Revista de la Sociedad Química de México, Vol. **46**, *Núm. 3 (2002) 251-253*

Investigación

Crystal and Molecular Structure of 2-Aminoacetophenone-*N*(3)-dimethylthiosemicarbazone

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Recibido el 4 de abril del 2002; aceptado el 6 de septiembre del 2002

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Abstract. Condensation of N(3)-dimethylthiosemicarbazide with 2-aminoacetophenone in anhydrous ethanol produces 2-aminoacetophenone-N(3)-dimethylthiosemicarbazone, ***1***, which is planar with the S1 and N1 atoms in a *syn* conformation. The amino group forms a bifurcated intramolecular hydrogen bond with the sulfur and the imine nitrogen, and an intermolecular hydrogen bond with the thione sulfur of a second molecule.
Keywords: Thiosemicarbazones, Crystal structure, X-Ray.

Resumen. La condensación de la N(3)-dimetiltiosemicarbazida con la 2-aminoacetofenona en etanol anhidro produce la 2-aminoacetofenona-N(3)-dimetiltiosemicarbazona, ***1***, la molécula es plana y los átomos S1 y N1 se encuentran en una conformación *syn*. El grupo amino forma un enlace de hidrógeno intramolecular bifurcado con el azufre y el nitrógeno de tipo imina, y un enlace de hidrógeno intermolecular con el azufre de una segunda molécula.
Palabras clave: Tiosemicarbazonas, estructura cristalina, Rayos X.

Introduction

Although there has been considerable interest in thiosemicarbazones derived from salicylaldehyde [1] and 2-hydroxyacetophenone [2], and in particular, those with substitution at the N(3)-position of the thiosemicarbazone moiety [3-5], less attention has been given to the 2-aminobenzaldehyde [6] and 2-aminoacetophenone thiosemicarbazones [7, 8]. The amino group provides additional hydrogen bonding possibilities, a major interest in the structural studies of thiosemicarbazones [9] and thioureas [10]. We previously prepared and characterized representative copper(II) [11], nickel(II) [12] and cobalt(II) [13] complexes of a selection of 2-aminoacetophenone N(3)-substituted thiosemicarbazones, as well as the unsubstituted thiosemicarbazone. Although we have not obtained suitable crystals of any of the complexes, in this paper we present the molecular and crystal structure of the 2-aminoacetophenone-N(3)-dimethylthiosemicarbazone, ***1***.

Results and Discussion

Table 1 summarizes the crystal data, collection information and refinement data of ***1***. Selected bond distances and angles are in Table 2, and Table 3 provides information about the hydrogen-bond geometries. Figure 1 shows the molecular geometry, thermal ellipsoids (30 %), and numbering scheme.

The S1 and N1 atoms of ***1*** are in a *syn* conformation with respect to the C8-N2 bond, and the amino group on the aromatic ring forms an intra-molecular bifurcated hydrogen bond with S1 and N2, giving the molecule the conformation presented in Fig. 1. The C8-S1 bond distance is consistent with its assignment as a formal double bond, and similar to distances found for the analogous bond in thioureas [10] and other thiosemicarbazones [9]. The C7-N1 bond is formally a double bond. The C2-N4, C8-N3 and C8-N2 bond lengths indicate delocalization [14], and the average bond angles around N2 (119.5°), N3 (120.0°) and N4(119.4°) correspond to an sp^2 hybridization. The N1-N2 bond distance is shorter than the

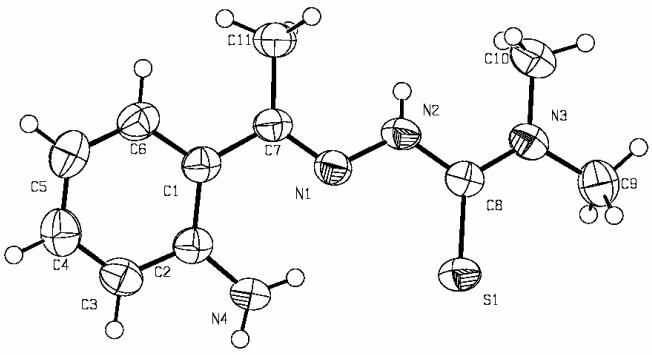

Fig. 1. Themal ellipsoid plot (30 %) of ***1***.

Table 1. Crystal Data and Details of the Structure Determination for ***1***.

Crystal data	
Empirical Formula	$C_{11}H_{16}N_4S$
Formula Weight	236.35
Crystal Color, Habit	yellow, prism
Crystal System	monoclinic
Space Group	$P2_1$ / c (No.14)
a, Å	11.102(2)
b, Å	7.585(2)
c, Å	14.522(3)
β, °	97.33(3)
Volume, Å^3	1212.9(5)
Z	4
Density (calcd.), g / cm^3	1.294
Absorption coefficient, mm^{-1}	2.197
F(000)	504
Crystal Size (mm)	$0.12 \times 0.20 \times 0.40$
Data collection	
Temperature, K	293(2)
Radiation, λ(Å)	CuKα, 1.54178
q min, max, °	4.0, 55.0
Index ranges	$0 \le h \le 11$
	$0 \le k \le 8$
	$-15 \le l \le 15$
Reflections collected	1610
Independent reflections, R_{int}	1517, 0.042
Observed reflects [$I > 2.0\ \sigma$ (I)]	1311
Refinement	
Data-to-parameter ratio	1517:155
R, wR2	0.0422, 0.1213,
Goodness-of-Fit	1.04
Largest diff. peak, hole, eÅ^{-3}	–0.32, 0.34

