Z. Kristallogr. NCS 221 (2006) 185-186 / DOI 10.1524/ncrs.2006.0032

Crystal structure of 1,3-bis(1-phenyl-1*H*-tetrazol-5-ylthio)propane, $C_3H_6(SCN_4C_6H_5)_2$

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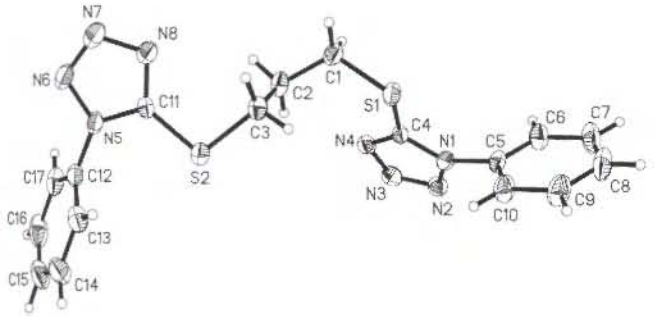
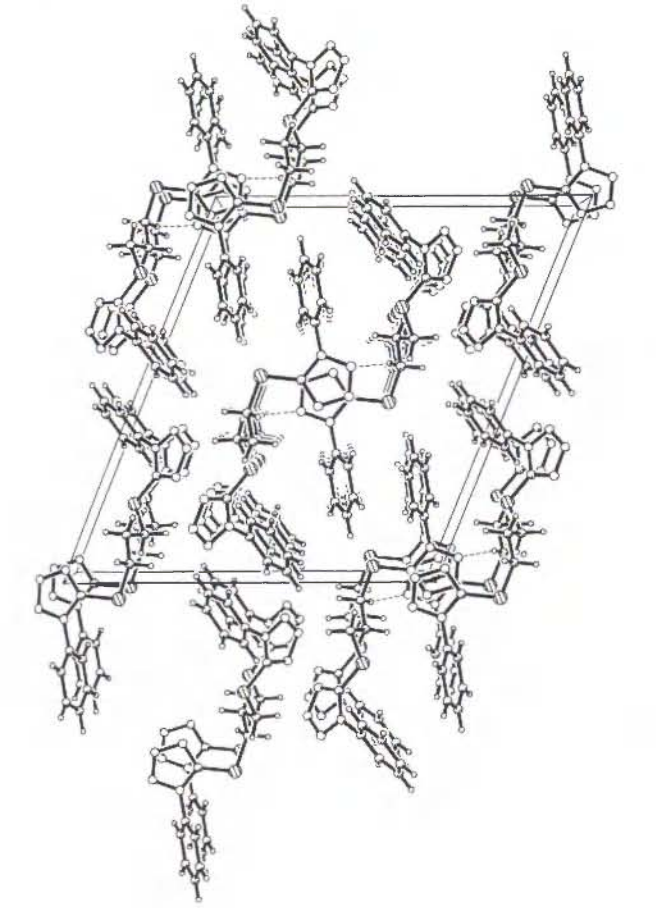
Received April 11, 2006, accepted and available on-line May 16, 2006; CCDC no. 1267/1760





Abstract

$C_{17}H_{16}N_8S_2$, monoclinic, $P12_1/n1$ (no. 14), a = 16.716(5) Å, b = 6.492(2) Å, c = 18.640(6) Å, β = 112.126(5)°, V = 1873.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.128, T = 298 K.

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Source of material

Sodium hydroxide (1.2 g, 0.03 mol) was added slowly to 5-mercapto-1-phenyltetrazole (5 g, 0.03 mol) in 20 ml of dry DMSO. The reaction mixture was stirred at 80 °C for 1 h. Then 1.4 ml (0.015 mol) of 1,3-dichloropropane was added in portions to the solution and resulted in the formation of grey suspension. The suspension was stirred for 4 h, cooled to room temperature and filtered. The solvent was removed under reduced pressure. The residue was recrystallized from ethanol to give a white crystalline product (m.p. 82-83 °C). Single crystals suitable for X-ray diffraction analysis were isolated after two weeks from a solution in ethanol.

Elemental analysis: found – C, 51.32 %; H, 4.48 %; N, 28.19 %; calc. for $C_{17}H_{16}N_8S_2$ – C, 51.50 %; H, 4.07 %; N, 28.26 %.

Discussion

The literature on tetrazoles is expanding rapidly. The functional group plays a role in coordination chemistry as a ligand, in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group [1,2], and in various materials science applications, including explosives [3]. Less appreciated, but of enormous potential, are many useful transformations that make tetrazoles versatile intermediates en route to substituted tetrazoles, and especially, to other 5-ring heterocycles via the Huisgen rearrangement [4].

