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Synthesis, X-ray crystal structure and spectroscopic studies of benzothiazole Schiff base

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The new Schiff base **3** was synthesized by reacting 6-methyl-2-aminobenzothiazole and 2-methoxy-1-naphtaldehyde in ethyl L- lactate as a green solvent. Compound **3** was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, single crystal X-ray diffraction study and elemental analysis. The compound crystallizes in the monoclinic space group P21/n, with a= 8.1077(15), b=17.302(3), c=22.790(4) Å, β= 95.799(7), V= 3180.7(1) Å^3, absorption coefficient= 0.212 mm^{-1}. The asymmetric unit contains two crystallographically independent molecules with intramolecular C-H···N and intermolecular C-H···Cg interactions.

Keywords: Benzothiazole, Schiff base, Ethyl L-lactate, X-ray structure

INTRODUCTION

The reaction of primary amines with aldehydes or ketones leads to Schiff bases containing the imine C=N double bond. The Schiff base formation reaction was carried out by Hugo Schiff in 1864 and the compounds obtained from this reaction were named Schiff bases [1]. If the aryl group is not bound to the carbon or nitrogen atom of the imine group, the Schiff base immediately polymerises or decomposes [2]. Schiff bases have an important role in the development of coordination chemistry, since the transition metals easily form stable complexes with many species [3-5].

Schiff bases are the most widely used organic compounds both as synthetic intermediates and in coordination chemistry [6]. Schiff bases are an important ligand that coordinates to metal ions *via* azomethine nitrogen. Some Schiff bases have been reported to have antibacterial, antifungal, anticancer and diuretic activities. It is also known that Schiff bases are widely used in food industry, paint industry, analytical chemistry, catalysis, fungicide, agricultural chemical and biological activities [7-9]. Imines are also intermediates in many enzymatic and pharmaceutical reactions. Conventional syntheses often require the use of toxic solvents such as methylene chloride [10] or refluxing in petroleum-based solvents such as toluene as azetropic agents [11]. More recently, green chemistry solvents are used in imine synthesis [12-17]. Here, new naphthaldehyde-derivatized Schiff bases were synthesized using ethyl lactate as a solvent and the process was identified as green synthesis. Water was used as a cosolvent. By optimizing the solvent polarity, the formation of the product is accelerated.

EXPERIMENTAL

Materials and Methods

6-Methyl-2-amino benzothiazole and 2-methoxy-1-naphthaldehyde were of commercial quality or purified before use. Organic solvents used were of HPLC grade. The melting point was determined using a Gallenkamp apparatus. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX FT NMR spectrometer (at 500 MHz and 125 MHz, respectively) at 298 K. Chemical shifts are given in δ (ppm) relative to TMS (DMSO-d_6) as the internal standard. The infrared spectrum was recorded on a Perkin Elmer Precisely Spectrum 100 FT-IR spectrophotometer as pressed KBr disc. Elemental analysis was performed on Elementar Analysensysteme GmbH vario MICRO CHNS (Turkish Technical and Scientific Research Council Laboratories, Ankara, Turkey). TLC was performed on pre-coated silica gel plates (Merck 60, F254, 0.25 mm).

Synthesis of (2-methoxy-1-naphthyl methylene)-6-methyl-benzothiazole-2-yl-amine (3)

General procedure A for preparation of (2-methoxy-1-naphthyl methylene)-6-methyl-benzothiazole-2-yl-amine (3): the Schiff base was synthesized by the method given in [18]. A mixture of 6-methyl-2-amino benzothiazole (**1**, 0.082115 g, 0.5 mmol) and methoxy-1-naphthalene (2, 0.093105 g, 0.5 mmol) in ethyl lactate - water

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system (3 mL, 80%) was stirred at room temperature for a period of time (Table 1).

