both conformers in the asymmetric unit is best observed in Fig. 2. The distance between

Table 3. Torsional/Dihedral Angles (deg) for 1

Anti conformer		Syn conformer	
C(5) - N(1) - C(6) - S(1)	171.2(5)	C(55) - N(51) - C(56) - S(2)	6.4(9)
C(5)-N(1)-C(6)-O(3)	-7.6(9)	C(55)-N(51)-C(56)-O(53)	-176.6(5)
C(6)-N(1)-C(5)-O(2)	-19.5(10)	C(56)-N(51)-C(55)-O(52)	12.9(10)
C(6) - N(1) - C(5) - C(4)	160.6(5)	C(56)-N(51)-C(55)-C(54)	-166.7(5)
C(6) - O(3) - C(7) - C(8)	-168.4(6)	C(56)-O(53)-C(57)-C(58)	173.9(5)
C(7) - O(3) - C(6) - N(1)	178.1(4)	C(57)-O(53)-C(56)-N(51)	-176.6(4)
C(7) - O(3) - C(6) - S(1)	-0.6(9)	C(57)-O(53)-C(56)-S(2)	0.5(7)
C(9)-C(8)-C(7)-O(3)	2.3(9)	C(59)-C(58)-C(57)-O(53)	123.1(6)
C(13) - C(8) - C(7) - O(3)	-179.2(5)	C(63)-C(58)-C(57)-O(53)	-59.2(7)
O(2) - C(5) - C(4) - O(1)	-5.5(9)	O(52)-C(55)-C(54)-O(51)	0.5(9)
O(2) - C(5) - C(4) - C(3)	170.9(6)	O(52)-C(55)-C(54)-C(53)	178.2(7)
N(1) - C(5) - C(4) - C(3)	-9.2(10)	N(51)-C(55)-C(54)-C(53)	-2.3(10)
N(1) - C(5) - C(4) - O(1)	174.4(4)	N(51)-C(55)-C(54)-O(51)	-179.9(5)



Fig. 2. Conformers I and II of O-benzyl-N-(2-furoyl)thiocarbamate in the same asymmetric unit, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

O(2) and H(71)–N(51) is 2.152 (2) Å (O(2) \cdots H(71)–N(51) = 171.75°), this value is significantly shorter than the sum of the van der Waals radii of Oxygen and Hydrogen (2.70 Å).⁸ The other intermolecular hydrogen bonding observed

is outside the asymmetric unit and has a distance of 2.152 Å for N(1)–H(21)····O(52) (N(1)– H(21)····O(52) = 151.16°) (symmetry code: x, y + 1, z) (Fig. 3). These two intermolecular bonding form a zigzag chain along the *b*-axis.



Fig. 3. Intermolecular hydrogen bonding inside and outside asymmetric unit along *b*-axis.

O-benzyl-N-(2-furoyl)thiocarbamate

The angle between the plane defined by N(1)–C(6)(S(1))–O(3)–C(7) (anti conformer) and the plane defined by N(51)–C(56)(S(2))– O(53)–C(57) (syn conformer) was $87.67(18)^\circ$, indicating that both conformers have an orthogonal position in the asymmetric unit.

The furan ring of one conformer and the aromatic ring of the other have a parallel orientation and the angle between those groups was $12.2(3)^{\circ}$. On the other hand, the furan ring of the syn conformer and the aromatic ring of the anti conformer have a different orientation and the angle between these groups is $74.7(4)^{\circ}$.

In the anti conformer, the torsional angle of the C(5)–N(1)–C(6)–O(3) moiety is $-7.6 (9)^{\circ}$ and the torsional angle of the C(5)-N(1)-C(6)-S(1) unit is $171.2(5)^{\circ}$. In the syn conformer the torsional angle formed between O(53)-C(56)-N(51)-C(55) and S(2)-C(56)-N(51)-C(55) atoms are $-176.6(5)^{\circ}$ and $6.4(9)^{\circ}$, respectively (Table 3). These last values are almost opposite for both conformers. The angle between the plane defined by the phenyl ring atoms (C(58)-C(59)-C(60)-C(61)-C(62)-C(63)),and the plane defined by the N(51)-C(56)(S(2))-O(53)-C(57) atoms is 59.3(3)° in the anti conformer. In the syn conformer those groups have a different position and therefore, the angle formed between them is $12.7(3)^{\circ}$.

The KBr IR spectrum of **1** displays absorptions at 1664 cm⁻¹ (C=O) and a broad, strong absorption at 3354 cm⁻¹ (NH). These bands are consistent with hydrogen bonding. In CHCl₃ solution, where the free (non H-bonded) form is present, the signal of both absorptions appear at higher frequencies: 3413 cm^{-1} (NH) and 1683 cm^{-1} (C=O).

The ¹H NMR spectrum of **1** shows a signal at 9.58 ppm in CDCl₃, and at 12.07 ppm in DMSO- d_6 , which corresponds to an acidic NH (thiocarbamate). Similar values are reported for 1-furoyl-3-benzylthiourea³ in DMSO- d_6 . Each furan proton and CH₂ shows two signals on each solvent. The ¹³C NMR spectrum in both solvents shows the same phenomena, indicating the existence of two structures in solution in spite of the different properties of the solvents studied. The C=S (at 187.8 and 188.8 ppm) and C=O (160.5 and 159.8 ppm) signals (in CDCl₃ and DMSO- d_6 , respectively) are within the expected chemical shifts.

Acknowledgments

We are grateful to CONACyT (Project 32718-E) for financial support. AM acknowledges CONACyT for a MSc fellowship. We are grateful to Dr. Alejandro Alvarez (UAEH) for the English review.

References

- Quas, L.; Schroder, V.; Beyer, L. Solvent Extr. Ion Exch. 2000, 18, 1167.
- Quas, L.; Ristau, T.; Schroder, V.; Dietze, F.; Beyer, L. Z. Anorg. Allg. Chem. 2001, 627, 1909.
- Otazo-Sánchez, E.; Pérez-Marin, L.; Estevez-Hernandez, O.; Rojas-Lima, S.; Alonso-Chamarro, J. J. Chem. Soc. Perkin Trans. 2001, 2, 2211.
- SHELXTL-NT Version 5.1; Bruker Analytical X-Ray Systems: Madison, USA, 1998.
- 5. Spek, A.L. Acta Cryst. Sect. C. 1990, A46, 34.
- SAINT+NT Version 6.01; Bruker Analytical X-ray Systems: Madison, USA, 1999.
- 7. Farrugia, L.J. J. Appl. Cryst. 1997, 30, 565.
- 8. Bondi, A. J. Phys. Chem. 1964, 68, 441.