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КРАТКИЕ СООБЩЕНИЯ

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CHARACTERIZATION AND CRYSTAL STRUCTURES OF 5-BROMO-2-METHOXY-4-(*p*-TOLYLIMINOMETHYL)PHENOL AND 2-BROMO-6-[(6-METHYLPYRIDIN-2-YLIMINO)METHYL]PHENOL

Y.-L. Dong, C. Li, X.-F. Meng, X. Zhou, J.-J. Ma

College of Sciences, Agricultural University of Hebei, Baoding, P. R. China
E-mail: majingjun71@126.com

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Two bromo-substituted Schiff bases 5-bromo-2-methoxy-4-(*p*-tolyliminomethyl)phenol (**1**) and 2-bromo-6-[(6-methylpyridin-2-ylimino)methyl]phenol (**2**) are prepared and characterized by elemental analysis, ^{1}H and ^{13}C NMR, and single crystal X-ray diffraction. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 6.228(1)$ Å, $b = 10.929(2)$ Å, $c = 21.312(2)$ Å, $\alpha = 104.230(2)°$, $\beta = 91.780(2)°$, $\gamma = 90.890(2)°$, $V = 1405.0(4)$ Å^3, $Z = 4$, $R_1 = 0.0359$, and $wR_2 = 0.0830$. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 8.180(2)$ Å, $b = 12.011(3)$ Å, $c = 12.843(3)$ Å, $\beta = 106.263(2)°$, $V = 1211.4(4)$ Å^3, $Z = 4$, $R_1 = 0.0364$, and $wR_2 = 0.0889$. X-ray diffraction indicates that the Schiff base molecules of the compounds display *trans* configuration with respect to the C=N double bonds. The crystal structures of the compounds are stabilized by hydrogen bonds and weak π···π interactions.

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Keywords: synthesis, Schiff base, crystal structure, X-ray diffraction, hydrogen bonding, π···π interaction.

Schiff bases derived from aldehydes with various primary amines are important compounds in biological and medical chemistry [1—3]. In the past decade, a number of Schiff base derivatives have been synthesized and investigated for their structures and biological applications [4—6]. A detailed study on the crystal structures seems to be essential for the understanding of the activities and applications of the compounds. In recent years, Schiff bases bearing halide groups have been proved to have interesting biological activities [4, 7, 8]. In this paper, we report the synthesis, characterization, and crystal structures of two new bromo-substituted Schiff bases: 5-bromo-2-methoxy-4-(*p*-tolyliminomethyl)phenol **1** and 2-bromo-6-[(6-methylpyridin-2-ylimino)methyl]phenol **2**.

Experimental. Materials and measurements. 2-Bromo-4-hydroxy-5-methoxybenzaldehyde, 3-bromo-2-hydroxybenzaldehyde, *p*-tolylamine, and 6-methylpyridin-2-ylamine were purchased from Aldrich. Methanol was commercially available and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental analyzer. ^{1}H and ^{13}C NMR spectra were obtained from a solution in DMSO-d_6 with Me_4Si as the internal standard using a Bruker AVANCE 500 MHz analyzer.

Synthesis of 1. 2-Bromo-4-hydroxy-5-methoxybenzaldehyde (1.0 mmol, 0.231 g) and *p*-tolylamine (1.0 mmol, 0.107 g) were dissolved in methanol (20 ml). The mixture was stirred at room temperature for 30 min to give a yellow solution. After keeping the solution in air for a few days, yellow block-shaped single crystals, suitable for X-ray diffraction, were formed. The crystals were isolated by

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filtration, washed with methanol and dried in air. Yield 0.23 g (72 %). Anal. calcd. for $C_{15}H_{14}BrNO_2$ (%): C 56.3, H 4.4, N 4.4; found (%): C 56.1, H 4.5, N 4.3. ^{1}H NMR (ppm): δ: 2.33 (*s*, 3H), 3.85 (*s*, 3H), 7.17—7.26 (*m*, 5H), 7.40 (*s*, 1H), 8.91 (*s*, 1H), 11.10 (*s*, 1H). ^{13}C NMR (ppm): δ: 21.5, 55.8, 115.3, 116.6, 120.7, 122.3, 128.7, 130.9, 136.6, 147.7, 149.2, 150.6, 160.1.