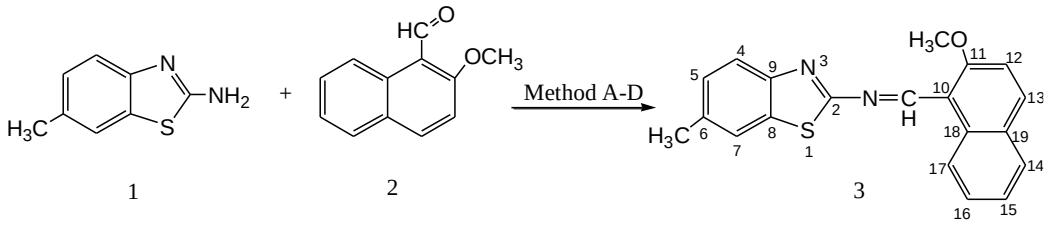
Table 1. Effect of solvent polarity and catalyst on the yield for the synthesis of (2-methoxy-1-naphthyl methylene)-6-methyl-benzothiazole-2-yl-amine[d] (**3**)

Procedure	Time (min)	Solvent (%EL)	%Yield[c]
A	60	80	77
B	120	70	72
C	30	100[a]	80
D	10	100[b]	90

[a] $Sc(OTf)_3$
[b] $Yb(OTf)_3$
[c] isolated yield
[d] reactions were carried out at room temperature

The reaction was terminated by TLC checking and left at room temperature overnight. The resulting precipitate was filtered off and washed with petroleum ether. The resulting crude product (3) was recrystallized from a mixture of ethyl acetate: n-hexane and ethanol solvent (1:6:0.008). Yield 77%.

General procedure B for preparation of (2-methoxy-1-naphthyl methylene)-6-methyl-benzothiazole-2-yl-amine (3): A mixture of 6-methyl-2-amino benzothiazole (**1**, 0.082115 g, 0.5 mmol) and 2-methoxy-1-naphthaldehyde (**2**, 0.093105 g, 0.5 mmol) in ethyl lactate - water system (3 mL, 70%) was stirred at room temperature for a period of time (Table 1).



1 2 3

A: 80% Ethyl L-lactate, room temperature, 60 min, yield 77%
B: 70% Ethyl L-lactate, room temperature, 120 min, yield 72%
C: Ethyl L-lactate, room temperature, 30 min, yield 80%
D: Ethyl L-lactate, room temperature, 10 min, yield 90%

Scheme 1. Schematic representation of the formation of (2-methoxy-1-naphthyl methylene)-6-methyl-benzothiazole-2-yl-amine (**3**)

The reaction was terminated by TLC checking and left at room temperature overnight. The resulting crude product (3) was recrystallized from a mixture of ethyl acetate: n-hexane and ethanol solvent (1:6:0.008). Yield 72%.

General procedure C for preparation of (2-methoxy-1-naphthyl methylene)-6-methyl-benzothiazole-2-yl-amine (3): A mixture of 6-methyl-2-amino benzothiazole (**1**, 0.082115 g, 0.5 mmol) and 2-methoxy-1-naphthaldehyde (**2**, 0.093105 g, 0.5 mmol) in ethyl L-lactate - water (3 mL, 99 %) and $Sc(OTf)_3$ (0.0098432 g, 0.02 mmol) was stirred at room temperature for period of time (Table 1). The reaction was terminated by TLC checking and left at room temperature overnight. The resulting crude product (3) was recrystallized from a mixture of ethyl acetate: n-hexane and ethanol solvent (1:6:0.008). Yield 80%

General procedure D for preparation of (2-methoxy-1-naphthyl methylene)-6-methyl-benzothiazole-2-yl-amine (3): A mixture of 6-methyl-2-amino benzothiazole (**1**, 0.082115 g, 0.5 mmol) and 2-methoxy-1-naphthaldehyde (**2**, 0.093105 g, 0.5 mmol) in ethyl L-lactate - water (3 mL, 99 %) and $Yb(OTf)_3$ (0.012405 g, 0.02 mmol) was stirred at room temperature for period of time (Table 1). The reaction was terminated by TLC checking and left at room temperature overnight. The resulting crude product (3) was recrystallized from a mixture of ethyl acetate: n-hexane and ethanol solvent (1:6:0.008). Yield 90%.

