SYNTHESIS AND X-RAY STRUCTURE OF 2-HYDRAZINYL-1,3-BENZOTHIAZOLE

Ratika Sharma,[a] Prakash S. Nayak,[b] B. Narayana,[b] Vivek K. Gupta[a] and Rajni Kant[a]*

Keywords: 2-hydrazinyl-1,3-benzothiazole; single crystal XRD; inter-molecular interactions; hydrogen bonding;

The title compound, $C_7H_7N_3S$, (2-hydrazinyl-1,3-benzothiophene) was prepared from the reaction of 2-amino-benzothiazole treated with hydrazine hydrate. It crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters a = 10.839(5), b = 5.752(5), c = 12.961(5) Å, β = 110.005(5)º, Z = 4. The crystal structure is stabilized by N-H…N [N2-H5...N3, N1-H12...N1] intermolecular interactions, N2-H5...N3 interaction is responsible for the formation of dimers corresponding to $R_2^2(8)$ graph-set motif and the dimers are further connected by N1-H12…N1 hydrogen bonding forming dimeric chains. Besides this, there is N1-H11… π interaction which is responsible for the stabilization of the crystal structure. The packing diagram of the title compound represents the dimeric chains extending along the b-axis.

Corresponding Authors*
Fax: +91 191 243 2051
E-Mail: rkvk.paper11@gmail.com
[a] Department of Physics& Electronics, Jammu University , Jammu Tawi -180 006, India.
[b] Department of Studies in Chemistry, Mangalore University, Mangalagangotri-574 199, Karnataka, India.

Introduction

Benzothiazoles are very important bicyclic ring compounds which are of great interest because of their biological activities. The substituted benzothiazole derivatives have emerged as significant components in various diversified therapeutic applications. The literature review reveals that benzothiazoles and their derivatives show considerable activity, including potent inhibition of human immunodeficiency virus type 1 (HIV-1) replication by HIV-1 protease inhibition, antitumor,[1] anthelmintic,[2] analgesic and anti-inflammatory,[3] antimalarial,[4] anticandidous activities [5] and various CNS activities.[6]

Experimental

Materials and methods

All chemicals were purchased commercially and used without prior purification. Melting point was taken in open capillary tube and was uncorrected. The purity of the compound was confirmed by thin layer chromatography using Merck silica gel 60 F_{254} coated aluminium plates.

Synthetic procedure of 2-hydrazinyl-1,3-benzothiazole (I)

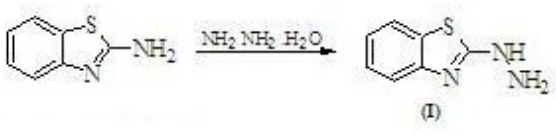
2-Amino-1,3-benzothiazole (0.03 mol) and hydrazine hydrate (85 %) (0.12 mol) in 50 ml of ethylene glycol were refluxed by stirring for 4 h at 333 K. A white solid was precipitated at the end of the reflux period. The mixture was cooled and the product was filtered and then washed with water several times. Then the product was air-dried and recrystallized by using ethanol. The single crystals were grown by slow evaporation from solvent ethanol and dichloromethane (1:1, v/v). Yield obtained 62 %.

X-ray Crystallography

X-ray intensity data of a crystal (0.30 X 0.20 X 0.10 mm) having well-defined crystal morphology were collected at 293(2)K on *X'calibur* CCD area-detector diffractometer equipped with graphite monochromated Mo$K\alpha$ radiation (λ=0.71073 Å*)*. The intensities were measured by employing ω scan mode for the diffraction angle ranging from 3.92 to 25.00º. A total number of 2657 reflections were measured of which 1335 were found to be unique. The criterion *(I >2σ(I))* was employed to the unique data set and hence 1080 reflections were treated as observed. Data were corrected for Lorentz and Polarization factors. The structure was solved by direct methods using SHELXS97.[7] All non-hydrogen atoms of the molecule were located in the best E-map. Full-matrix least-squares refinement was carried out using SHELXL97.[7] The final refinement cycles converged to R = 0.0372 and $wR(F^2)$ = 0.0825 for 1080 observed reflections. Residual electron densities ranged from -0.227 to 0.157 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4).The crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2. An ORTEP[8] view of the title compound with atomic labeling is shown in Fig. 1. The geometry of the molecule was calculated using the PLATON[9]and PARST[10] software.

