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# Synthesis, Spectroscopic Studies and Structure of 2-[(Benzo[*d*]thiazol-2-ylamino)methyl]phenol

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**Abstract** Schiff base (*E*)-2-[(benzo[*d*]thiazol-2-ylimino) methyl]phenol (1) has been synthesized from the reaction of 2-hydroxy-benzaldehyde with 2-aminobenzothiazole. The 2-[(benzo[d]thiazol-2-ylamino)methyl]phenol (2) was prepared reduction of the Schiff base 1 with sodium borohydride. The compounds 1 and 2 have been characterized by elemental analysis, FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and UV-visible spectroscopic techniques. The structure of the compound 2 has also been examined crystallographically. The compound 2 crystallizes in the monoclinic space group P2/c. The unit cell parameters were found as a = 10.017(1),  $b = 11.725(1), c = 10.341(1) \text{ Å}, V = 1208.1(1) \text{ Å}^3, D_x =$ 1.409 g cm<sup>-3</sup> and Z = 4. The crystal structure was solved by direct methods and refined by the full-matrix least squares method and found as  $R_1 = 0.0308$  and  $wR_2 = 0.0818$  for 2032 for the observed reflections  $[I > 2\sigma(I)]$ .

Keywords Crystal structure  $\cdot$  Spectroscopic studies  $\cdot$  FT-IR  $\cdot$  UV–visible  $\cdot$  NMR

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### Introduction

Thiazole and its derivatives are important in diverse fields medicine due to their medicinal activities, and thiazole derivatives are widely used in the synthesis of the medicinal products such as sulphathiazole [1]. Apart from the medicinal activities, benzothiazoles are also used for production of dyes with photosensitizing properties [2]. Metal complexes of Schiff bases derived from salicylaldehyde, substituted salicylaldehyde and aminobenzothiazoles containing nitrogen, sulphur and/or oxygen as ligand atoms are of interest as simple structural models of more complicated biological systems [3, 4]. However, metal complexes of Schiff bases with heterocyclic compounds also find applications as potential drugs [5, 6]. Various heterocycles, especially thiazoles, occupy an important place owing to their versatile bioactivities due to the presence of multifunctional groups [7-10]. It has been reported that the 2-aminobenzothiazole is found as structural unit in antioxidant, anti-inflammatory, herbicides, antibiotics, thermoplastic polymers [11], flavouring and odour agents and in the luciferine responsible for the bioluminescence of fire flies [12]. It shows namely two important properties such as the tautomerism of its delocalized dienyl system N-C-N and as it has been reported earlier. C=N-H imine group is also a base and a very reactive acid [13] which makes it a good candidate for coordination studies. The Schiff base ligands and their complexes derived from the reaction of salicylaldehyde, substituted salicylaldehyde and 2-hydroxy-1-naphthaldehyde with 2-aminobenzothiazole have been extensively studied earlier. However, the similar statement could not be given for the reduction product of 2-aminobenzothiazole Schiff bases and their complexes.

In this present work, molecular structure of Schiff bases 1 and its reduction product 2 (Scheme 1) were studied in





order to reveal the presence of either the enol-imine or keto-amine forms related with hydrogen bonding by using FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV–visible spectroscopic and X-ray crystallographic techniques.

# Experimental

## Reagents and Techniques

The <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer operating at 400 and 101.6 MHz. Infrared absorption spectra were obtained from a Perkin Elmer BX II spectrometer in KBr discs and were reported in cm<sup>-1</sup> units. The UV–visible spectrums were taken by using a SHIMADZU 1208 series spectrometer. Carbon, nitrogen and hydrogen analyses were performed on a LECO CHNS-932 analyzer. Melting points were determined with an Electro Thermal IA 9100 apparatus using a capillary tube. THF (tetrahydrofuran), 2-aminobenzothiazole, 2-hydroxy-benzaldehyde, C<sub>2</sub>H<sub>5</sub>OH, CHCl<sub>3</sub>, n-hexane, DMSO (dimethyl sulfoxide) and NaBH<sub>4</sub> were purchased from Merck (Germany).