Elemental analysis (%): Formula $C_{20}H_{16}N_2SO$: Found: C- 72.19; H- 4.79; N- 8.40; O- 4.78; S- 9.61 % ; Calculated: C- 72.26; H- 4.85; N- 8.43; O- 4.81; S- 9.65% ; IR (KBr): 3012.72 cm^{-1} (m, Ar-H), 2974.14 cm^{-1} (m, CH_3), 2939.43 cm^{-1} (m, CH_3), 1622.08 cm^{-1} (m, CH=N), 1585.44 cm^{-1} (s, Ar-H), 1512.15 cm^{-1} (s, Ar-H), 1458.14 cm^{-1} (s, Ar-H); ^{1}H-NMR (DMSO-*d*6, 500 MHz, δ ppm): 1.6 (s, 3H, CH_3-benzothiazole); 4.1 (s, 3H, OCH_3 - naphthaldehyde); 7.29 (d, J=6.26 Hz, 1H, H4); 7.33 (d, J=9.10 Hz, 1H, H12); 7.48 (t, J=7.47 Hz, 1H, H15); 7.66 (s, 1H, H7); 7.7 (t, J=7.79 Hz, 1H, H16); 7.83 (d, J=8.03 Hz, 1H, H-17); 7.92 (d, J= 8.25 Hz, 1H, H5); 8.07 (d, J=9.11 Hz, 1H, H-13); 9.8 (d, J= 8.68 Hz, 1H, H14); 9.9 (s, 1H, −CH=N−); ^{13}C-NMR (CDCl3, 125 MHz, δ ppm): 21.63; 56.67; 112.14; 115.29; 121.46; 122.55; 124.77; 126.56; 127.80; 128.49; 128.97; 129.59; 132.11; 134.38; 135.00; 136.72; 150.07; 162.01; 164.06; 172.49.

X-Ray Crystallography

The suitable crystals of the title compound were crystallized from ethyl acetate : *n*-hexane : ethanol (1:6:0.008) at room temperature. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K_α radiation (λ=0.71073 Å) at T=150(2) K. Multi-scan absorption correction was applied [19]. The structure was elucidated by direct methods and clarified by full-matrix least squares against F^2 using all data [20]. All of the H atoms were anisotropically refined. Methine H atoms, aromatic H atoms and methylene H atoms were geometrically located at 0.95 (CH), 0.95 (aromatic) and 0.98 (CH_3) distances from the parent O and C atoms; the U_{iso} (H) values during refinement process were limited to 1.2 U_{eq} (for aromatic carrier atoms) and 1.5 U_{eq} (for methyl carrier atoms) using a sliding model.

RESULTS AND DISCUSSION

The novel Schiff base (3) was synthesized according to the route shown in Scheme 1. We performed an effective synthesis using ethyl lactate, a green solvent. The reaction was carried out using the ethyl lactate-water system and then the polarity of the reaction medium was adjusted with water. In the medium where 100% ethyl lactate and Yb $(OTf)_3$ were used, it was observed that the reaction was very rapid and yielded a product with maximum efficiency (Table 1). The structure of Schiff base 3 was deterined through spectroscopic and elemental analysis. When the IR spectrum of compound 3 was examined, it was observed that the peak observed at 1622 cm^{-1} belonged to the azomethine group. ^{1}HNMR spectrum of compound 3 showed a characteristic singlet signal at 9.9 ppm, which might be attributed to the CH=N group. Two sharp singlets were also observed at δ 4.1 and 1.6 ppm for methoxy (OCH_3-napht) and methyl protons (CH_3-benzth), respectively. For the aromatic ring protons, two triplets, six doublets and one singlet signal were assigned at δ 7.7, 7.48, 9.8, 8.07, 7.33, 7.83 and 7.66 ppm, corresponding to H16, H15, H14, H13, H12, H17 and H7 protons, respectively (Scheme 1). In the ^{13}C NMR spectrum of the compound 3, the signals observed at 56.67 and 21.63 ppm were assigned to methoxy and methyl carbons, respectively. Furthermore, one downfield signal observed at 172.49 ppm was assigned to azomethine carbon (C=N). Finally, by single crystal X-ray analysis of compound 3, the relative stereochemical outcome was determined.

X-Ray Structure

The crystal structure of the compound and the atomic numbering scheme of the compound are shown in Fig. 1.

