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Synthesis and Crystal Structure of N-(*p*-Nitro)benzoyl-N'-(3-pyridyl)thiourea

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In this study, N-(*p*-nitro)benzoyl-N'-(3-pyridyl)thiourea with the molecular formula $C_{13}H_{10}N_4O_3S$ has been synthesized and characterized structurally by ^1H NMR and X-ray crystallography. There is a strong intramolecular N2-H2···O1 hydrogen bond. In the crystal structure, intermolecular N1-H1···N4 hydrogen bonds link neighbouring molecules into an infinite zigzag chain supramolecular structure.

Key Words: Thiourea, Synthesis, Crystal structure.

INTRODUCTION

The extensive applications of thiourea derivatives are paid much attention. Besides their good biological activities[1-3], some thioureas have good inhibition effect on the corrosion of mild steel in hydrochloric acid medium and are excellent neutral ion carrier[4,5], which are also organic reaction catalyst in the metal-catalyzed asymmetric reduction of carbonyl compounds and carbonylative cyclization of *o*-hydroxy arylacetylenes[6,7]. Studies of a number of substituted thioureas including N-benzoyl-N'-thiourea indicate an intramolecular hydrogen bond between NH group and oxygen atom[8,9]. ^1H NMR spectrum shows that there is intramolecular hydrogen bond between the pyridyl nitrogen atom and NH group[10,11] and there is also internolecular hydrogen bond between NH group and pyridyl nitrogen atom of a neighboring molecule[12]. Here we report the synthesis and crystal structure of N-(*p*-nitro)benzoyl-N'-(3-pyridyl)thiourea.

EXPERIMENTAL

p-Nitrobenzoyl chloride, 3-aminopyridine and polyethylene glycol-400 were purchased and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra in the range 4000-400 cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. The ^1H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using $CDCl_3$ as solvent. X-Ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points was measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

Synthesis: The *p*-nitrobenzoyl chloride (1.86 g, 10 mmol) was reacted with ammonium thiocyanate (1.14 g, 15 mmol) in CH_2Cl_2 (25 mL) solution under soild-liquid phase transfer catalysis, using polyethylene glycol-400 (0.18 g) as the catalyst, to give the corresponding *p*-nitrobenzoyl isothiocyanate, which was reacted with 3-aminopyridine (0.85 g, 10 mmol), to give the title compound. Yield 67.8 %, m.p. 443-445 K. Anal. calcd. (%) for $C_{13}H_{10}N_4O_3S$: C, 51.65; H, 3.33; N, 15.88. Found (%): C, 51.47; H, 3.45; N, 15.69. Selected IR data (KBr, ν_{max}, cm^{-1}, pellet): 3344, 3173 (NH), 1680 (C=O), 1171 (C=S). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.49 (dd, J = 8.4, 4.8 Hz, 1H, PyH), 8.12 (t, J = 8.2 Hz, 1H, PyH), 8.21 (dd, J = 20.4, 8.8 Hz, 2H, ArH), 8.34 (dd, J = 20.4, 8.8 Hz, 2H, ArH), 8.45 (dd, J = 27, 6.6 Hz, 1H, PyH), 8.74 (s, 1H, PyH), 12.13 (s, 1H, NH), 12.31 (s, 1H, NH).

A THF solution of the N-(*p*-nitro)benzoyl-N'-(3-pyridyl)-thiourea was placed in a diethyl ether atmosphere, after several days, along with diffusion of diethyl ether into the THF solution of the title compound, colourless needle-shaped single crystals suitable for X-ray crystallographic analysis were obtained.

X-Ray structure determination: The single crystal of N-(*p*-nitro)benzoyl-N'-(3-pyridyl)thiourea, with approximate dimensions of 0.37 mm × 0.17 mm × 0.15 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the title compound are given

in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 647074.

TABLE-1
CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE TITLE COMPOUND

Empirical formula	$C_{13}H_{10}N_4O_3S$
Formula weight	302.31
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions	a = 9.3802(13) Å, b = 15.567(2) Å, c = 9.6041(14) Å β = 110.217(2)
Volume	1316.0(3) $Å^3$
Z	4
Density (calculated)	1.526 mg/m^3
Absorption coefficient	0.263 mm^{-1}
$F_{(000)}$	624
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 18$, $-7 \le l \le 11$
Reflections collected/unique	6580/2318 [$R_{(int)}$ = 0.0441]
Independent reflections	2318
Data/restraints/parameters	2318/0/190
Goodness of fit indicator	1.019
R [I > 2σ(I)]	R_1 = 0.0425, wR_2 = 0.0786
Largest diff. peak and hole	0.243 and -0.195 e Å

