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Crystal structure of 3-(benzo[*d*]thiazol-2-yl)-5-bromo-2-hydroxybenzaldehyde, $C_{14}H_8BrNO_2S$

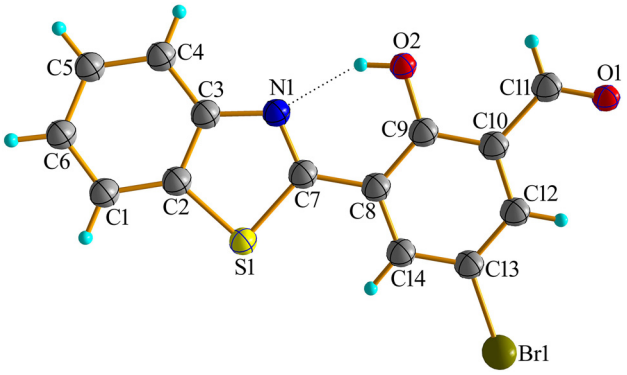

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.20 × 0.19 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	3.40 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.0°, 98 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10,724, 2440, 0.047
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2189
$N(param)_{refined}$:	173
Programs:	Olex2 [1], Bruker [2], SHELX [3], Diamond [4]

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Abstract

$C_{14}H_8BrNO_2S$, orthorhombic, $P2_12_12_1$ (no. 19), a = 4.7405(2) Å, b = 14.5781(5) Å, c = 18.3358(6) Å, V = 1267.14(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0318, $wR_{ref}(F^2)$ = 0.0774, T = 273(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

Weigh 5-bromo-2-hydroxybenzaldehyde (1.07 g, 5 mmol) and 2-aminobenzenethiol (0.47 g, 5 mmol) and add to a round bottom flask with a volume of 100 mL. Add 30 mL of methanol and stir at room temperature for 30 min. Add I_2 (5 mmol, 0.32 g) and continue stirring at room temperature for 8 h to produce a precipitate. Filter and wash the precipitate three times with methanol to obtain 2-(benzo[d]thiazol-2-yl)-4-bromophenol.

Weigh the above product (2.5 mmol, 0.76 g) and add it to a round bottom flask. Then add 11 mL of trifluoroacetic acid and stir until it is completely dissolved. Then add hexamethylenetetramine (5 mmol, 0.70 g) and heat for reflux reaction for 24 h. Cool the solution to room temperature, pour a small amount into ice water multiple times, precipitate the solid, filter, and recrystallize with ethanol to obtain the target product of 0.58 g, with a yield of 70 %.

2 Experimental details

Using Olex2 [1], the structure was solved using Charge Flipping and refined with the ShelXL [3] refinement. All hydrogen atoms were positioned geometrically, withthe d (C–H) = 0.97–0.99 Å, U_{iso}(H) = 1.2 times U_{eq}(C) and U_{iso}(H) = 1.5 times U_{eq}(O).

3 Comment

Schiff base is a compound with a C=N double bond obtained by condensation reaction between compounds containing aldehyde groups and compounds containing primary amino groups. Because of the non-bonding pair of electrons on the nitrogen atom in the C=N double bond, it is easy to coordinate with different metal ions, resulting in novel structures and excellent properties of the complex [5, 6]. Researchers have utilized this characteristic to advance the field of metal ion recognition and detection [7, 8].

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.25879 (11)	0.36204 (3)	0.84827 (2)	0.04844 (18)
S1	0.4628 (3)	0.53789 (8)	0.67261 (7)	0.0391 (3)
O1	1.1881 (10)	0.0748 (3)	0.6600 (2)	0.0694 (12)
O2	0.6237 (8)	0.2500 (2)	0.57828 (18)	0.0470 (9)
H2	0.5030	0.2881	0.5678	0.070*
N1	0.3532 (7)	0.4061 (2)	0.5825 (2)	0.0337 (8)
C1	0.0811 (10)	0.6395 (3)	0.5865 (3)	0.0460 (12)
H1	0.1086	0.6925	0.6137	0.055*
C2	0.2238 (10)	0.5586 (3)	0.6026 (2)	0.0350 (10)
C3	0.1882 (8)	0.4785 (3)	0.5610 (2)	0.0329 (10)
C4	−0.0016 (10)	0.4786 (4)	0.5032 (3)	0.0425 (12)
H4	−0.0301	0.4260	0.4754	0.051*
C5	−0.1457 (11)	0.5577 (4)	0.4881 (3)	0.0492 (14)
H5	−0.2754	0.5584	0.4500	0.059*
C6	−0.1022 (11)	0.6373 (4)	0.5285 (3)	0.0509 (13)
H6	−0.1998	0.6904	0.5160	0.061*
C7	0.5075 (9)	0.4262 (3)	0.6393 (2)	0.0313 (9)
C8	0.7096 (8)	0.3630 (3)	0.6717 (2)	0.0291 (8)
C9	0.7595 (10)	0.2766 (3)	0.6389 (2)	0.0330 (9)
C10	0.9595 (10)	0.2173 (3)	0.6695 (3)	0.0373 (10)
C11	1.0164 (12)	0.1239 (3)	0.6359 (3)	0.0484 (13)
H11	0.9127	0.1053	0.5955	0.058*
C12	1.1033 (10)	0.2432 (3)	0.7319 (3)	0.0372 (10)
H12	1.2331	0.2031	0.7526	0.045*
C13	1.0568 (9)	0.3275 (3)	0.7637 (2)	0.0325 (10)
C14	0.8619 (9)	0.3864 (3)	0.7345 (2)	0.0323 (10)
H14	0.8303	0.4429	0.7567	0.039*

Excited State Intramolecular Proton Transfer (ESIPT) is characterized by the presence of both a proton donor group (–NH_2 or –OH) and a proton acceptor group (C=O or =N–) within a molecule. The molecule absorbs photons and transitions to the excited state, causing the charge of the molecule to rearrange and the proton to transfer to nearby proton acceptors. The alcohol like structure of the molecule in the ground state changes to the quinone like structure in the excited state. Quinone like structures are more stable and have lower energy in the excited state compared to alcohol like structures, and the fluorescence released by radiative transitions back to the ground state shows a red shift. Therefore, these molecules typically have a large Stokes shift, avoiding self-absorption and internal filtering effects, and their fluorescence often exhibits double emission, making them widely used in the design and development of fluorescent probes [9, 10].

The design and synthesis of aldehyde compounds with ESIPT are of great significance [11]. Here, we design and sythesised 3-(benzo[d]thiazol-2-yl)-5-bromo-2-hydroxybenzaldehyde with aldehyde groups and ESIPT effect. The target compound is first obtained by reacting 2-hydroxy-5-bromobenzaldehyde with 2-phenylaminophenylthiophenol to obtain 2-(benzo[d]thiazol-2-yl)-4-bromophenol, and then introducing an aldehyde group to obtain it. The crystal structure proves that the compound has been successfully acylated, and the bond length of the C=O bond is 1.170(6) Å [12]. The benzothiazole ring and the phenyl ring have a dihedral angle of 6.02°. The hydroxyl oxygen atom and the nitrogen atom of the thiazole ring form an O2–H2···N1 intramolecular hydrogen bond. Molecules extend into one-dimensional structures through atypical C14–H14···O1 hydrogen bonds.

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