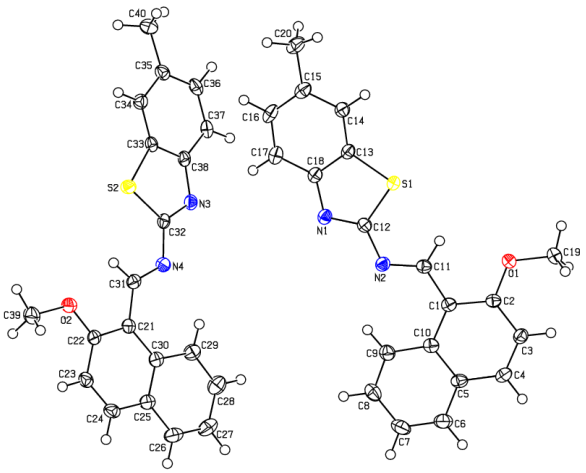


Fig. 1. ORTEP-3 [21] the atom numbering drawing scheme of compound 3. Displacement ellipsoids are drawn at the 50% probability level.

Table 2. Crystal data and structure refinement for compound **3**

Empirical formula	$C_{40}H_{32}N_4O_2S_2$
Colour/shape	yellow/block
Formula weight	664.82
T (K)	99(2)
Radiation used, graphite monochr.	Mo K_α (λ = 0.71073 Å)
Crystal system	Monoclinic
Space group	P 2_1/n
a (Å)	8.1077 (15)
b (Å)	17.302 (3)
c (Å)	22.790 (4)
α(°)	90
β(°)	95.799 (7)
γ(°)	90
V (Å^3)	3180.7 (1)
Z	4
Absorption coefficient (mm^{-1})	0.212
ρ_{calc} (mg mm^{-3})	1.388
Crystal dimensions (mm)	0.31 × 0.24 × 0.21
θ(Max.) (°)	23.25
θ(Min.) (°)	2.76
Reflections measured	4535
Range of *h*, *k*, *l*	-8 <*h* <8 -19 <*k* < 19 -25 <*l* < 25
No of reflections with $I>2\sigma(I)$	4222
Corrections applied	Lorentz-polarization
Structure solution	Direct methods
Treatment of H atoms	Geometric calculations
No. of parameters var	437
Goodness-of-fit S	1.079
$R = \|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.0296
R_w	0.0867
R_{int}	0.0279
$(\Delta/\rho)_{max}$ (e Å^{-3})	0.165
$(\Delta/\rho)_{min}$ (e Å^{-3})	-0.257

Table 3. Bond lengths (Å), bond angles (º) and torsion angles (º) for compound **3**

