

Unusual isolation of a hemiaminal product from 4-cyclohexyl-3-thiosemicarbazide and di-2-pyridyl ketone: Structural and spectral investigations

V. Suni^a, M.R. Prathapachandra Kurup^{a,*}, Munirathinam Nethaji^b

^aDepartment of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India

^bDepartment of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received 20 December 2004; revised 25 March 2005; accepted 29 March 2005

Available online 31 May 2005

Abstract

Stable hemiaminal product was isolated as single crystals from the condensation reaction of di-2-pyridyl ketone with 4-cyclohexyl-3-thiosemicarbazide and structurally and spectrochemically characterized. The compound is the first report of a stable hemiaminal product of the condensation reaction of a substituted thiosemicarbazone. Spectral characterization was carried out using IR, UV–vis., ¹H NMR, ¹³C NMR, COSY and HMQC. The compound crystallizes into a triclinic lattice with space group *P*-1. The molecule reveals a highly strained *Z**E* conformation and a one-dimensional packing is effected by a network of intermolecular hydrogen bonding interactions in the unit cell.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Di-2-pyridyl ketone; Thiosemicarbazone; Hemiaminal; COSY; HMQC; Crystal structure

1. Introduction

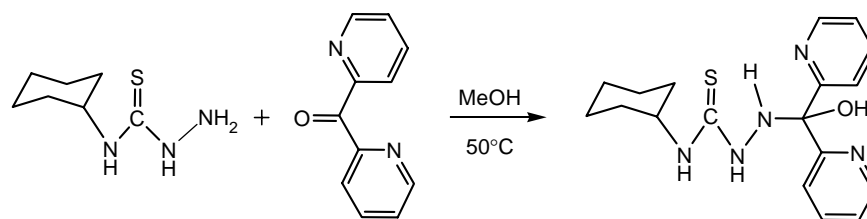
The mechanistic pathway for the condensation of amines with carbonyl compounds involves the formation of a tetrahedral addition intermediate followed by its dehydration to yield imines [1]. These reaction intermediates, formerly referred to as ‘carbinolamines’, are thermodynamically unstable and are presently termed as ‘hemiaminals’ by IUPAC. The rate of formation of hemiaminals with the variation of substituents and pH has been the subject of several investigations and many conclusions were established with regard to their mechanisms. Isolation of the hemiaminal product was immaterial in the above studies and the products of the reactions of aldehydes with thiosemicarbazides were the corresponding thiosemicarbazones. However, here we report the isolation of the hemiaminal derivative, HL of a substituted thiosemicarbazone as crystalline product from a reaction between 4-cyclohexyl-3-thiosemicarbazide and di-2-pyridyl ketone

(Scheme 1). The structure of the compound (Fig. 1) is established by single crystal X-ray diffraction and spectral studies.

Unsubstituted or alkyl substituted imines are highly reactive and imines are stabilized by one or more aryl groups attached to carbon or nitrogen. In such cases, the compounds are easily isolated and are called Schiff bases. Enhanced stability is imparted by aryl substituents due to the conjugative effect of the aryl group and the carbon–nitrogen double bond. For Schiff bases such as hydrazones and semicarbazones, additional stability is imparted by a second nitrogen attached to the azomethine nitrogen [1]. In the light of these facts, a stable thiosemicarbazone is always expected as the final product of the condensation between a thiosemicarbazide and a carbonyl compound as observed from our previous findings [2–13]. From this standpoint also, the present study is interesting, since in spite of the stability factors such as aromatic substitution and hydrazinic nitrogen linkage, the imine product is not separated out here. This is contrary to the observations so far, since stable thiosemicarbazones are the commonly and easily obtained products after the condensation of a thiosemicarbazide with any carbonyl compound.

Previous reports of stable hemiaminal crystals were in the form of covalent intermediates during the reaction of an

* Corresponding author. Tel.: +91 484 2575804; fax: +91 484 2577595.
E-mail address: mrp@cusat.ac.in (M.R.P. Kurup).



Scheme 1.

aldehyde with lysine [14]. However, to the best of our knowledge, the title compound is the first report of the isolation of a hemiaminal product as single crystals from the condensation of a substituted thiosemicarbazide with any carbonyl compound.

