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

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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 P2₁2₁2₁. 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-aryloxythiocarbamates are useful as selective extractants of heavy metal ions in water solutions. These compounds are also employed in studies of liquid–liquid extraction of Ag(I).

The structure of O-alkyl-N-furoylthiocarbamates is similar to that reported for furoylthioureas, 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 ion-recognition 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
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 yellow needles (m.p. 378 K). Spectroscopic analysis—IR (KBr, cm⁻¹): 3554 (NH), 3132 (CH₃), 2944 (CH₅), 1581 and 1469 (C=C), 1664 (C≡O), 1286 (COC), 1011 (furan), 1509 (thioureide), 771 (thioureide IV). 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,¹ data reduction was carried out using the SAINT-NT⁵