Nana Xin, Jun Zheng and Qingpeng He*

The crystal structure of *N,N'*-(Disulfanediyl)-2,1-phenylene)di(6'-methylpyridine)-2-carboxamide, $C_{26}H_{22}N_4O_2S_2$

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Abstract

$C_{26}H_{22}N_4O_2S_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9495(7)$ Å, $b = 11.2494(12)$ Å, $c = 13.7829(13)$ Å, $\alpha = 81.433(2)^\circ$, $\beta = 76.536(1)^\circ$, $\gamma = 82.641(2)^\circ$, $V = 1179.7(2)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0727$, $wR_{ref}(F^2) = 0.2189$, $T = 298(2)$ 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.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.23 × 0.21 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.26 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX II, φ and ω
θ_{max} , completeness:	25.0°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	6008, 4109, 0.067
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2424
$N(param)_{refined}$:	309
Programs:	Bruker [1], SHELX [2]

Source of material

In the typical case, 6-methyl-2-pyridinecarboxylic acid (1.2 mmol), *N*-methyl morpholine (0.4 mmol), and ethylchloroformate (0.4 mmol) were successively added to the 10 mL dry tetrahydrofuran (THF) and stirred at -15°C for 20 min. After 20 min of stirring, 2-(2-(2-aminophenyl)disulfanyl)-benzenamine (0.3 mmol) was added to the solution, and the reaction mixture was stirred for 2 h at -15°C . The stirring was later continued at room temperature for an additional 12 h. The reaction was monitored by using thin

*Corresponding author: Qingpeng He, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252000, Shandong, China, E-mail: heqingpenglc@163.com

Nana Xin and Jun Zheng, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252000, Shandong, China

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
N1	0.7177 (5)	0.7664 (3)	0.2043 (3)	0.0588 (10)
H1	0.670456	0.716123	0.253320	0.071*
N2	0.6380 (6)	0.5491 (4)	0.2069 (3)	0.0718 (12)
N3	1.0316 (5)	0.7030 (3)	0.3478 (2)	0.0538 (9)
H3'	0.997609	0.753084	0.391490	0.065*
N4	1.1458 (5)	0.9091 (3)	0.3548 (3)	0.0614 (10)
O1	0.8270 (7)	0.7863 (4)	0.0357 (3)	0.1122 (16)
O2	1.2059 (5)	0.6831 (3)	0.1943 (3)	0.0941 (13)
S1	0.54357 (15)	0.79815 (11)	0.41849 (8)	0.0582 (4)
S2	0.70671 (16)	0.71049 (10)	0.51002 (8)	0.0572 (4)
C1	0.6675 (6)	0.9025 (4)	0.3295 (3)	0.0534 (11)
C2	0.6883 (7)	1.0132 (4)	0.3573 (4)	0.0672 (13)
H2	0.643264	1.029291	0.423095	0.081*
C3	0.7743 (7)	1.0987 (5)	0.2886 (4)	0.0756 (15)
H3	0.785486	1.172740	0.307529	0.091*
C4	0.8438 (7)	1.0744 (5)	0.1919 (4)	0.0714 (14)
H4	0.902745	1.132176	0.145583	0.086*
C5	0.8274 (6)	0.9656 (4)	0.1626 (3)	0.0609 (12)
H5	0.875053	0.950463	0.096787	0.073*
C6	0.7399 (6)	0.8781 (4)	0.2308 (3)	0.0510 (11)
C7	0.7597 (7)	0.7257 (5)	0.1128 (4)	0.0683 (13)
C8	0.7114 (7)	0.6009 (4)	0.1161 (4)	0.0624 (12)
C9	0.7419 (7)	0.5429 (5)	0.0286 (4)	0.0732 (14)
C10	0.6893 (9)	0.4266 (6)	0.0439 (5)	0.0928 (19)
H10	0.706046	0.384018	−0.011033	0.111*
C11	0.6149 (9)	0.3740 (6)	0.1356 (6)	0.097 (2)
H11	0.580265	0.296503	0.144218	0.116*
C12	0.5915 (8)	0.4382 (5)	0.2167 (4)	0.0835 (16)
H12	0.541239	0.402251	0.280347	0.100*
C13	0.8273 (10)	0.5978 (6)	−0.0750 (4)	0.110 (2)
H13A	0.831778	0.542691	−0.122594	0.165*
H13B	0.943163	0.613764	−0.075150	0.165*
H13C	0.761290	0.672054	−0.093152	0.165*
C14	0.8085 (6)	0.5824 (4)	0.4495 (3)	0.0490 (10)
C15	0.7402 (6)	0.4719 (4)	0.4800 (3)	0.0575 (12)
H15	0.641084	0.465493	0.531268	0.069*
C16	0.8191 (7)	0.3712 (4)	0.4345 (4)	0.0629 (12)
H16	0.775195	0.296642	0.455838	0.076*
C17	0.9627 (6)	0.3826 (4)	0.3576 (4)	0.0611 (12)
H17	1.012461	0.315849	0.324980	0.073*
C18	1.0348 (6)	0.4901 (4)	0.3277 (3)	0.0559 (11)
H18	1.134389	0.494795	0.276634	0.067*
C19	0.9592 (6)	0.5924 (4)	0.3734 (3)	0.0493 (10)
C20	1.1469 (6)	0.7423 (4)	0.2644 (3)	0.0559 (11)
C21	1.1947 (6)	0.8672 (4)	0.2649 (3)	0.0527 (11)
C22	1.2820 (6)	0.9350 (4)	0.1781 (3)	0.0579 (12)
C23	1.3214 (6)	1.0475 (5)	0.1901 (4)	0.0724 (14)
H23	1.379576	1.095328	0.134613	0.087*
C24	1.2765 (7)	1.0902 (4)	0.2820 (4)	0.0715 (14)
H24	1.305139	1.165410	0.289570	0.086*
C25	1.1884 (7)	1.0185 (4)	0.3621 (4)	0.0673 (13)
H25	1.156608	1.047116	0.424353	0.081*
C26	1.3245 (8)	0.8923 (5)	0.0747 (4)	0.0847 (17)
H26A	1.414779	0.826687	0.072271	0.127*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H26B	1.362995	0.957700	0.024447	0.127*
H26C	1.222498	0.865556	0.062098	0.127*

