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The crystal structure of 6,6'-((1*E*,1'*E*)-hydrazine-1,2-diylidenebis(methaneylylidene))bis(2-bromo-4-nitrophenol) – dimethylsulfoxide (1/2), $C_{14}H_8Br_2N_4O_6 \cdot 2(C_2H_6OS)$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.30 × 0.25 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.40 mm ⁻¹
Diffractometer, scan mode:	Bruker photon 100, φ and ω
$\theta_{\max}$, completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8435, 2602, 0.068
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1586
$N(\text{param})_{\text{refined}}$:	167
Programs:	Bruker [1, 2], SHELX [3, 4]

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Abstract

$C_{14}H_8Br_2N_4O_6 \cdot 2(C_2H_6OS)$, triclinic, $P\bar{1}$ (no. 2), $a = 6.1463(12)$ Å, $b = 8.3637(16)$ Å, $c = 12.461(3)$ Å, $\alpha = 85.578(5)^\circ$, $\beta = 85.942(5)^\circ$, $\gamma = 86.310(5)^\circ$, $V = 635.9(2)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0601$, $wR_{\text{ref}}(F^2) = 0.0983$, $T = 296$ 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.

Source of materials

All chemicals were analytical reagent grade and used without further purification. The title compound was prepared according to the synthetic route as following. Into a 100 mL round-bottom flask with a reflux condenser, 3-bromo-5-nitro-2-hydroxybenzaldehyde (10 mmol, 2.4668 g) were dissolved in 40 mL ethanol and added hydrazine hydrate (1 mmol, 60 μ L) into it, refluxing 2 h later, the pale yellow precipitate of the compound was obtained (yield 89%). A few days later, yellow block crystals were obtained from DMSO. ¹H NMR (600 MHz, DMSO-*d*₆) (ppm): 9.262 (s, 2H, –HC=N–), 8.658 (s, 2H, Ph–H), 8.551 (s, 2H, Ph–H).

Experimental details

Data integrations were performed by the SAINT program [1], and the absorption data were modified by using the multiscan program SADABS [2]. Structural solutions and refinements were performed by using the SHELXS [3] and SHELXL programs [4]. The H atoms attached to C atoms were placed in calculated idealized positions and refined by a riding model.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Br1	0.80364 (7)	0.88181 (6)	0.37022 (4)	0.0516 (2)
S1 ^a	0.1498 (8)	0.7024 (7)	0.1549 (4)	0.098 (2)
S1A ^b	0.2235 (6)	0.6030 (5)	0.0933 (3)	0.1053 (17)
O3	0.1045 (10)	0.5372 (6)	0.1930 (4)	0.149 (2)
N1	0.6809 (8)	0.8227 (6)	0.7922 (4)	0.0699 (13)
O1	0.3997 (5)	0.7028 (4)	0.3952 (2)	0.0489 (8)
H1	0.297260	0.643909	0.401273	0.073 [*]
N2	0.0921 (5)	0.5454 (4)	0.4953 (3)	0.0393 (9)
O2	0.5654 (7)	0.7917 (6)	0.8726 (3)	0.1033 (15)
O4	0.8570 (7)	0.8809 (5)	0.7921 (3)	0.1037 (15)
C1	0.6473 (7)	0.8123 (5)	0.4991 (4)	0.0378 (11)
C2	0.4607 (6)	0.7271 (5)	0.4921 (3)	0.0338 (10)
C3	0.3478 (6)	0.6703 (5)	0.5883 (3)	0.0363 (11)
C4	0.4199 (7)	0.7021 (5)	0.6864 (4)	0.0428 (11)
H4	0.344511	0.666738	0.750255	0.051 [*]
C5	0.6048 (7)	0.7866 (5)	0.6891 (4)	0.0453 (12)
C6	0.7191 (7)	0.8418 (5)	0.5959 (4)	0.0427 (12)
H6	0.843601	0.898375	0.599224	0.051 [*]
C7	0.1569 (6)	0.5777 (5)	0.5845 (4)	0.0388 (11)
H7	0.081932	0.541919	0.648422	0.047 [*]
C9	0.0650 (12)	0.7526 (11)	0.0366 (7)	0.170 (4)
H9A	0.110755	0.669922	−0.010857	0.255 [*]
H9B	0.125301	0.851714	0.008777	0.255 [*]
H9C	−0.091628	0.766109	0.041511	0.255 [*]
C10	0.4294 (12)	0.7151 (10)	0.1345 (5)	0.143 (3)
H10A	0.490694	0.724014	0.202445	0.215 [*]
H10B	0.460538	0.808077	0.087158	0.215 [*]
H10C	0.492417	0.620443	0.102721	0.215 [*]

^aOccupancy: 0.418(7), ^bOccupancy: 0.582(7).

half of the hydrazine compound in the asymmetric unit. The aromatic carbon-carbon bond lengths deviate significantly, that the values of the C(3)–C(4) and C(1)–C(6) bond-distances are 1.380(6) and 1.359(6) Å respectively, which are shorter than the values of the remaining bond distances [9, 10]. The length of double bond C(7)–N(2), 1.261(5) Å, is very consistent with the value of 1.259(5) Å given by Safin for the length of carbon-nitrogen double bond of *N,N'*-bis(5-bromosalicylidene)diamines [10]. The two benzene rings are in trans configuration connected by N2–N2A bond, and are nearly coplanar (C6–C1–C2–O1: 179.9(4)°, O1–C2–C3–C7: 1.2(6)°, C3–C7–N2–N2A: 179.5(4)°, C4–C3–C7–N2: 178.6(4)°. In addition, there are weak interactions in the structure. Firstly, the intramolecular O1–H1...N2 hydrogen bonds form a six-membered ring, generating a S(6) ring motif [11]. Secondly, $\pi\cdots\pi$ interactions between aromatic rings are also contained in the structure. The molecules are nearly planar and are arranged in parallel packing, meanwhile the distance between atom N2 and Cg (C1–C2–C3–C7–Br1–O1–N2) is 3.33 Å.

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Comment

Salicylaldehyde azine (SAA) consists of salicylaldehyde and hydrazine, is a Schiff base with ESIPT process and its derivatives exhibit obvious aggregation-induced emission (AIE) characters with recognizable fluorescence performance which have been used widely in bioimaging and ions detection [5, 6]. Different SAA derivatives with specific spectral properties can be obtained [7, 8]. In this report a SA derivative, named 3-bromo-2-hydroxy-5-nitrobenzaldehyde which has an electron drawing group (–NO₂) *para* to the hydroxyl group, was chosen to study the fluorescence properties and we got the crystal structure of the title compound unexpectedly.

The single-crystal X-ray diffraction revealed that title compound crystallized in the triclinic space group and it contains one dimethylsulfoxide (DMSO) molecule and one

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