Crystal structure of 4-bromo-2-(pyridin-4-ylmethyliminomethyl)phenol, $C_{13}H_{11}BrN_2O$

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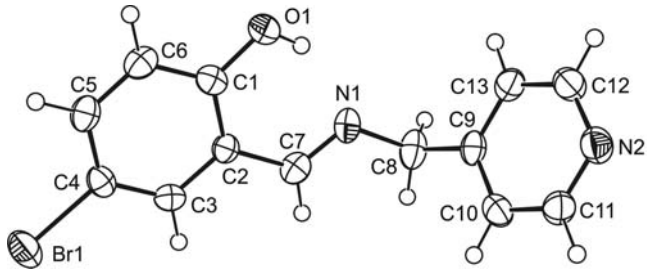

Abstract

$C_{13}H_{11}BrN_2O$, monoclinic, $P12_1/c1$ (no. 14), a = 13.945(2) Å, b = 6.1164(7) Å, c = 14.163(2) Å, β = 102.771(2)°, V = 1178.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.098, T = 200 K.

Source of material

4-(Aminomethyl)pyridine (1.0811 g, 9.997 mmol) and 5-bromosalicylaldehyde (2.0097 g, 9.998 mmol) in EtOH (20 ml) were stirred for 1 h at room temperature. After addition of pentane (30 ml) to the reaction mixture, the formed precipitate was then separated by filtration, washed with ether/pentane, and dried at 50 °C to give a yellow powder (2.4091 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a methanol solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) or 0.99 Å (CH_2) and U_{iso}(H) = 1.2 U_{eq}(C). The hydroxy H atom was located from difference Fourier map and refined isotropically with d(O—H) = 0.82(3) Å. The highest peak (0.60 e·Å^{-3}) and the deepest hole (–0.56 e·Å^{-3}) in the difference Fourier map are located 1.87 Å and 0.83 Å from the atoms H5 and Br1, respectively.

Discussion

The title compound is a polydentate Schiff base, which can act as a monobasic bi- or tridentate ligand, that is, the two N and one O donor atoms can coordinate a metal ion or metal ions. The compound crystallized in the monoclinic space group $P2_1/c$, whereas the previously reported analogous compound 4-bromo-2-(pyridin-2-ylmethyliminomethyl)phenol crystallized in the triclinic space group $P\bar{1}$ [1]. The Schiff base reveals intramolecular O–H···N hydrogen bonding between the hydroxy O atom and the imino N atom with d(O···N) = 2.610(4) Å forming a nearly planar six-membered ring. The dihedral angle between the phenol ring and the pyridyl ring is 67.81(8)°. The N1—C7/C8 bond lengths and the C7–N1–C8 bond angle indicate that the imino N1 atom is sp^2 hybridized (d(N1=C7) = 1.278(4) Å and d(N1—C8) = 1.468(4) Å; ∠C7–N1–C8 = 118.0(3)°). In the crystal structure, the molecules are stacked in columns along [001]. In the columns, several intermolecular π-π interactions between adjacent six-membered rings are present. The centroid-centroid distance between Cg1 (the centroid of ring C1-C6) and Cg1^{i} (symmetry code i: 1–x,1–y,1–z) is 3.814(2) Å, the ring planes are parallel and shifted by 1.309 Å.

Table 1. Data collection and handling.

Crystal:	yellow stick, size 0.18 × 0.25 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	34.73 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8377, 2922
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1736
$N(param)_{refined}$:	158
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP [3], PLATON [4]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.346(2)	0.270(6)	0.343(2)	0.03(1)
H(3)	4*e*	0.5706	0.7694	0.3396	0.037
H(5)	4*e*	0.7085	0.2444	0.4807	0.042
H(6)	4*e*	0.5596	0.0604	0.4585	0.041
H(7)	4*e*	0.3923	0.7784	0.2813	0.041
H(8A)	4*e*	0.1843	0.5921	0.1814	0.051
H(8B)	4*e*	0.2385	0.8138	0.2235	0.051
H(10)	4*e*	0.1845	1.0047	0.3536	0.045
H(11)	4*e*	0.0702	1.0392	0.4483	0.048
H(12)	4*e*	–0.0275	0.4479	0.3830	0.048
H(13)	4*e*	0.0804	0.3967	0.2836	0.043

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4*e*	0.77538(3)	0.66959(7)	0.42960(3)	0.0344(2)	0.0564(3)	0.0555(3)	–0.0116(2)	0.0037(2)	–0.0065(2)
O(1)	4*e*	0.3890(2)	0.1931(4)	0.3763(2)	0.035(1)	0.034(1)	0.054(2)	–0.003(1)	0.012(1)	0.007(1)
N(1)	4*e*	0.3033(2)	0.5419(5)	0.2905(2)	0.028(2)	0.044(2)	0.037(2)	0.006(1)	0.009(1)	0.001(1)
N(2)	4*e*	0.0097(2)	0.7492(5)	0.4243(2)	0.035(2)	0.046(2)	0.044(2)	–0.002(1)	0.013(1)	–0.005(2)
C(1)	4*e*	0.4743(2)	0.3053(5)	0.3872(2)	0.034(2)	0.033(2)	0.027(2)	–0.004(2)	0.012(1)	–0.001(2)
C(2)	4*e*	0.4769(2)	0.5192(5)	0.3518(2)	0.028(2)	0.030(2)	0.026(2)	0.002(1)	0.009(1)	–0.001(1)
C(3)	4*e*	0.5676(2)	0.6257(5)	0.3643(2)	0.036(2)	0.026(2)	0.031(2)	–0.002(1)	0.009(2)	–0.002(1)
C(4)	4*e*	0.6523(2)	0.5244(5)	0.4119(2)	0.027(2)	0.038(2)	0.028(2)	–0.003(2)	0.009(1)	–0.005(2)
C(5)	4*e*	0.6496(2)	0.3134(6)	0.4476(2)	0.033(2)	0.042(2)	0.030(2)	0.008(2)	0.006(1)	0.004(2)
C(6)	4*e*	0.5613(2)	0.2052(5)	0.4347(2)	0.042(2)	0.033(2)	0.031(2)	0.006(2)	0.015(2)	0.008(2)
C(7)	4*e*	0.3877(2)	0.6331(5)	0.3035(2)	0.038(2)	0.035(2)	0.030(2)	0.005(2)	0.009(2)	0.003(2)
C(8)	4*e*	0.2171(2)	0.6683(6)	0.2415(3)	0.033(2)	0.056(2)	0.039(2)	0.014(2)	0.010(2)	0.012(2)
C(9)	4*e*	0.1455(2)	0.6959(6)	0.3063(2)	0.025(2)	0.040(2)	0.030(2)	0.008(2)	0.002(1)	0.005(2)
C(10)	4*e*	0.1410(2)	0.8873(6)	0.3575(3)	0.029(2)	0.040(2)	0.042(2)	–0.005(2)	0.005(2)	–0.003(2)
C(11)	4*e*	0.0724(2)	0.9060(6)	0.4143(3)	0.035(2)	0.040(2)	0.043(2)	0.000(2)	0.006(2)	–0.015(2)
C(12)	4*e*	0.0156(2)	0.5642(6)	0.3760(3)	0.034(2)	0.040(2)	0.045(2)	–0.004(2)	0.008(2)	0.003(2)
C(13)	4*e*	0.0804(2)	0.5314(6)	0.3170(2)	0.034(2)	0.036(2)	0.037(2)	0.005(2)	0.005(2)	–0.003(2)

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