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

GANG LI*, MENG-MENG ZHAO, LI WANG, YU-HUA YANG, YU-JIE ZHANG and XIU-YAN DONG

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: li_gang78@126.com

(Received: 26 April 2012;

Accepted: 11 February 2013)

AJC-12958

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 activities¹⁻³, 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 intermolecular hydrogen bond between NH group and pyridyl nitrogen atom of a neighboring molecule¹². 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 solid-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 $\times$ 0.17 mm $\times$ 0.15 mm was placed on a Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_{α} radiation (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 ₄ O ₃ S
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 ≤ h ≤ 11, -16 ≤ k ≤ 18, -7 ≤ l ≤ 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 ⁻³

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 C₁₃H₁₀N₄O₃S molecule, in which all bond lengths are in normal ranges. The X-ray diffraction analysis 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 = 136.9°) 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)° and 13.6(4)°, 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 = 130.33°) 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 (°) 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. Diagram showing the intramolecular O-H...N and intermolecular O-H...N

$-z + 3/2$) ($d(H1 \cdots N4) = 2.22 \text{ \AA}$; $d(N1 \cdots N4) = 2.993(3) \text{ \AA}$; $\angle N1-H1 \cdots N4 = 150.0^\circ$) (Fig. 2)¹³⁻¹⁵.

ACKNOWLEDGEMENTS

The authors thank the Young Scholars Science Foundation of Lanzhou Jiaotong University for financial support of this work.

REFERENCES

1. S.G. Teoh, S.H. Ang and H.K. Fun, *J. Organomet. Chem.*, **580**, 17 (1999).
2. V. Ravichandran and R.K. Agrawal, *Med. Chem. Lett.*, **17**, 2197 (2007).
3. R. Campo, J.J. Criado and E. Garcia, *J. Inorg. Biochem.*, **89**, 74 (2002).
4. S.D. Shetty and P. Shetty, *Mater. Lett.*, **61**, 2347 (2007).
5. M.R. Ganjali, P. Norouzi and T. Alizadeh, *Sens. Actuators B*, **120**, 487 (2007).
6. Y. Nan, H. Miao and Z. Yang, *Org. Lett.*, **2**, 297 (2000).
7. J.A.J. Breuzard, M.L. Tommasino and F. Toucard, *J. Mol. Catal. A: Chem.*, **156**, 223 (2000).
8. W.K. Dong, X.Q. Yang, L.Q. Chai, Y.Q. Tian and J.H. Feng, *Phosphorus Sulfur Silicon Rel. Elem.*, **183**, 1181 (2008).
9. W.K. Dong, X.Q. Yang and J.H. Feng, *Acta Crystallogr.*, **E62**, o3459 (2006).
10. J. Valdés Martínez, S. Hernández Ortega and L.J. Ackeman, *J. Mol. Struct.*, **524**, 51 (2000).
11. D.X. West, J.K. Swearingen and A.K. Hernetet, *J. Mol. Struct.*, **522**, 27 (2000).
12. V.M. Jesus, H.O. Simon and R. Manuel, *J. Chem. Crystallogr.*, **34**, 533 (2004).
13. W.K. Dong, G. Wang, S.S. Gong, J.F. Tong, Y.X. Sun and X.H. Gao, *Transition Met. Chem.*, **37**, 271 (2012).
14. W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009).
15. W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).