Synthesis of (*E*)-2-[(Benzo[*d*]thiazol-2-ylimino)methyl]phenol (1)

2-Aminobenzothiazole (1.50 g;  $1 \times 10^{-2}$  mol) was added to a dry THF (100 mL) solution of 2-hydroxy-benzaldehyde (1.22 g;  $1 \times 10^{-2}$  mol). The mixture was stirred and heated for 2 h. Compound (1) was obtained from the evaporation of THF. It was crystallized from chloroform/n-heptane as yellow crystals, m.p. 123–124 °C, 2.34 g (92%) yield. The obtained results were; C, 66.10; H, 3.93; N, 11.01. Calc. for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>OS; C, 66.12; H, 3.96; N, 11.02%. IR(KBr, cm<sup>-1</sup>); \_vO–H; 3417 w, vAr–H; 3059 m, vC=N; 1629 s, vC=C; 1533 s, vC–N; 1446 s, vC–O; 1330 m, 1278 s. <sup>1</sup>H-NMR(DMSO); δ ppm, 10.27(s, 1H, Ar–O<u>H</u>); 9.45 (s, 1H, Ar–C<u>H</u>=N–Ar); 8.80 (d, 1H, Benzothiazole-<u>H</u>); 8.01 (d, 1H, Benzothiazole-<u>H</u>); 7.97–7.94 (m, 2H, Benzothiazole-H); 6.82–7.70 (m, 4H, Ar–H).

Synthesis of 2-[(Benzo[*d*]thiazol-2-ylamino)methyl] phenol (**2**)

Sodium borohydride (3.80 g;  $1.0 \times 10^{-2}$  mol) was added drop wise to a stirred solution of compound 1 (2.54 g;  $1.0 \times 10^{-2}$  mol), in C<sub>2</sub>H<sub>5</sub>OH (250 cm<sup>3</sup>) at room temperature for over 24 h. Then the mixture was stirred and heated for 1 h. The precipitated compound was filtered off and the solvent removed by rotary evaporation and the crude product was washed and dried under vacuo. The sample was crystallized from chloroform/n-heptane as colourless crystals (2), m.p. 182-183 °C, 2.52 g (98%) yield. The results were found as C, 65.58; H, 4.68; N, 10.91. Calc. for C14H12N2OS; C, 65.60; H, 4.72; N, 10.93%. IR(KBr, cm<sup>-1</sup>); vN-H; 3412 s, vAr-H; 3046 m, vC-H; 2930-2874 m, vC=C; 1549 s, vC-N; 1497 m, 1449 s, vC-O; 1351 m, 1271 s, 1247 s. <sup>1</sup>H-NMR(DMSO);  $\delta$  ppm, 9.84 (s, 1H, OH); 8.40 (t, 1H, N–H); 7.68 (d, 1H, Benzothiazole-H); 7.66 (d, 1H, Benzothiazole-H); 7.39-7.37 (m, 2H, Benzothiazole-H); 7.24-6.99 (m, 4H, Ar-H); 4.51 (d, 2H, Ar-CH<sub>2</sub>).

# X-ray Crystallography

The single crystal of the 2-[(benzo[*d*]thiazol-2-ylamino)methyl]phenol (**2**) was mounted on goniometer of a STOE IPDS 2 diffractometer with a graphite monochromatized Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). Data collection, reduction and corrections for absorption and decomposition were achieved by using X-AREA, X-RED software [14]. The structure was solved by SHELXS-97 and refined with SHELXL-97 [15, 16]. The positions of the Ζ 4  $D_{\rm c} \, ({\rm g} \, {\rm cm}^{-3})$  $1.41 \text{ g cm}^{-3}$  $\mu$ (Mo-K $\alpha$ )  $1.109 \text{ mm}^{-1}$ *F*(000) 536 52.00°  $2\theta_{\rm max}$ h, k, l range  $-9 \le h \le 12$  $-14 \leq k \leq 14$  $-12 \leq l \leq 12$ No. of measured reflections 6,004 No. of independent reflections 2,348 No. of observed reflections 2,032 Goodness-of-fit on  $F^2$ 1.042 Measurement STOE IPDS 2 Program system STOE X-AREA SHELXS-97 Full-matrix least-Structure determination refinement method squares on  $F^2$ 0.031. 0.082  $R_1, wR_2 (I > 2\sigma(I))$  $0.176, -0.246 \text{ e. } \text{\AA}^{-3}$  $(\Delta \rho)_{\rm max}, (\Delta \rho)_{\rm min}$ C12 H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model. The details of the X-ray data collection, structure solution and structure C13

refinements are given in Table 1. The selected bond distances and angles are listed in Table 2. The molecular structure with the atom-numbering scheme is shown in Fig. 1 [17].