S1-C13	1.7340(17)	O1-C19	1.427(2)	N3-C32	1.301(2)	C11-C1	1.447(2)
S1-C12	1.7875(18)	O2-C22	1.360(2)	N3-C38	1.389(2)	C21-C31	1.449(2)
S2-C33	1.7325(17)	O2-C39	1.432(2)	C20-C15	1.510(3)	C31-N4	1.290(2)
S2-C32	1.7840(18)	N1-C12	1.295(2)	C12-N2	1.381(2)	N4-C32	1.384(2)
O1-C2	1.362(2)	N1-C18	1.390(2)	N2-C11	1.289(2)	C35-C40	1.507(3)
C13-S1-C12	88.46(8)	N1-C12-N2	122.35(16)	N1-C18-C13	115.90(15)	C38-C33-S2	109.59(13)
C33-S2-C32	88.71(8)	N1-C12-S1	115.44(13)	O1-C2-C1	116.58(15)	N3-C38-C37	125.61(16)
C2-O1-C19	118.04(14)	N2-C12-S1	122.19(13)	O1-C2-C3	121.51(16)	N3-C38-C33	115.82(15)
C22-O2-C39	118.69(14)	C11-N2-C12	117.94(15)	C22-C21-C31	116.59(16)	O2-C22-C21	116.66(15)
C12-N1-C18	110.48(15)	N2-C11-C1	125.88(16)	N3-C32-N4	121.81(16)	O2-C22-C23	121.44(16)
C32-N3-C38	110.60(15)			N3-C32-S2	115.25(13)	N1-C18-C13	115.90(15)
C14-C13-S1	128.55(14)	C2-C1-C11	116.62(15)	N4-C32-S2	122.94(13)	N1-C18-C17	125.12(17)
C18-C13-S1	109.64(13)	C10-C1-C11	124.87(16)	C34-C33-S2	128.60(14)	C33-S2-C32-N4	-178.76(15)
C20-C15-C14-C13	179.57(16)	N2-C11-C1-C2	-174.43(17)	C10-C1-C2-O1	174.96(15)	C33-C34-C35-C40	175.32(17)
C15-C14-C13-C18	-1.8(3)	N2-C11-C1-C10	6.3(3)	C11-C1-C2-O1	-4.3(2)	C32-N3-C38-C37	-178.28(17)
C15-C14-C13-S1	179.85(14)	C20-C15-C16-C17	-178.04(17)	O1-C2-C3-C4	-178.30(17)	C32-N3-C38-C33	0.7(2)
C18-N1-C12-N2	-178.23(15)	C33-S2-C32-N3	1.91(14)	C22-C21-C31-N4	-179.85(16)	S2-C33-C38-C37	179.78(13)
C18-N1-C12-S1	3.21(19)	C12-N1-C18-C13	-2.4(2)	C30-C21-C31-N4	0.5(3)	C39-O2-C22-C21	175.46(16)
C13-S1-C12-N1	-2.53(14)	S1-C13-C18-C17	2.3(3)	C31-N4-C32-N3	-175.67(16)	C39-O2-C22-C23	-4.7(2)
N1-C12-N2-C11	161.10(16)	C19-O1-C2-C1	-178.71(17)	C12-N1-C18-C17	177.10(17)	C12-N2-C11-C1	177.72(16)
S1-C12-N2-C11	-20.4(2)	C19-O1-C2-C3	1.5(3)	C31-N4-C32-S2	5.0(2)	C21-C31-N4-C32	-178.69(16)

Table 4. Hydrogen-bond geometry (Å, º)

D-H···A	D-H	H···A	D···A	D-H···A
C9-H9···N2	0.95	2.28	2.929(2)	125
C29-H29···N4	0.95	2.26	2.927(2)	126
C36-H36···Cg3^{i}	0.95	2.90	3.590(2)	130
C36-H36···Cg4^{i}	0.95	2.98	3.777(2)	142

Symmetry code: (i) -1+x, y, z. Cg3 and Cg4 are the centroids of the rings C(N1/S1/C12/C13/C18) and D(C13-C18), respectively.

The asymmetric unit contains two crystallographically independent molecules, while the bond lengths and angles are in the normal range. The crystallographic data, and the selected bond lengths, bond angles and torsion angles are given in Tables 2 and 3, respectively.

The C1-C11=N2-C12 [177.72(16)º] and C21-C31=N4-C32 [-178.69(16)º] torsion angles show that the configurations about the C=N bond s are *anti* (1*E*). The planar rings A(C1-C5/C10), B(C5-C10), C(N1/S1/C12/C13/C18) D(C13-C18) and E(C21-C25/C30), F(C25-C30), G(N3/S2/C32/C33/C38), H(C33-C38) are oriented at dihedral angles of A/B=4.65(5)º, C/D=0.95(5)º and E/F=0.35(6)º, G/H=2.45(6)º. So, rings C, D and E, F are coplanar. The coplanar rings I(N1/S1/C12-C18) and J(C21-C30) are oriented with respect to rings A, B and G, H at dihedral angles of A/I=15.12(4)º, B/I=2.24(5)º and G/J=5.84(4)º, H/J=5.58(4)º. The compound 3 has intramolecular C–H…N hydrogen bonds (Table 4).

Molecules are stacked along the a-axis in the crystal structure, extending along the c-axis (Fig. 2). The π···π contacts between the rings, Cg3---Cg1^{i}, Cg3---Cg2^{i}, Cg7---Cg5, Cg1---Cg1^{ii} and Cg5---Cg8 where Cg1, Cg2, Cg3, Cg5, Cg7 and Cg8 are the centroids of the rings A, B, C, E, G and H with centroid-centroid distances of 3.595(1) Å, 3.784(1) Å, 3.600(1) Å, 3.900(1) Å and 3.554 (1) Å, respectively, and the C-H···π interactions may be effective in the stabilization of the crystal packing (Table 4).

