Crystal structure of bis(2-pyrimidylthio)methane, $C_9H_8N_4S_2$

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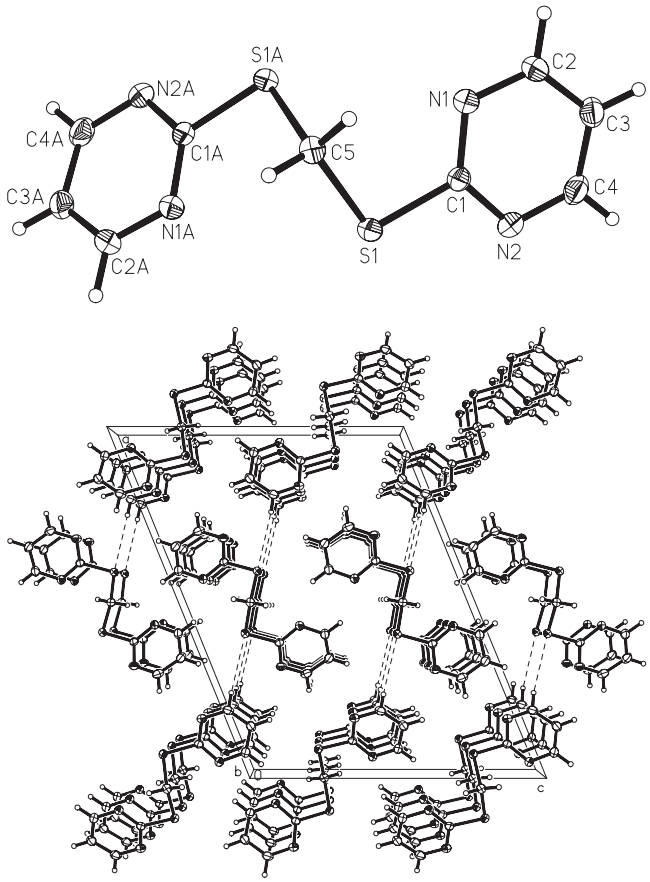

Abstract

$C_9H_8N_4S_2$, monoclinic, $P12/c1$ (No. 13), a = 18.757(4) Å, b = 3.9876(8) Å, c = 14.668(3) Å, β = 112.15(3)°, V = 1016.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.030, $wR_{ref}(F^2)$ = 0.080, T = 100 K.

Source of material

2-Mercaptopyrimidine (224 mg, 2.0 mmol) was added to a solution of NaOH (200 mg, 5 mmol) in 15 mL of absolute ethanol. After stirring for 2 hours, 4 mL of CH_2Cl_2 diluted with 5 mL of absolute ethanol was added drop-wise to the sodium salt so-obtained, and the mixture was stirred at reflux overnight. The resulting suspension was filtered and the filtrate was concentrated, affording colorless needle crystalline product (yield 73%). Analysis: calculated for $C_9H_8N_4S_2$ – C, 45.74%; H, 3.41%; N, 23.71%; found – C, 45.66%; H, 3.40%; N, 23.58%. ^{1}H-NMR, MS and IR data are included in the deposited CIF-file.

Discussion

Many classes of ligands have been designed to synthesize supramolecular networks with rich structural types [1]. Among them, the S,N′-donor ligands are particularly attractive because they can be used as constituents of protein models [2]. Many new S,N′-ligands with a nitrogenated aromatic ring system such as pyridine or benzimidazole have been synthesized to act as spacers for the construction of transition metal coordination polymer, the main interesting point is that the strengths of the M—N and M—S bonds vary inversely to each other as the metal M changes [3]. Recently the coordination chemistry of the bis(2-pyridylthio)-methane as a versatile ligand has been well investigated, showing a variety of different coordination modes based upon the flexibility of the M—N and M—S bonds [4]. With this in mind, we have attempted to extend the rich structural chemistry of the similar versatile S,N′-ligands. In the present paper we report the structure of bis(2-pyrimidylthio)methane.

In structure of the title compound consists of two pymS units bridged by a methylene group. The two pyrimidyl rings are essentially planar; the dihedral angle between them is 29.6(2)°. Both distances, C(CH_2)—S and C(pym)—S are closer to the average value for a single C—S bond (1.82 Å) than to that of double C=S bonds (1.62 Å), although the lengths of *S*-pym bonds C1—S1 and C6—S2 (1.762(2) Å and 1.761(1) Å, respectively) suggest a slightly greater bond order than those of the *S*-methylene bonds C5—S1 and C10—S2 (1.801(1) Å and 1.799(1) Å, respectively). The orientation of the two pym rings places the two N atoms 5.822(3) Å apart. The S···S# distance is 3.077(2) Å. There are weak intermolecular C–H···S hydrogen-bonded contacts (d(C···S) = 3.799(2) Å) which stabilize the crystal packing (bottom figure). The molecules of $(pymS)_2CH_2$ are packed in the crystal with the closest rings of nearest neighbours in the b direction only 4.293(2) Å apart, which is close enough for a very weak π-π interaction

Table 1. Data collection and handling.