# **Result and Discussion**

FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and UV-Visible Spectroscopic Studies

The IR spectra of the compounds 1 and 2 are given in synthetic procedures. Vibration bands with the wave numbers of 3417 and 3412 ( $v_{O-H}$  and  $v_{N-H}$ ), 3059 and 3046 cm<sup>-1</sup> ( $v_{C-H}$ , Ar–H), 1533 and 1549 cm<sup>-1</sup> ( $v_{C=C}$ ), 1446 and 1497–1449 ( $v_{C-N}$ ), 1330–1278 cm<sup>-1</sup> and 1351– 1271 cm<sup>-1</sup> ( $v_{C-O}$ , Ar–O) were observed for compounds 1 Table 2 Some selected bond lengths (Å), bond angles (°) and torsion angles (°)

C1-C6	1.4005(19)	C8-N2	1.4587(18)
C1-S1	1.7428(15)	C8–C9	1.502(2)
C6-N1	1.3940(18)	C9C14	1.389(2)
C7-N1	1.3028(17)	C9–C10	1.3991(17)
C7-N2	1.3368(19)	C10-O1	1.3671(16)
C7–S1	1.7605(12)		
C2C1S1	128.96(12)	O1-C10-C11	121.72(12)
C6C1S1	109.28(10)	O1-C10-C9	117.78(12)
C5-C6-N1	125.42(13)	C7-N2-C8	121.38(12)
N1-C6-C1	115.50(12)	C7-N2-H2A	117.9(12)
N1-C7-N2	124.70(12)	C8-N2-H2A	120.5(12)
N1-C7-S1	115.69(10)	C10O1H1	110.5(13)
N2-C7-S1	119.61(10)	C1-S1-C7	88.96(6)
N2-C8-C9	113.24(12)		
S1-C1-C2-C3	178.57(12)	C1-C6-N1-C7	-1.86(17)
C4-C5-C6-N1	-179.34(15)	N1-C7-N2-C8	-1.5(2)
N2-C8-C9-C14	-19.9(2)	S1-C7-N2-C8	179.32(11)
N2-C8-C9-C10	159.17(13)	C9-C8-N2-C7	-77.27(18)
C14-C9-C10-O1	-179.63(12)	C2C1S1C7	-177.88(15)
C8-C9-C10-O1	1.29(19)	C6-C1-S1-C7	0.30(11)
O1-C10-C11-C12	-179.58(14)	N1-C7-S1-C1	-1.44(12)
N2-C7-N1-C6	-177.11(14)	N2-C7-S1-C1	177.81(12)
C5-C6-N1-C7	177.60(14)		



C6

and 2, respectively. The C=N bond was observed at  $1620 \text{ cm}^{-1}$  for compound **1**. This band was not observed between 2000 and  $1600 \text{ cm}^{-1}$  for compound **2**. The stretching frequency observed at 2849, 2701 cm<sup>-1</sup> and 2875, 2725 cm<sup>-1</sup> in compounds **1** and **2** show the presence of O-H…N intramolecular hydrogen bond [18, 19]. The C=N bond which is accountable partially for the existence enol-imine form can also be inferred from the IR spectra of compound 1. The compound 1 with strong band at 1278 cm<sup>-1</sup> possesses highest percentage of enol-imine tautomer due to the stabilization of phenolic C-O bond

Table 1 Crystal and experimental data



[20]. The C–O bond was observed  $1271 \text{ cm}^{-1}$  for compound **2**.

The <sup>1</sup>H NMR data for compound **1** shows that the tautomeric equilibrium favours the enol-imine in DMSO. The OH protons are observed 10.27 ppm singlets and 9.84 ppm singlets for ligands **1** and **2**. The azomethine proton is observed as singlets 9.46 for **1**. The amine proton is observed at 8.40 ppm ( ${}^{3}J_{CHNH} = 5.14$  Hz) triplets for **2**. The phenyl protons resonate at  $\delta = 8.80-7.94$  ppm and  $\delta = 7.68-6.99$  ppm multiplet for compounds **1** and **2**, respectively. The ArCH<sub>2</sub> proton of the compound **2** gave a doublet at  $\delta = 4.51$  ppm ( ${}^{3}J_{NHCH} = 5.14$  Hz). According to the <sup>13</sup>C NMR spectra compounds **1** and **2** are given in Scheme 2.

The UV–visible spectra of the compounds were studied in DMSO. The Schiff bases show absorption in the range greater than 400 nm in polar and nonpolar solvents [18, 19, 21–28]. The UV–visible spectrum of *ortho* hydroxylated Schiff bases which exists mainly as enol-imine structure indicate the presence of a band at <400 nm and compounds of either as keto-amine or as mixture of enol-imine/ketoamine forms show a new band, especially in polar and nonpolar solvents in both acidic and basic media at >400 nm [18, 19, 27, 29–32]. The compound **1** showed no absorption above 400 nm in DMSO. The enol-imine tautomer was found to be dominant only in DMSO.