Synthesis of 2. 3-Bromo-2-hydroxybenzaldehyde (1.0 mmol, 0.201 g) and 6-methylpyridin-2-ylamine (1.0 mmol, 0.108 g) were dissolved in methanol (20 ml). The mixture was stirred at room temperature for 30 min to give a yellow solution. After keeping the solution in air for a few days, yellow block-shaped single crystals, suitable for X-ray diffraction, were formed. The crystals were isolated by filtration, washed with methanol and dried in air. Yield 0.25 g (86 %). Anal. calcd. for $C_{13}H_{11}BrN_2O$ (%): C 53.6, H 3.8, N 9.6; found (%): C 53.5, H 3.8, N 9.7 %. ^{1}H NMR (ppm): δ: 2.54 (*s*, 3H), 6.82 (*d*, 1H), 6.99 (*t*, 1H), 7.39—7.70 (*m*, 4H), 8.62 (*s*, 1H), 10.37 (*s*, 1H). ^{13}C NMR (ppm): δ: 23.7, 112.0, 112.9, 120.5, 122.2, 122.9, 130.7, 133.5, 137.7, 159.0, 159.8, 161.0, 162.1.

X-ray crystallography. Suitable single crystals were carefully selected under a microscope. Crystal data for the compounds were collected on a Bruker SMART APEX II-CCD diffractometer at 298(2) K using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by the global refinement of the positions of all collected reflections. An empirical absorption correction was applied. The structures were solved by a direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 software [9]. All the non-hydrogen atoms were refined anisotropically. All H atoms were added theoretically. Some relevant crystallographic data and structure determination parameters are summarized in Table 1. Selected bond lengths and angles for the compounds are given in Table 2.

Table 1

Crystal data for the compounds

Compounds	**1**	**2**
Color / shape	Yellow / block	Yellow / block
Empirical formula	$C_{15}H_{14}BrNO_2$	$C_{13}H_{11}BrN_2O$
Formula weight	320.2	291.2
Temperature, K	298(2)	298(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions *a*, *b*, *c*, Å	6.228(1), 10.929(2), 21.312(2)	8.180(2), 12.011(3), 12.843(3)
α, β, γ, deg.	104.230(2), 91.780(2), 90.890(2)	β 106.263(2)
Volume, Å^3	1405.0(4)	1211.4(4)
Z	4	4
Density (calculated), g/cm^3	1.514	1.596
Absorption coefficient, mm^{-1}	2.923	3.377
$F(000)$	648	584
Crystal size, mm	0.20×0.17×0.17	0.20×0.20×0.18
θ range for data collection, deg.	2.96—25.50	2.37—25.50
Limiting indices	$-7 \le h \le 7$, $-13 \le k \le 13$, $-25 \le l \le 25$	$-7 \le h \le 9$, $-14 \le k \le 14$, $-15 \le l \le 13$
Reflections collected	12846	6159
Observed reflections ($I \ge 2\sigma(I)$)	5242	2255
Data / restraints / parameters	4256 / 0 / 349	1679 / 0 / 156
R_{int}	0.0332	0.0278
Goodness-of-fit on F^2	1.041	1.024
Final *R* indices ($I \ge 2\sigma(I)$)	$R_1 = 0.0359$, $wR_2 = 0.0830$	$R_1 = 0.0364$, $wR_2 = 0.0889$
R indices (all data)	$R_1 = 0.0498$, $wR_2 = 0.0910$	$R_1 = 0.0544$, $wR_2 = 0.0970$
Largest diff. peak and hole, e/Å^3	0.646, –0.540	0.565, –0.523

Table 2

Selected bond lengths (Å) *and angles* (deg.) *for the compounds*

1				2	
Bond distances					
C8—N1	1.269(3)	C9—N1	1.425(3)	C7—N1	1.277(4)
C21—N2	1.271(3)	C22—N2	1.424(3)	C8—N1	1.421(4)
Bond angles					
C8—N1—C9	117.1(2)	C21—N2—C22	119.3(2)	C7—N1—C8	120.3(3)

Results and discussion. The compounds were readily prepared by the reaction of equimolar quantities of 2-bromo-4-hydroxy-5-methoxybenzaldehyde with *p*-tolylamine and 3-bromo-2-hydroxybenzaldehyde with 6-methylpyridin-2-ylamine, respectively, in methanol. The elemental analyses are in agreement with the empirical formulae given by the single crystal X-ray determination. Single crystals of the compounds can easily be formed by slow evaporation of their methanol solutions. All the compounds are soluble in methanol, ethanol, acetonitrile, dichloromethane, and chloroform.