RESULTS AND DISCUSSION

X-Ray crystallographic analysis revealed the crystal structure of the title compound. And the structure is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. The single crystal structure of the title compound is built up by only the $C_{13}H_{10}N_4O_3S$ molecule, in which all bond lengths are in normal ranges. The X-ray diffraction anylisis of the title compound revealed there is an intramolecular hydrogen bonding N2-H2···O1 (d(H2..O1) = 1.98 Å; d(N2···O1) = 2.675(4) Å; ∠N2-H2···O1 = 136.9º) between the carbonyl group and the N2-H2 group, the six atoms (C2/N1/C1/N2/H2/O1) in the hydrogen-bonded ring almost coplanar, the torsion angles of C(2)-N(1)-C(1)-N(2) and C(1)-N(1)-C(2)-O(1) are -0.2(4)º and 13.6(4)º, respectively. The C=O bond length is 1.221(3) Å, longer than the average C=O bond length (1.200 Å), which is due to intramolecular hydrogen bonding interactions.

A view of the intra- and inter- molecular hydrogen bonds in a stacking of the title compound in the crystal lattice shows it contains four molecules in a crystal packing. These molecules are linked with another neighboring molecule by the intermolecular hydrogen bondings of N2-H2···O1 (-x + 1, -y + 2, -z + 2) (d(H2··O1) = 2.569 Å; d(N2···O1) = 3.194(4) Å; ∠N2-H2···O1 = 130.33º) and N1-H1···N4 (-x + 3/2, y - 1/2,

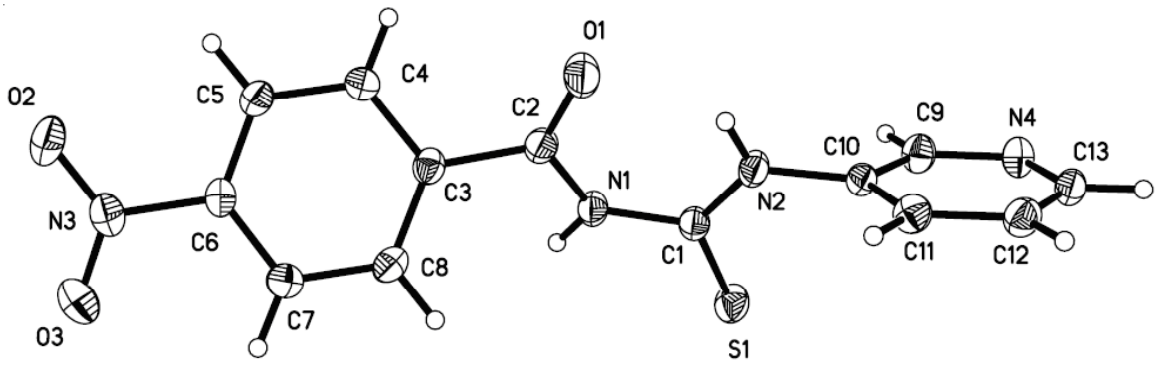

Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (º) FOR THE TITLE COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
N(1)-C(2)	1.366(3)	N(4)-C(13)	1.338(3)	C(6)-C(7)	1.369(3)
N(1)-C(1)	1.390(3)	O(1)-C(2)	1.222(3)	C(7)-C(8)	1.380(3)
N(2)-C(1)	1.334(3)	S(1)-C(1)	1.660(3)	C(9)-C(10)	1.379(3)
N(2)-C(10)	1.421(3)	C(2)-C(3)	1.490(4)	C(10)-C(11)	1.371(3)
N(3)-O(3)	1.218(3)	C(3)-C(8)	1.381(4)	C(11)-C(12)	1.372(3)
N(3)-O(2)	1.219(3)	C(3)-C(4)	1.385(3)	C(12)-C(13)	1.372(3)
N(3)-C(6)	1.474(3)	C(4)-C(5)	1.381(3)	–	–
N(4)-C(9)	1.331(3)	C(5)-C(6)	1.375(3)	–	–
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C(2)-N(1)-C(1)	129.4(2)	O(1)-C(2)-C(3)	121.8(2)	C(6)-C(7)-C(8)	118.9(3)
C(1)-N(2)-C(10)	124.9(2)	N(1)-C(2)-C(3)	114.7(2)	C(7)-C(8)-C(3)	120.1(3)
O(3)-N(3)-O(2)	123.7(3)	C(8)-C(3)-C(4)	119.7(2)	N(4)-C(9)-C(10)	123.4(3)
O(3)-N(3)-C(6)	117.9(3)	C(8)-C(3)-C(2)	121.7(2)	C(11)-C(10)-C(9)	118.7(2)
O(2)-N(3)-C(6)	118.4(2)	C(4)-C(3)-C(2)	118.6(2)	C(11)-C(10)-N(2)	120.1(2)
C(9)-N(4)-C(13)	116.9(2)	C(5)-C(4)-C(3)	120.8(3)	C(9)-C(10)-N(2)	121.2(2)
N(2)-C(1)-N(1)	114.6(2)	C(6)-C(5)-C(4)	117.9(2)	C(10)-C(11)-C(12)	118.9(3)
N(2)-C(1)-S(1)	125.7(2)	C(7)-C(6)-C(5)	122.6(2)	C(13)-C(12)-C(11)	118.8(3)
N(1)-C(1)-S(1)	119.72(19)	C(7)-C(6)-N(3)	119.0(2)	N(4)-C(13)-C(12)	123.4(2)
O(1)-C(2)-N(1)	123.5(2)	C(5)-C(6)-N(3)	118.4(2)	–	–