In conclusion, UV–Visible, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopic results show that the compound **1** exist enolimine form in DMSO solution.



Scheme 2 The <sup>13</sup>C-NMR data for the compounds

#### Structure Determination

Conjugated organic molecules containing both donor and acceptor groups are of great interest for molecular electronic devices. Second-order nonlinear optics (NLO) organic materials, which contain stable molecules with large molecular hyperpolarizabilities in noncentrosymmetric packing, are also of great interest for device applications [33]. However, according to a statistical study, a great majority of achiral molecules crystallize centrosymmetrically [34].

The title molecule (2) is not planar. The plane **A** [C8–C14, O1; planar with a maximum deviation of 0.019(1) Å for the C8 atom] and **B** [N1, N2, S1, C1–C7; planar with a maximum deviation of 0.052(1) Å for the N2 atom] are inclined at angle of 87.44(2)° reflecting mainly a twist about C8–N2 [C9–C8–N2–C7 =  $77.3(2)^\circ$ ].

The X-ray data revealed that there is a strong interaction between C14, H14 and N2 atoms and the distance between them 2.46(2) Å. In compound **2** the C9–C14–H14 angle is [116.0(1)°] smaller than the other C–C–H [C12– C11–H11 = 120.5(11)°, C13–C12–H12 = 121.4(1)°, C14– C13–H13 = 121.9(11)°] angles. C–H···X hydrogen bonds has been postulated to stabilize the geometries of many organic compounds in the solid state [35, 36]. The crystal structure is stabilized by a strong intermolecular hydrogen bonds between O1···N1<sup>i</sup> [O1···N1 2.762(2) Å, O1–H1 0.83(2) Å, H1···N1 1.94(2) Å, O1–H1···N1 174.0(2)°; symmetry code: (i) 1 – x, -1/2 + y, 3/2 - z] and N2···O1<sup>ii</sup> [N2···O1 3.088(2) Å, N2–H2A 0.82(2) Å, H2A···O1 2.37(2) Å, N2–H2A···O1 147.0(2)°; symmetry code: (ii) 1 – x, 1 – y, 1 – z] atoms (see Fig. 2).

The phenyl rings show small distortions from ideal geometry, with the C=C distances for the phenyl rings close to the expected value for aromatic rings [1.394(5) Å] [37]. The bond lengths C11–Cl0 and C4–C5 were determined within the expected ranges. Both N2 and C8 atoms



Fig. 2 A perspective view of the molecule 2 in the unit cell. The intermolecular hydrogen bond has been indicated by *dashed lines* 

exhibit distorted tetrahedral configuration. The bond angles of C7-N2-H2A (117.9°), C8-N2-H2A (120.5°) and N2-C8-H8A (107.7, N2-C8-C9 (113.3) are significantly smaller than that of 120.0°. The bond length of C7-N1 (1.303 (2) Å) is remarkably shorter than normal C–N (1.47 Å) and close to the C=N double bond distance (1.308(7) Å) [38], which is indicative of significant double bond character. This shows a good agreement with the expected values [39, 40]. The N2-C7 single bond length (1.337(2) Å) is shorter than the reported values [39, 40], which suggests the existence of a delocalized double bond in the benzothiazole moiety. Although the N2-C8 bond distance (1.458 (2) Å) is longer than a typical C=N bond distance, it is shorter than a normal C-N. In compound 2 the phenol group seems to have a weak electron withdrawing character. Thus, the length of N2-C7 and N2-C8 bonds are shorter than a typical N-C (1.47 Å) bond distance. The single bond lengths of C8-C9 and C7-S1 are 1.502(2), 1.761(1) Å, respectively, which are longer than typical C-C (1.54 Å), and C-S (1.85 Å) [41].

Clearly, the amine form is favoured rather than the imine form for compound **2**. These are evident from the observed C8–N2 bond distances of 1.458(2) Å, which are consistent with a single bond. However, the C7=N1 bond distances are 1.303(2) Å, and this is an indicative of a double bond.

#### **Supplementary Material**

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number 689396. Copies of the data can be obtained free of charge on application to CCDC12 Union Road, Cambridge CB21 EZ, UK (Fax: (+44) 1223-336-033; e-mail: data\_request@ccdc.cam.ac.uk).