Crystal structure description of 1. Fig. 1 gives the perspective view of compound **1** with the atomic labeling system. The asymmetric unit of the compound contains two independent molecules (*A* and *B*). All the bond lengths in the compounds are within normal ranges [10], and are comparable to those of the similar Schiff bases [11—13]. The C8—N1 and C21—N2 bond lengths confirm them as double bonds. The dihedral angles between the two benzene rings are 52.6(3)° for molecule *A* and16.6(3)° for molecule *B*. Both molecules of the compound exist in *trans* configuration with respect to the C=N double bonds of the central methylidene units. The C1—C8—N1—C9 and C20—C21—N2—C22 torsion angles are 176.3(3)° and 179.3(3)° respectively. In the crystal structure of **1** (Fig. 2) the molecules are stacked along the *a* axis *via* π-electron ring–π-electron ring interactions (Table 3).

Crystal structure description of 2. Fig. 3 gives the perspective view of compound **2** with the atomic labeling system. All the bond lengths in the compounds are within normal ranges [10] and are comparable to those of the similar Schiff bases [14—16]. The C7—N1 bond length confirms it as a double bond. The dihedral angle between the C1—C6 benzene ring and the C8—C12/N2 pyridine ring is 4.8(2)°. The molecules of the compound exist in *trans* configuration with respect to the C=N double bond of the central methylidene unit. The C1—C7—N1—C8 torsion angle is 0.3(3)°. In the crystal structure of **2** (Fig. 4) the molecules are stacked along the *a* axis *via* π-electron ring—π-electron ring interactions (Table 3).

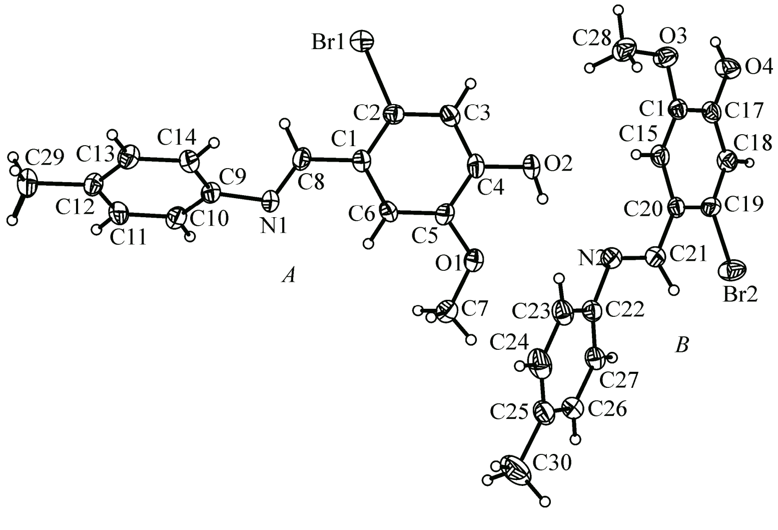

Fig. 1. Molecular structure of **1** showing 30 % probability displacement ellipsoids