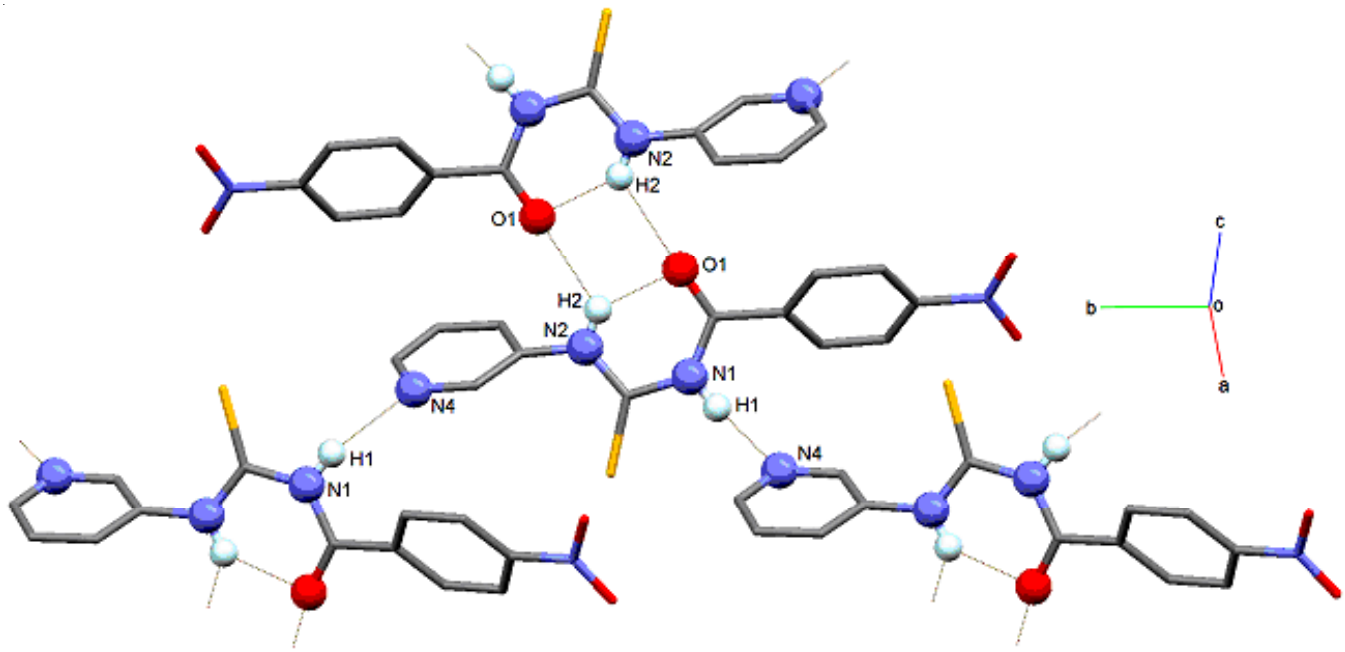

Fig. 2. Digram showing the intramolecular O-H···N and intermolecular O-H···N

-z + 3/2) (d(H1··N4) = 2.22 Å; d(N1···N4) = 2.993(3) Å; ∠N1-H1···N4 = 150.0°) (Fig. 2)[13-15].

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