2. Experimental

2.1. Materials

Cyclohexyl isothiocyanate (Fluka), hydrazine hydrate (Lancaster) and di-2-pyridyl ketone (Aldrich) were used as received. Infrared spectrum was recorded on ABB Bomem FTIR instrument as KBr pellets in the range 4000–500 cm^{-1} . The ^1H NMR, ^{13}C NMR, COSY and HMQC spectra were recorded using Bruker DRX 500, with CDCl_3 as solvent and TMS as the standard at Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India. The solid state reflectance spectrum was recorded on Ocean Optics, SD2000 Fibre Optic Spectrometer.

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

The X-ray diffraction data were measured at room temperature (293 K) using a Bruker SMART APEX CCD diffractometer, equipped a fine focus sealed tube. Selected crystal data and data collection parameters are given in Table 1. The SMART software was used for data acquisition and the SAINT software for data extraction [15]. Empirical absorption corrections were made on the intensity data and the structure was refined by full-matrix least squares using the SHELXL system of programs [16] and the graphics tool was DIAMOND [17]. All non-hydrogen atoms were refined

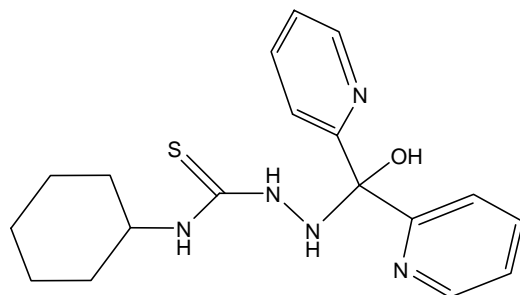


Fig. 1. Structure of compound HL.

anisotropically. The hydrogen atoms were treated with a mixture of independent and constrained refinement and used for structure factor calculation only. The selected bond lengths and bond angles are listed in Table 2.

2.3. Synthesis of HL

The hemiaminal, HL was prepared by adapting the following procedure. Ethanolic solutions of cyclohexyl isothiocyanate (0.706 g, 5 mmol) and hydrazine hydrate (0.250 g, 5 mmol) were mixed with constant stirring. The stirring was continued for one more hour and the white product, *N*(4)-cyclohexylthiosemicarbazide formed was washed, dried and recrystallised from ethanol. A methanolic solution of the *N*(4)-cyclohexyl thiosemicarbazide (0.865 g, 5 mmol) was then refluxed with di-2-pyridyl ketone (0.921 g, 5 mmol) in 5 ml methanol continuously for 4 h after adding 1–2 drops of acetic acid and the pH of

Table 1
Crystal data and structural refinement for HL

Parameters	HL
Empirical formula	$\text{C}_{18}\text{H}_{25}\text{N}_5\text{O}_2\text{S}$
Formula weight, M	375.49
Temperature, T (K)	293(2)
Wavelength, Mo $K\alpha$ (\AA)	0.71073
Crystal system	Triclinic
Space group	$P-1$
Lattice constants a (\AA), b (\AA), c (\AA), α ($^\circ$), β ($^\circ$), γ ($^\circ$)	8.571(5), 10.700(6), 11.104(6), 95.089(9), 104.996(8), 91.481(9)
Volume V (\AA^3)	978.5(9)
Z calculated density, ρ (Mg m^{-3})	2, 1.274
Absorption coefficient, μ (mm^{-1})	0.188
$F(000)$	400
Crystal size (mm)	$0.35 \times 0.33 \times 0.30$
θ Range for data collection	1.91–26.25
Limiting indices	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$
Reflections collected	10253
Unique reflections	3978 [$R_{\text{int}} = 0.0145$]
Completeness to θ	26.25 (91.1%)
Absorption correction	Multi-scan
Max. and min. transmission	0.9459 and 0.9373
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3978/0/335
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0443$, $wR_2 = 0.1165$
R indices (all data)	$R_1 = 0.0496$, $wR_2 = 0.1211$
Largest difference peak and hole (e \AA^{-3})	0.304 and -0.265

Download English Version:

<https://daneshyari.com/en/article/9769997>

Download Persian Version:

<https://daneshyari.com/article/9769997>

[Daneshyari.com](https://daneshyari.com)