Results and discussion

The title compound was prepared from 2-amino-1,3-benzothiazole and hydrazine hydrate in ethylene glycol under 4 h reflux with 62 % yield.



(I)

The white solid was recrystallized from ethanol and single crystals were grown from EtOH:CH2Cl2 (1:1, v/v) mixture.

Table 1. Crystal data and other experimental details

CCDC Number	983692
Crystal description	Block
Crystal size	0.30 x 0.20 x 0.10 mm
Empirical formula	$C_7H_7N_3S$
Formula weight	165.22
Radiation, Wavelength	Mo *Kα,* 0.71073 Å
Unit cell dimensions	*a* = 10.839(5), *b* = 5.7552(5), *c* = 12.961(20) Å, *β* = 110.005(5)º
Crystal system, Space group	Monoclinic, $P2_1/n$
Unit cell volume	759.3(8)Å^3
No. of molecules per unit cell, Z	4
F(000)	344
θ range for entire data collection	3.92< θ < 25.00
Reflections collected / unique	2657/1335
Reflections observed(I > 2σ(I))	1080
Range of indices	*h*= -12 to 10, *k*= -4 to 6, *l*= -9 to 15
No. of parameters refined	112
Final *R*-factor	0.0372
$wR(F^2)$	0.0825
Goodness-of-fit	1.073
(Δ/σ)max	0.000
Final residual electron density	-0.227< Δρ >0.157 eÅ^{-3}

The N1-N2 (=1.413 Å) bond length is comparable to the pure single bond length.[11] The nitrogen-carbon distance [N3-C5=1.389(3)Å] is shorter than the distance characteristics of single C-N bond length (1.45 Å) but is comparable with the values reported in the analogous structures.[12,13] The benzothiazole moiety is planar and the hydrazinyl group is slightly deviated with respect to the plane of benzothiazole moiety [deviation being -0.01717 Å].

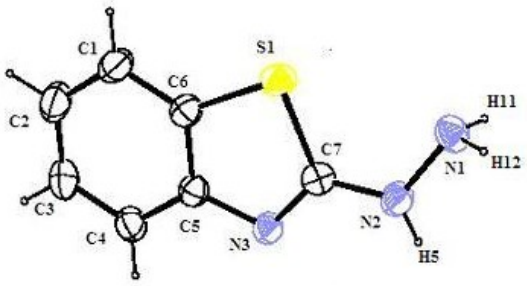


Figure 1. Ortep view of the molecules with displacement ellipsoids at the 40 % probability level. H atoms shown as small spheres of arbitrary radii.

Table 2. Selected bond lengths (Å) and bond angles (º) for non-hydrogen atoms (e.s.d.'s are given in parentheses)

Bond lengths, Å		**Bond angles, °**	
N2-N2	1.413(3)	C6-S1-C7	88.2(1)
N3-C7	1.305(3)	C7-N2-N1	117.7(2)
N2-C7	1.341(3)	N3-C7-N2	123.1(2)
N3-C5	1.389(3)	N3-C7-S1	120.5(2)
S1-C7	1.759(3)	C7-N3-C5	110.2(2)
S1-C6	1.748(2)		

In the crystal structure, molecules are inter-linked *via* intermolecular N2-H5…N3 and N1–H12…N1 interactions. N2-H5…N3 hydrogen bond is responsible for the formation of dimers (Fig. 2) corresponding to $R_2^2(8)$ graph-set motif[14] and the dimers are further connected by N1-H12…N1 hydrogen bonding forming dimeric chains along the *b*- axis (Fig. 3).

