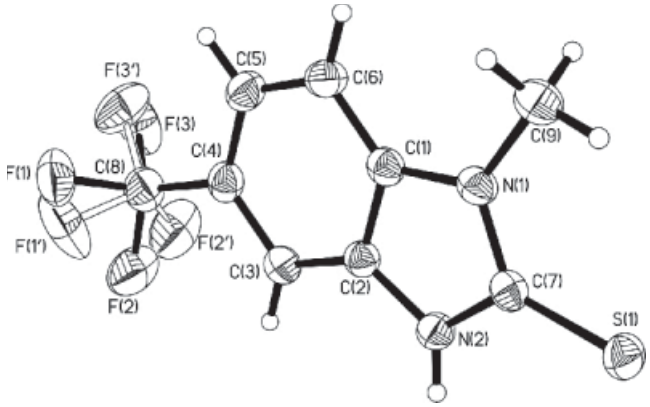
Crystal structure of 1-methyl-5-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-2(3*H*)-thione, $C_9H_7F_3N_2S$

Guang-Zhou Zhu[I], Zai-Sheng Lu[I,*], Huan-Le Shi[II] and Xiang-Shan Wang[I]

[I] School of Chemistry & Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, Jiangsu Province, P. R. China
[II] Lianyungang Henrychem Science Co., Ltd., Lianyungang, Jiangsu 222000, P. R. China

Received October 16, 2012, accepted December 03, 2012, available online April 05, 2013, CCDC no. 1267/3913



Abstract

$C_9H_7F_3N_2S$, monoclinic, $P2_1/c$ (no. 14), a = 8.695(4) Å, b = 4.676(2) Å, c = 24.13(1) Å, β = 97.861(4)°, V = 972.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.0386, $wR_{ref}(F^2)$ = 0.1074, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.109×0.188×0.204 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.43 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	49.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6381, 1710
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1540
$N(param)_{refined}$:	170
Programs:	SHELX [9], DIAMOND [10]

Source of material

The title compound was synthesized by addition of carbondisulfide (1.6 ml, 26 mmol) to the methanol solution (50 ml) of *N*-methyl-4-(trifluoromethyl)-1,2-benzendiamine (2.47 g, 13 mmol). The mixture solution was stirred at 0°C over night to give a colourless solution. The solution was evaporated to dryness getting a white solid (yield 70%). Colourless block crystals suitable for X-ray analysis of title compound were obtained from THF by slow evaporation within a few days.

Experimental details

The H atoms were calculated geometrically and refined as riding, with C–H = 0.93-0.97 Å, except for H2, and with $U_{iso}(H) = 1.2U_{eq}$ (parent atom).

Discussion

Benzimidazole-2-thione and its derivatives have been widely studied because of their importance as pharmaceutical intermediates [1] and ligands [2,3]. X-ray structure analysis reveals that the title compound in the solid state prefers the thio form with N2 protonted rather than the alternative tautomeric ene-thiol form [4-6]. The bond length of C7–S1 is with a value of 1.673(3) Å slightly shorter than that in the nucleoside containing a benzimidazole (1.693(4) Å) [7] and 1-methyl-1*H*-benzimidazole-2(3*H*)-thione (1.684(2) Å) [8]. In the imizole ring, the bond lengths of N1–C1, N1–C7, N2–C2 and N2–C7 are 1.383(3), 1.364(3), 1.379(3) and 1.356(3) Å respectively, between C-N single bond and C=N double bond. The benzene ring and imizo ring are coplanar, with the dihedral angle 1.27(0.16)°. In the the title structure the three fluorine atoms of trifluoromethyl exhibt disorder status with occupancy ratio of 0.6:0.4. Each pair of two neighbouring molecules are connected by two crystallographically dependant intermolecular hydrogen bonds (d(N···S) = 3.301(2) Å; ∠N–H···S = 179(3)°) forming a dimer.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	4*e*	0.7480	0.9575	0.6160	0.055
H(5A)	4*e*	0.5011	0.5014	0.7149	0.064
H(6A)	4*e*	0.2696	0.6836	0.6692	0.062
H(9A)	4*e*	0.0411	1.2169	0.5623	0.072
H(9B)	4*e*	0.0736	1.0851	0.6225	0.072
H(9C)	4*e*	0.0557	0.8846	0.5699	0.072
H(2)	4*e*	0.548(3)	1.292(6)	0.541(1)	0.053(8)