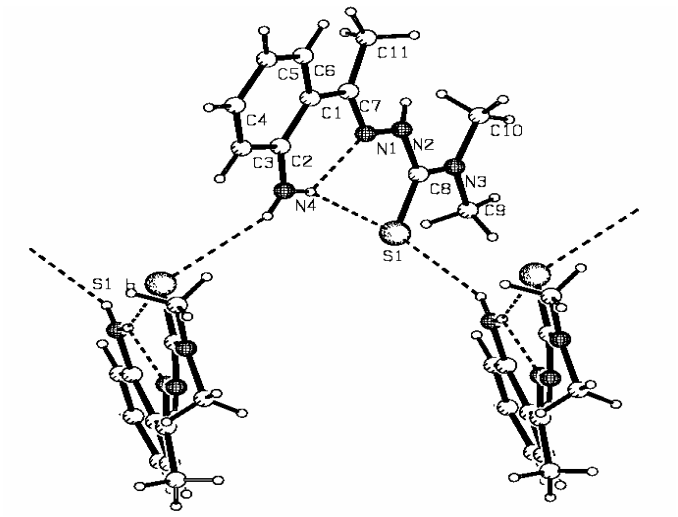

Fig. 2. Intra-and intermolecular hydrogen bonding in ***1***.

Table 2. Selected bond distances (Å), angles (°) and torsion angles (°), for ***1***.

S1-C8	1.686(3)
N1-N2	1.369(3)
N2-C8	1.365(3)
C8-N3	1.332(3)
N3-C9	1.458(3)
N3-C10	1.457(4)
C2-N4	1.368(3)
C7-N1	1.287(3)
C7-C11	1.506(4)
N1-C7-C1	116.1(2)
N1-C7-C11	122.4(2)
C1-C7-C11	121.5(2)
N4-C2-C1	123.2(2)
C7-N1-N2	118.6(2)
C8-N1-N2	119.0(2)
N3-C8-N2	115.3(2)
N3-C8-S1	124.0(2)
N2-C8-S1	120.7(2)
C8-N3-C10	122.7(2)
C8-N3-C9	121.1(2)
C9-N3-C10	116.2(2)
C6-C1-C2-N4	179.2(3)
C7-C1-C2-N4	0.6(4)
C6-C1-C7-C11	14.3(4)
C2-C1-C7-N1	14.3(3)
C6-C1-C7-N1	165.6(2)

Table 3. Hydrogen Bonds (Å, °), for ***1***.

D-H…A	D-H	DHA	D…A	DHA
N4-H4B..S1	0.84(3)	2.87(3)	3.674(3)	161(3).
N4-H4B..N1	0.84(3)	2.03(3)	2.631(4)	128(3).
N4-H4A..S1*	0.81(3)	2.87(3)	3.623(3)	157(3)

*1 – *x*, 1/2 + *y*, 1/2 – *z*

observed value (1.401 Å) in single N-N bonds [14]. In agreement with the bonding delocalization observed in the molecule, torsion angles indicate the molecule is planar. All the atoms other than hydrogens lay in essentially the same plane, with C11 (0.277(3) Å) and N4 (0.275(3) Å) showing the largest deviation from the mean plane of the molecule.

In addition to the intramolecular hydrogen bonds, the amino group is involved in an intermolecular N4-H...S1 (1 – *x*,1/2 + *y*, 1/2 – *z*) hydrogen bond, which generates infinite chains, as shown in Fig. 2. To improve this intermolecular hydrogen bond the NH_2 needs to deviate from the mean plane of the molecule, this deviation is reflected in the 13.8° angle observed between the mean plane of the aromatic ring and the mean plane formed by C11-C7-N1-N2-C8-S1-N3. The hydrogen atom on N2 does not participate in hydrogen bonding probably due to the steric hindrance of the C10 and C11 methyl groups.

Experimental

2-aminoacetophenone was purchased from Aldrich and used without further purification. N(3)-dimethylthiosemicarbazide was prepared following the method of Scovill [15]. The thiosemicarbazide was refluxed for *ca.* 2 h. with 2-aminoacetophenone in ethanol containing a few drops of conc. H_2SO_4 as reported previously [11].

Crystals of ***1*** were obtained by slow evaporation of dilute ethanol solutions and mounted in random orientation on glass fibers. Reflections were acquired with a Nicolet P3/F diffractometer. Three standard reflections every 97 reflections were used to monitor the crystal stability. The structure was solved by direct methods, missing atoms were found by difference-Fourier synthesis, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters using SHELX-97 [16]. Hydrogen atoms attached to nitrogens were found on a difference Fourier map and refined isotropically while hydrogens attached to carbons were located in their calculated positions (C-H, 0.93-0.97 Å), and refined using a riding model. Scattering factors are from the International Tables for Crystallography (1974, Vol IV) [17]. The graphics used are PLATON [18].

Supporting Information Available. CCDC 185211 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts / retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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