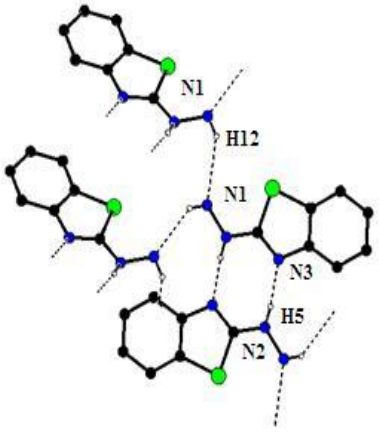


Figure 2. Intermolecular N2-H5….N3 hydrogen bond giving rise to dimer

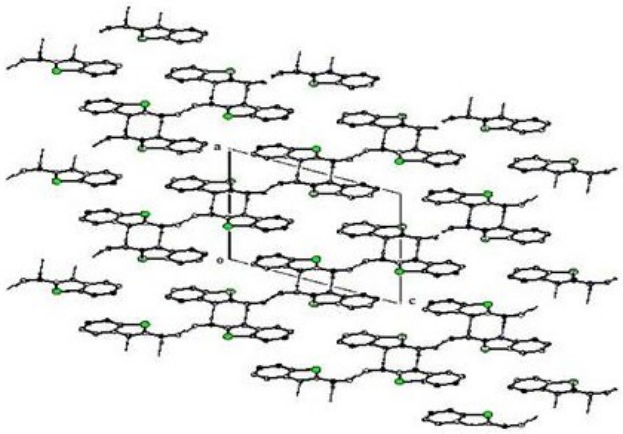


Figure 3. Unit cell molecular packing viewed down the b-axis

The crystal packing also features N1-H11…π interaction, where atom N1 acts as hydrogen- bond donor to the six membered ring (C1/C2/C3/C4/C5/C6), helps in the stabilization of the crystal structure. Hydrogen bond parameters are presented in Table 3.

Acknowledgement

One of the authors (Rajni Kant) acknowledges the Department of Science & Technology for single crystal X-ray diffractometer as a National Facility under Project No. SR/S2/CMP-47/2003. RS acknowledges University Grant Commission (UGC) for the award of NET-JRF scholarship under ref. No. 23/12/2012 (ii) EU-V dated 01.07.2013. BN thanks UGC for financial assistance through BSR grant. PSN thanks PURSE-DST project for financial assistance.

Table 3. Geometry of N-H…H and N-H…π hydrogen bonding geometry

D-H…A	D-H, Å	H…A, Å	D…A, Å	θ[D-H…A,º]
N2- H5…N3^{i}	0.90(3)	2.04(3)	2.936(4)	174
N1- H12…N1^{ii}	0.82(3)	2.54(2)	3.232(4)	144
N1- H11…Cg1^{iii}	2.442	2.45(3)	3.345(4)	167

Symmetry Codes: (i) –x+1, -y+1, -z+2 (ii) –x+1/2+1, y+1/2, -z+1/2+2 (iii) –x,1-y,1-z

References

[1]Kini, S., Swain, S. P., Gandhi, A. M., *Indian J. Pharm. Sci.,* **2007**, *9*, 46–50.

[2]Munirajasekhar, D., Himaja, M., Sunil, V. M., *Int. Res. J. Pharm.*, **2011,** *2*, 114–117.

[3]Gurupadayya, B. M., Gopal, M., Padmashali, B., Manohara, Y. N., *Indian J. Pharm. Sci.,* **2008,** *70*, 572–577.

[4]Bowyer, P. W., Gunaratne, R. S., Grainge, M., Withers-Martinez, C., Wickramsinghe, S. R., Tate, E. W., Leatherbarrow, R. J., Brown, K. A., Holder, A. A., Smith, D. F., *Biochem. J.,* **2007,** *408*, 173–180.

[5]Pozas, R., Carballo, J., Castro, Rubio J., *Bioorg. Med. Chem. Lett.,* **2005,** *15*, 1417–1421.

[6]Rana, A., Siddiqui, N., Khan, S., *Eur. J. Med. Chem.,* **2008,** *43*, 1114–1122.

[7]Sheldrick, G. M., *Acta Cryst.,* **2008,** *A64*, 112.

[8]Farrugia, L. J., *J. Appl. Cryst.*, **2012,** *45*, 849-854.

[9]Spek, A. L., *Acta Cryst.,* **2009,** *D65*, 148-155.

[10]Nardelli, M. J., *Appl. Cryst.,* **1995,** *28,* 659.

[11]Burke-Laing, M., Laing, M., *Acta Cryst.,* **1976,** *B32*, 3216-3224.

[12]Hoong-Kun, F., Ching Kheng Q., Sarojini, B. K., Mohanb, B. J., Narayanac B., Acta Cryst., **2012,** *E68*, o2682.

[13]Md. Abu, A., Philip G. J., Md. Abdus S., Siti Nadiah B. A. H., Edward, R. T. T., *Acta Cryst.,* **2013,** *E69*, o1273.

[14]Bernstein, J., Davis, R. E., Shimoni, L., Chang, N.L., *Angew. Chem. Int. Ed. Engl.,* **1995**, *34,* 1555–1573.

Received: 12.03.2014.
Accepted: 14.03.2014.