* Correspondence author (e-mail: lzs@jsnu.edu.cn)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*		0.23641(7)	1.4664(2)	0.49658(3)	0.0404(4)	0.0639(5)	0.0547(5)	0.0042(3)	0.0023(3)	0.0112(3)
N(2)	4*e*		0.4823(2)	1.2047(5)	0.55716(9)	0.035(1)	0.051(1)	0.045(1)	–0.0010(9)	0.0074(9)	0.006(1)
N(1)	4*e*		0.2599(2)	1.0855(5)	0.58251(8)	0.036(1)	0.047(1)	0.046(1)	–0.0035(9)	0.0077(9)	–0.0018(9)
C(1)	4*e*		0.3726(3)	0.9340(5)	0.6164(1)	0.043(1)	0.041(1)	0.040(1)	–0.003(1)	0.006(1)	–0.006(1)
C(4)	4*e*		0.6450(3)	0.7156(6)	0.6706(1)	0.056(2)	0.044(1)	0.045(1)	0.002(1)	0.000(1)	–0.003(1)
C(2)	4*e*		0.5152(3)	1.0124(5)	0.6005(1)	0.041(1)	0.039(1)	0.040(1)	–0.001(1)	0.005(1)	–0.002(1)
C(3)	4*e*		0.6534(3)	0.9052(6)	0.6269(1)	0.042(1)	0.047(1)	0.048(1)	–0.000(1)	0.005(1)	–0.002(1)
C(7)	4*e*		0.3272(3)	1.2504(5)	0.5458(1)	0.039(1)	0.044(1)	0.041(1)	–0.001(1)	0.004(1)	–0.005(1)
C(5)	4*e*		0.5029(3)	0.6322(6)	0.6859(1)	0.068(2)	0.046(2)	0.046(1)	–0.004(1)	0.005(1)	0.005(1)
C(6)	4*e*		0.3644(3)	0.7397(6)	0.6590(1)	0.055(2)	0.052(2)	0.049(1)	–0.009(1)	0.012(1)	0.001(1)
C(8)	4*e*		0.7916(4)	0.6087(6)	0.7028(1)	0.070(2)	0.052(2)	0.068(2)	0.004(2)	–0.009(2)	0.009(2)
C(9)	4*e*		0.0934(3)	1.0664(7)	0.5845(1)	0.039(1)	0.076(2)	0.067(2)	–0.003(1)	0.012(1)	0.006(2)
F(1)	4*e*	0.599	0.8047(9)	0.718(2)	0.7568(2)	0.088(4)	0.107(4)	0.066(2)	–0.005(3)	–0.022(2)	–0.003(2)
F(2)	4*e*	0.599	0.9201(5)	0.701(2)	0.6862(3)	0.047(2)	0.163(6)	0.101(4)	0.012(3)	0.000(2)	0.064(4)
F(3)	4*e*	0.599	0.794(1)	0.336(1)	0.7139(4)	0.114(5)	0.044(2)	0.145(6)	0.014(3)	–0.057(5)	–0.014(3)
F(1')	4*e*	0.401	0.859(2)	0.773(2)	0.7407(7)	0.101(7)	0.059(4)	0.170(9)	0.004(4)	–0.074(6)	–0.017(5)
F(2')	4*e*	0.401	0.887(1)	0.509(3)	0.6663(4)	0.064(4)	0.160(8)	0.099(5)	0.047(5)	0.012(4)	0.034(5)
F(3')	4*e*	0.401	0.772(2)	0.363(2)	0.7283(5)	0.105(5)	0.092(7)	0.086(5)	0.036(4)	0.022(4)	0.046(5)

Acknowledgments. We are grateful to a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions, the National Natural Science Foundation of China (20802061), and Natural Science Foundation of Jiangsu Education Deparatment (02KJB 150007) for financial support.

References

1. Mavrova, A.. T.; Denkova, P.; Tsenov, Y. A.; Anichina, K. K.; Vutchev, D. I.: Synthesis and antitrichinellosis activity of some bis(benzimidazol-2-yl)amines. Bioor. Med. Chem. **15** (2007) 6291-6297.
2. Ozturk, I. I.; Hadjikakou, S. K.; Hadjiliadis, N.; Kourkoumelis, N.; Tasiopoulos, A. J.; Scleiman, H.; Barsan, M. M.; Butler, I. S.; Balzarini, J.: New antimony(III) bromide complexes with thioamides: synthesis, characterization, and cytostatic properties. Inorg. Chem. **48** (2009) 2233-2245.
3. Dennehy, M.; Quinzani, O. V.; Faccio, R.; Freire, E.; Mombru, A.: The conformations of copper(I) complexes of 1*H*-benzimidazole-2(3*H*)-thione and thiosaccharinate. Acta Crystallogr. **C68** (2012) m12-m16.
4. Prusiner, P.; Sundaralingam, M.: Crystal and structure of 2-thio-1-(β-D-ribofuranosyl)-3*H*-benzimidazole. Acta Crystallogr. **B29** (1993) 2328-2334.
5. Simanek, R. E.; Tsoi, A.; Wang, C. C. C.; Whitesides, G. M.: Benzimidazolene-2-thione: A new class of molecules for the engineering of molecular tapes in the organic solid state: Chem. Mater. **9** (1997) 1954-1961.
6. McBride, M. T.; Luo, T. M..; Palmore, G. T. R.: Hydrogen-bonding interactions in crystalline solids of cyclic thioureas. Cryst. Growth Des. **1** (2001) 39-46.
7. Kitano, Y. K.; Ishitani, A.; Sato, H.; Imamura, S.; Ashida, T.: Structure of 4,5,6,7-tetrahydro-1,3-benzimidazole-2-thione. Acta Crystallogr. **C47** (1991) 1269-1271.
8. Khan, H.; Badshah, A.; Shaheen, F.; Gieck, C.; Qureshi, R. A.: 1-Methyl-1*H*-benzimidazole-2(3*H*)-thione. Acta Crystallogr. E64 (2008) o1141.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
10. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.