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The crystal structure of 2,5-bis(3,5-dimethylphenyl)thiazolo[5,4-*d*]thiazole, C₂₀H₁₈N₂S₂

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Abstract

C₂₀H₁₈N₂S₂, monoclinic, *P*₂/n (no. 14), *a* = 7.92140(10) Å, *b* = 6.08080(10) Å, *c* = 17.8091(3) Å, β = 90.592(2)°, *V* = 857.79(2) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0382, *wR*_{ref}(*F*²) = 0.1051, *T* = 149.99(10) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of rubeanic acid (10 mmol, 1.2 g), 3,5-dimethylbenzaldehyde (30 mmol, 4.0 g) were dissolved in anhydrous *N,N*-dimethylformamide (50 mL) and stirred for 20 min at room temperature. Subsequently, the solution was bubbled by nitrogen for 30 min, heated to reflux and kept 425 K in the nitrogen atmosphere. After 8 h, the

Table 1: Data collection and handling.

Crystal:	Yellowish green block
Size:	0.10 × 0.05 × 0.03 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	2.82 mm ⁻¹
Diffractometer, scan mode:	XtaLAB AFC12 (RINC), ω
θ _{max} , completeness:	73.2°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	3637, 1658, 0.021
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1583
<i>N</i> (<i>param</i>) _{refined} :	111
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

reaction system was cooled slowly to room temperature. So the yellowish green crystals were deposited. The mixture was filtered and washed by *N,N*-dimethylformamide (10 mL) three times. And then the pure title compound was obtained. Yield: 1.8 g (51%, based on rubeanic acid). **Anal. Calcd.** for C₂₀H₁₈N₂S₂ (%): C, 68.53; H, 5.18; N, 7.99; S, 18.30. Found: C, 68.25.; H, 5.31; N, 7.46; S, 18.14.

Experimental details

Crystallographic data collection and reduction were performed using the program CrysAlis^{PRO} [1]. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program and refined on *F*² with the ShelXL [4] refinement package. Hydrogen atoms were added using the typical AFIX commands of the SHELX system [4]. The *U*_{iso} values were set to be 1.5*U*_{eq} of the carrier atom for methyl hydrogen atoms and 1.2*U*_{eq} for aryl hydrogen atom.

Comment

As well-known, the thiazolo[5,4-*d*]thiazole moiety with a rigid conjugated plane has good photo-electricity activity, which has been applied to many fields, such as fluorescence [5–9], photothermal therapy [10], laser [11, 12], light-harvester [13, 14] and photocatalysis [15–18]. Moreover, the photo-electricity activities of thiazolo[5,4-*d*]thiazole derivatives vary with the substitution. Therefore, it is very

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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}
S1	0.63907 (5)	0.81753 (7)	0.57515 (2)	0.02482 (18)
N1	0.3325 (2)	0.8064 (2)	0.51701 (9)	0.0238 (3)
C1	0.4359 (2)	0.7038 (3)	0.56499 (10)	0.0208 (4)
C2	0.4183 (2)	0.9822 (3)	0.48821 (9)	0.0218 (4)
C3	0.3875 (2)	0.5067 (3)	0.60717 (9)	0.0205 (4)
C4	0.2284 (2)	0.4145 (3)	0.59522 (10)	0.0236 (4)
H4	0.1533	0.4814	0.5618	0.028*
C5	0.1804 (2)	0.2242 (3)	0.63251 (10)	0.0248 (4)
C6	0.2935 (2)	0.1287 (3)	0.68337 (10)	0.0249 (4)
H6	0.2618	0.0021	0.7089	0.030*
C7	0.4524 (2)	0.2179 (3)	0.69683 (10)	0.0228 (4)
C8	0.4990 (2)	0.4068 (3)	0.65800 (10)	0.0219 (4)
H8	0.6056	0.4671	0.6660	0.026*
C9	0.0116 (3)	0.1186 (4)	0.61652 (13)	0.0363 (5)
H9A	0.0273	−0.0096	0.5859	0.054*
H9B	−0.0601	0.2213	0.5905	0.054*
H9C	−0.0399	0.0770	0.6630	0.054*
C10	0.5724 (3)	0.1112 (3)	0.75218 (11)	0.0314 (4)
H10A	0.6854	0.1597	0.7425	0.047*
H10B	0.5664	−0.0458	0.7469	0.047*
H10C	0.5417	0.1518	0.8023	0.047*

significant to design the thiazolo[5,4-*d*]thiazole derivatives containing the different electronegative substituent groups.

The title compound crystallizes in the monoclinic crystal system with *P*₂₁/*n* space group. Its asymmetric unit contains half of the title molecule (the figure). In the crystal structure, all atoms in thiazolo[5,4-*d*]thiazole moiety are in the same plane, and the thiazolo[5,4-*d*]thiazole plane (p1) is almost coplanar with the benzene ring plane (p2) (*a* = −*x*+1, −*y*+2, −*z*+1; cf. the figure). The dihedral angle between the two planes (p1 and p2) is only 2.66(8)°. The title molecules are alternately π -stacked, with thiazole rings overlaid and slightly offset to the benzene rings. The Cg...Cg distances are 3.5981(10) and 3.6391(10) Å, respectively (Cg is the centroid of the benzene ring or the thiazole ring). The slippage value ranges from 0.933 to 1.087 Å. Phenyl H6 is involved in C–H... π interactions with the pendant benzene rings in the neighboring molecules. The H6...Cg3b and C6...Cg3b distances are 2.95 and 3.75 Å, respectively (Cg3 is the centroid of the benzene ring C3–C8; symmetry code: *b* = −*x*+0.5, *y*−0.5, −*z*+1.5). The C–H...Cg angle is 146°. Angle of the X–H bond with the benzene plane is 68°. Through π – π and C–H... π interactions, the title molecules are stacked to form two-dimensional layers, which are further assembled by Van der Waals forces to extend into a three-dimensional structure. All bond lengths and bond angles within the title structure are in the normal range [19–25].

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