Crystal:	colorless needle fragment, size 0.35 × 0.45 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.92 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5801, 2405
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2217
$N(param)_{refined}$:	137
Programs:	SHELXTL-plus [5], SHELXTL-97 [6], SADABS [7]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	4*g*	0.0589	0.2246	0.5751	0.029
H(3A)	4*g*	0.1747	0.5070	0.6549	0.031
H(4A)	4*g*	0.2475	0.6529	0.5623	0.032
H(5A)	4*g*	0.0080	–0.1940	0.3057	0.023
H(7A)	4*g*	0.2495	1.1169	0.8185	0.032
H(8A)	4*g*	0.3256	1.0036	0.9828	0.034
H(9A)	4*g*	0.4424	0.7301	1.0169	0.032
H(10A)	4*g*	0.5085	0.2746	0.7024	0.022

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}
S(1)	4*g*	0.08711(2)	0.18343(8)	0.27315(2)	0.0179(2)	0.0229(2)	0.0171(2)	0.0011(1)	0.0082(1)	0.0012(1)
S(2)	4*g*	0.41285(2)	0.64950(8)	0.68788(2)	0.0165(2)	0.0236(2)	0.0150(2)	0.0000(1)	0.0046(1)	–0.0002(1)
N(1)	4*g*	0.06589(7)	0.1984(3)	0.44353(9)	0.0189(6)	0.0254(6)	0.0185(6)	–0.0008(5)	0.0078(5)	0.0016(5)
N(2)	4*g*	0.17893(7)	0.4565(3)	0.43636(9)	0.0167(5)	0.0303(6)	0.0230(6)	–0.0014(5)	0.0070(5)	0.0002(5)
N(3)	4*g*	0.31843(7)	0.9138(3)	0.76007(9)	0.0156(5)	0.0268(6)	0.0249(6)	–0.0009(5)	0.0062(5)	–0.0012(5)
N(4)	4*g*	0.43476(7)	0.6850(3)	0.87861(9)	0.0195(6)	0.0282(6)	0.0177(6)	–0.0015(5)	0.0070(5)	0.0009(5)
C(1)	4*g*	0.11238(7)	0.2880(3)	0.3982(1)	0.0157(6)	0.0204(6)	0.0176(6)	0.0030(5)	0.0055(5)	0.0025(5)
C(2)	4*g*	0.09003(8)	0.2831(4)	0.5393(1)	0.0236(7)	0.0310(7)	0.0198(7)	0.0021(6)	0.0106(6)	0.0020(6)
C(3)	4*g*	0.15795(8)	0.4511(4)	0.5871(1)	0.0238(7)	0.0323(8)	0.0187(6)	0.0035(6)	0.0047(6)	–0.0018(6)
C(4)	4*g*	0.20061(8)	0.5345(4)	0.5314(1)	0.0178(6)	0.0315(8)	0.0252(7)	–0.0020(6)	0.0029(6)	–0.0023(6)
C(5)	2*e*	0	–0.0512(5)	1/4	0.0204(9)	0.0180(8)	0.0188(9)	0	0.0067(7)	0
C(6)	4*g*	0.38687(8)	0.7582(3)	0.7876(1)	0.0168(6)	0.0201(6)	0.0186(6)	–0.0038(5)	0.0073(5)	–0.0008(5)
C(7)	4*g*	0.29717(8)	1.0039(4)	0.8337(1)	0.0190(7)	0.0289(7)	0.0342(8)	–0.0033(6)	0.0124(6)	–0.0051(6)
C(8)	4*g*	0.34179(9)	0.9393(4)	0.9313(1)	0.0269(7)	0.0349(8)	0.0280(8)	–0.0076(6)	0.0164(6)	–0.0083(6)
C(9)	4*g*	0.41066(9)	0.7779(4)	0.9505(1)	0.0260(7)	0.0356(8)	0.0188(7)	–0.0064(6)	0.0095(6)	–0.0026(6)
C(10)	2*f*	1/2	0.4175(5)	3/4	0.0181(8)	0.0178(8)	0.0192(9)	0	0.0067(7)	0

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