#### References

- 1. Borisenko VE, Koll A, Kolmakov EE, Rjasnyi AG (2006) J Mol Struct 783:101
- Ivanovskii VI (1978) Chemistry of hetero cyclic compounds. High School Publishing House, Moscow
- 3. Sharma RC, Varshney VK (1999) J Inorg Biochem 41:299
- Vicini P, Geronikaki A, Incerti M, Busonera B, Poni G, Cabrasc CA, Collac PL (2003) Bioorg Med Chem 11:4785
- Konstantinivi SS, Radovanovi BC, Caki Z, Vasic V (2003) J Ser Chem Soc 68:641
- 6. Anderson O (1999) Chem Rev 99:2683
- 7. Venugaopala KN, Jayashree BS (2003) Indian J Heterocycl Chem 12:307

- 8. Vashi K, Naik HB (2004) Eur J Chem 1:272
- 9. Joseyphus RS, Dharmaraj CJ, Nair MS (2006) Trans Met Chem 31:699
- Chohan ZH, Pervez H, Rauf A, Khan KM, Supuran CT (2004) J Enzym Inhib Med Chem 19:417
- Katritzky AR, Rees CW (1984) Comprehensive heterocyclic chemistry 6. Pergamon Press, New York; Toronto; Sydney; Paris, p 250
- 12. Kabalka GW (1994) Current topics in the chemistry of boron. The Royal Society of Chemistry, Cambridge, p 406
- Bakhmutova EV, Nöth H, Contreras R, Wrackmeyer B (2001) Z Anorg Allg Chem 627:1846
- 14. Stoe & Cie (2002), X-AREA (Version 1.18) and X-RED32 (Version 1.04). Stoe&Cie, Darmstadt, Germany
- Sheldrick GM (1997) SHELXS–97, Program for the solution of crystal structures. University of Goettingen, Germany
- 16. Sheldrick GM (1997) SHELXL-97, Program for the refinement of crystal structures. University of Goettingen, Germany
- 17. Farrugia LJ (1997) J Appl Crystallogr 30:565
- 18. Yıldız M, Kılıç Z, Hökelek T (1998) J Mol Struct 441:1
- 19. Nazır H, Yıldız M, Yılmaz H, Tahir MN, Ülkü D (2000) J Mol Struct 524:241
- Yeap GY, Ha ST, Ishizawa N, Suda K, Boey PL, Mahmood WAK (2003) J Mol Struct 658:87
- Salman SR, Shawkat SH, Al-Obaidi GM (1990) Can J Spectrosc 35:25
- Salman SR, Shawkat SH, Al-Obaidi GM (1989) Spectrosc Lett 22:1265
- Ünver H, Yıldız M, Zengin DM, Özbey S, Kendi E (2001) J Chem Crystallogr 31:211
- 24. Yıldız M (2004) Spectrosc Lett 37:367
- 25. Ünver H (2001) Spectrosc Lett 34:783
- Salman SR, Lindon JC, Farrant RD (1991) Spectrosc Lett 24:1071
- 27. Salman SR, Lindon JC, Farrant RD (1993) Magn Reson Chem 31:991
- 28. Salman SR, Kamounah FS (2002) Spectrosc Lett 35:327
- Ünver H, Zengin DM, Güven K (2000) J Chem Crystallogr 30:359
- Ünver H, Yıldız M, Dülger B, Özgen Ö, Kendi E, Durlu TN (2005) J Mol Struct 737:159
- Yıldız M, Ünver H, Dülger B, Erdener D, Ocak N, Erdönmez A, Durlu TN (2005) J Mol Struct 738:253
- Yıldız M, Ünver H, Erdener D, Ocak N, Erdönmez A, Durlu TN (2006) Cryst Res Technol 41:600
- Bosshard C, Sutter K, Schlesser R, Günter P (1993) J Opt Soc Am B10:867
- Jacques J, Collet A, Willen SH (1981) Enantiomers, racemates and resolutions. Wiley Interscience, New York, pp 1–23
- Kazak C, Aygün M, Turgut G, Odabaşoğlu M, Özbey S, Büyükgüngör O (2000) Acta Crystallogr C56:1044
- Aygün M, Işık Ş, Öcal N, Tahir MN, Kaban Ş, Büyükgüngör O (1998) Acta Crystallogr C54:527
- 37. Sutton LE (1965) Chem Soc Spec Publ Suppl 18:516
- Ünver H, Yıldız M, Kiraz A, Ocak N, Erdönmez A, Dülger B, Durlu TN (2006) J Chem Crystallogr 36:229
- Büyükgüngör O, Çalışkan N, Davran C, Batı H (2004) Acta Crystallogr E 60:01414
- Cui L, Yin H, Yang M, Quan L, Wang D (2008) Acta Crystallogr E 64:01974
- 41. Zhang G, Song B, Yang S, Jin L, Hu D, He W (2005) Anal Sci 21:105