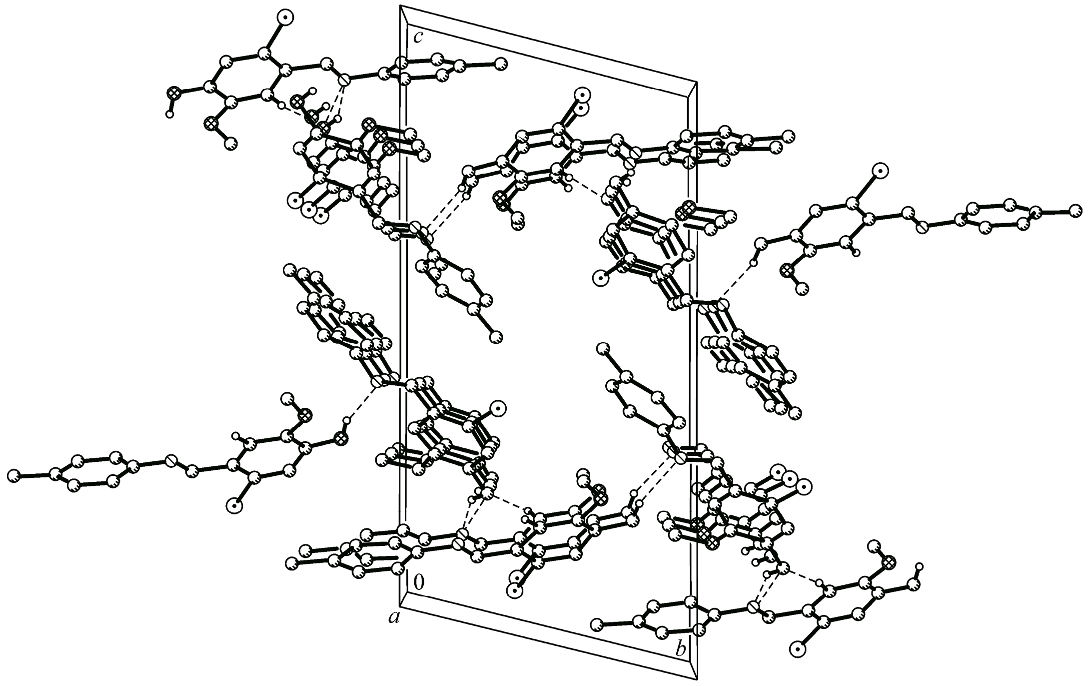

Fig. 2. Molecular packing of **1**. Hydrogen bonds are shown as dashed lines

Table 3

π—π *Interactions* (Å) *of the compounds*

1		**2**			
$Cg1\cdots Cg1^{iv}$	4.094	$Cg3\cdots Cg4^{vi}$	3.872	$Cg3\cdots Cg4^{vii}$	4.386
$Cg2\cdots Cg2^{v}$	4.788	$Cg4\cdots Cg4^{vii}$	4.892		

*Cg*1 and *Cg*2 are the centroids of the C9—C14 and C22—C27 benzene rings, respectively, in **1**. *Cg*3 and *Cg*4 are the centroids of the N2—C8—C12—C11—C10—C9 pyridine ring and C1—C6 benzene ring, respectively, in **2**. Symmetry codes: ^{iv} $1-x, -y, -z$; ^{v} $1-x, 2-y, 1-z$; ^{vi} $-x, 1-y, -z$; ^{viii} $1-x, 1-y, -z$.

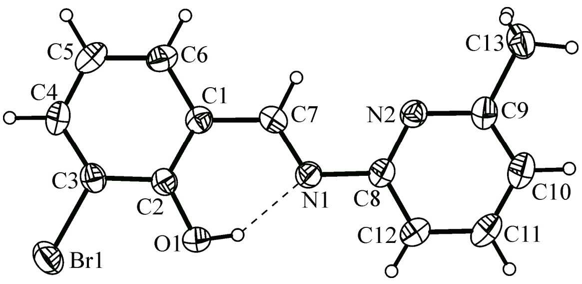

Fig. 3. Molecular structure of **2** showing 30 % probability displacement ellipsoids. Intramolecular hydrogen bond is drawn as a dashed line

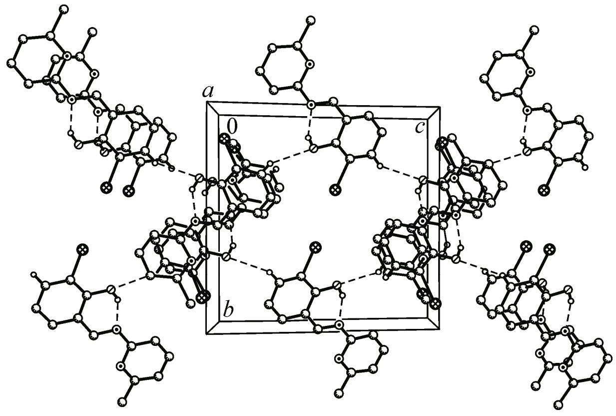

Fig. 4. Molecular packing of **2**. Hydrogen bonds are shown as dashed lines

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Nos. 969431 (*1*) and 969432 (*2*). Copies of the available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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