layer chromatography. After the reaction was completed, the reaction mixture was concentrated to remove the THF and then extracted into ethyl acetate. The organic layer was dried over sodium sulfate and was concentrated under vacuum, to get crude solid, which was recrystallized from chloroform-acetonitrile to get diffraction-quality crystals. Yield 72%. **Anal. Calc.** for C₂₆H₂₂N₄O₂S₂: C, 64.18; H, 4.56; N, 11.51; S, 13.18; found: C, 64.37; H 4.32; N 11.48; S, 13.15.

Experimental details

Hydrogen atoms were assigned with common isotropic displacement factors $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C, benzene ring; N, amide})$ and $U_{\text{iso}}(\text{H}) = 1.5$ times $U_{\text{eq}}(\text{C, methyl carbon})$. All the H atoms were refined as riding on their parent atom.

Comment

In nature, disulfide compounds have received much attention in the field of coordination chemistry, pharmaceutical chemistry, biochemistry, and organic synthesis [3–5]. It is particularly noteworthy that the disulfide bonds played an important role in the areas of folding, structure, and stability of the proteins because the S–S bonds are the only readily reversible covalent chemical cross-linking bonds presented in the native proteins [6, 7]. Consequently, the syntheses of new disulfide compounds has become a hot spot. For instance, Sobczak et al. firstly described that the heterodimeric product 1-[(4-chlorophenyl)disulfanyl]-2-nitrobenzene was synthesized by the reaction of bis 4-chlorophenyl disulfide [(4-ClPhS)₂] and bis 2-nitrophenyl disulfide [(2-NO₂PhS)₂] [8]. Singh's group synthesized three hexadentate disulfide ligands and tested their performance for binding with library of metal ions [9]. So far, despite some thrilling work has been achieved, newly designed disulfide compounds are long-sought-after yet still unmet.

The molecular structure of the title disulfide compound is shown in the figure. Single crystal X-ray diffraction analysis reveals that the title structure consists of one diphenyl disulfide unit and two (6'-methylpyridine)-2-carboxamide units, in two halves of the molecule (about S–S bond) the phenyl ring and the substituted pyridine are forming very different dihedral angles ($31.91(2)$; $6.60(2)^\circ$) between the phenyl plane (C14/C15/C16/C17/C18/C19) and the pyridine plane (C21/C22/C23/C24/C25/N4) and the phenyl plane (C1/C2/C3/C4/C5/C6) and the pyridine plane (C8/C9/C10/C11/C12/N2), respectively, suggesting that one-half is relatively more planar than the other. The torsion angle C1–S1–S2–C14 is 90.32° in the molecular structure of the title compound and shows a kink around the S–S bond making the two halves out of plane with each other. The bond distance of S–S is $2.0758(17)$ Å, which is similar with that of the reported *N,N'*-(disulfanediy-bis(4-(morpholin-4-yl)-2,1-phenylene)) bis(1,3-benzothiazol-2-amine) chloroform solvate [10]. Additionally, the title compound adopts weak $\pi \cdots \pi$ interactions between the pyridine ring (C21/C22/C23/C24/C25/N4) and phenyl ring (C1/C2/C3/C4/C5/C6) with a centroid to centroid distance as 3.83 Å, which was similar to that of the reported *N,N'*-(disulfanediyldi-2,1-phenylene)dipyridine-2-carboxamide [11].

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