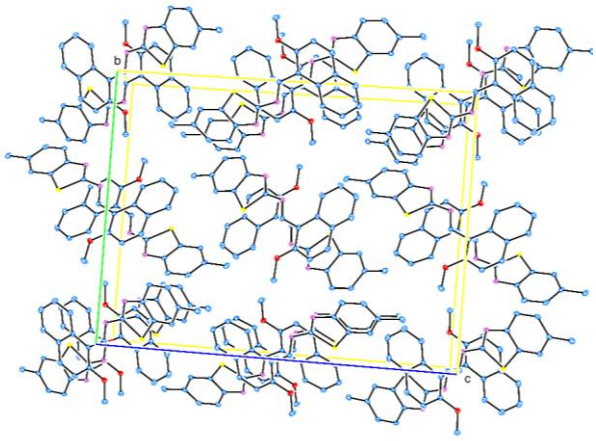


Fig. 2. A partial packing scheme that looks down on an axis. Hydrogen atoms are omitted for clarity.

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REFERENCES

1. H. Schiff, *Ann. Chem. Pharm. Suppl.* **3**, 343 (1864).
2. G. Wilkinson, R. Gillard, J. A. McCleverty, Comprehensive Coordination Chemistry. The Synthesis, Reactions, Properties and Applications of Coordination Compounds, in: Coordination Compounds en gros and en détail, **28,** 786, Pergamon Press, Oxford, 1987
3. H. Demirelli, M. Tümer, A. Gölcü, *Bull. Chem. Soc. Jpn*, **79 (6)**, 867 (2006).
4. A. Gölcü, M. Tumer, H Demirelli., R. A. Wheatley, *Inorg. Chim. Acta*, **358 (6)**, 1785 (2005).
5. Dolaz M., Tümer M. *Transition Met. Chem.*, **29 (5)**, 516 (2004).
6. T. T. Tidwell, *Angew. Chem., Int. Ed.* **47 (6)**, 1016, (2008).
7. S. Gaur, *Asian J. Chem.*, **15 (1)**, 250 (2003).
8. A. Prakash, D. Adhikari, *Int. J. ChemTech Res.*, **3 (4)**, 1891 (2011)
9. V. Mirkhani, R. Kia, A. R. Vartooni, H.-K. Fun, *Polyhedron*, **29 (6)**, 1600 (2010).
10. M. S. Manhas, M. Ghosh, A.K. Bose, *J. Org. Chem.*, **55 (2)**, 575 (1990).
11. J. H. Billman, K. M. Tai, *J. Org. Chem.*, **23 (4)**, 535 (1958).
12. J. Schmeyers, F. Toda, J. Boyb, G. Kaupp, *J. Chem. Soc., Perkin Trans.*, **2**, 4, 989 (1998).
13. R. S. Varma, R. Dahiya, S. Kumar, *Tetrahedron Lett.*, **38 (12)**, 2039 (1997).
14. P. C. Andrews, A. C. Peatt, C. L. Raston, *Tetrahedron Lett.*, **45 (2)**, 243 (2004).
15. K. Tanaka, R. Shiraishi, *Green Chem.*, **2 (6)**, 272 (2000).
16. A. Simion, C. Simion, T. Kanda, S. Nagashima, Y. Mitoma, T. Yamada, K. Mimura, M. Tashiro, *J. Chem. Soc., Perkin Trans.* **1** (17), 2071 (2001).
17. K. P. Guzen, A. S. Guarezemini, A. T. G. Órfão, R. Cella, C. M. P. Pereira, H. A. Stefani, *Tetrahedron Lett.*, **48 (10)**, 1845 (2007).
18. A. Dandia, A. K. Jain, A. K. Laxkar, *Tetrahedron Lett.*, **54 (30)**, 3929 (2013).
19. Bruker SADABS. Bruker AXS Inc. Madison, Wisconsin, USA, 2005.
20. G. M. Sheldrick, *Acta Cryst. Sect. A, Found. Cryst.*, **64**, 112 (2008).
21. L. J. Farrugia, *J. Appl.Cryst.*, **30 (5)**, 565 (1997).