The crystal structure of the title compound [1,3-bis(1-phenyl-1*H*-tetrazol-5-ylthio)propane], a new ligand, consists of the title molecule (figure, top) and its centrosymmetric equivalent. The benzene ring and tetrazole ring planes form a dihedral angle of 110.6°. The C—N distances are 1.346(4) Å for C4—N1 and 1.326(4) Å for C4—N4, which agree well with the corresponding distances for 1,6-bis(1-phenyl-1*H*-tetrazol-5-ylthio)hexane (1.318(2) Å and 1.349(2) Å [5]) and 1,3-bis(1-methyl-1*H*-tetrazol-5-ylthio)propane (1.329(2) Å and 1.334(2) Å [6]). While the C4—S1 distance (1.729(4) A) agrees with the corresponding distance in 1,6-bis(1-phenyl-1*H*-tetrazol-5-ylthio)hexane (1.732(2) Å [5]), the corresponding distance is shorter with 1.817(2) Å in 1,3-bis(1-methyl-1*H*-tetrazol-5-ylthio)propane [6]. The C4–S1–C1 and C11–S2–C3 bond angles are 101.4(2)° and 100.5(2)°, respectively. The N2–N1–C5–C6 and N6–N5–C12–C17 torsion angles are 67.4(5)° and 53.6(5)°, respectively. In addition, two kinds of aromatic π-π stacking interactions occur between parallel phenyl rings and tetrazolyl rings, respectively (figure, bottom). There exists a strengthening part of the π-π stacking interactions by inter hydrogen bonds. So, the distances between the tetrazolyl rings centroids are 3.325 Å and 3.333 Å. Also, parallel phenyl rings are stacked with their centroids separated by 3.782 Å. The molecules are assembled into a two-dimensional sheet structure by the hydrogen bonds and aromatic stacking interactions mentioned above.

Table 1. Data collection and handling.

Crystal:	colorless platelet, size 0.12 × 0.49 × 0.55 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.04 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9385, 3294
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1615
$N(param)_{refined}$:	244
Programs:	SHELXS-97 [7], SHELXL-97 [8]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.2317	0.6248	0.9463	0.059
H(1B)	4e	0.1419	0.5277	0.9338	0.059
H(2A)	4e	0.1318	0.7172	0.8261	0.062
H(2B)	4e	0.0718	0.8142	0.8644	0.062
H(3A)	4e	0.2304	0.9751	0.8714	0.056
H(3B)	4e	0.1841	1.0602	0.9245	0.056
H(6)	4e	0.0685	0.4978	1.1898	0.074
H(7)	4e	0.1464	0.5239	1.3223	0.095
H(8)	4e	0.2196	0.8211	1.3731	0.095
H(9)	4e	0.2137	1.0962	1.2946	0.091
H(10)	4e	0.1364	1.0735	1.1616	0.073
H(13)	4e	0.1065	1.5385	0.6986	0.071
H(14)	4e	0.0012	1.7879	0.6516	0.090
H(15)	4e	−0.1214	1.7188	0.5443	0.102
H(16)	4e	−0.1426	1.4019	0.4873	0.099
H(17)	4e	−0.0394	1.1448	0.5367	0.075

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}
N(1)	4e	0.0458(2)	0.7693(5)	1.0831(2)	0.038(2)	0.040(2)	0.038(2)	−0.002(2)	0.016(2)	−0.001(2)
N(2)	4e	−0.0412(2)	0.7573(5)	1.0558(2)	0.046(2)	0.048(2)	0.046(2)	0.000(2)	0.018(2)	0.003(2)
N(3)	4e	−0.0666(2)	0.7356(5)	0.9817(2)	0.044(2)	0.047(2)	0.053(2)	0.001(2)	0.014(2)	0.003(2)
N(4)	4e	0.0020(2)	0.7348(5)	0.9586(2)	0.044(2)	0.042(2)	0.037(2)	0.002(2)	0.011(2)	0.001(2)
N(5)	4e	0.1068(2)	1.1641(5)	0.6526(2)	0.050(2)	0.062(3)	0.034(2)	0.004(2)	0.023(2)	0.009(2)
N(6)	4e	0.1408(2)	1.0614(6)	0.6069(2)	0.069(3)	0.088(3)	0.045(2)	0.012(2)	0.034(2)	0.005(2)
N(7)	4e	0.1950(2)	0.9305(7)	0.6514(2)	0.077(3)	0.094(4)	0.057(3)	0.015(2)	0.042(2)	0.005(2)
N(8)	4e	0.1975(2)	0.9394(6)	0.7256(2)	0.054(2)	0.070(3)	0.048(2)	0.010(2)	0.027(2)	0.006(2)
S(1)	4e	0.17870(6)	0.7650(2)	1.03344(5)	0.0451(6)	0.0690(9)	0.0332(6)	0.0024(6)	0.0163(5)	0.0042(6)
S(2)	4e	0.11121(7)	1.1674(2)	0.79837(6)	0.0650(7)	0.0644(9)	0.0377(6)	0.0132(6)	0.0234(6)	0.0082(6)
C(1)	4e	0.1734(2)	0.6566(6)	0.9420(2)	0.062(3)	0.050(3)	0.048(3)	−0.001(2)	0.032(2)	0.001(2)
C(2)	4e	0.1316(2)	0.7910(6)	0.8713(2)	0.061(3)	0.062(3)	0.032(2)	−0.009(2)	0.018(2)	−0.003(2)
C(3)	4e	0.1745(2)	0.9962(6)	0.8749(2)	0.048(2)	0.055(3)	0.036(2)	−0.002(2)	0.013(2)	0.001(2)
C(4)	4e	0.0715(2)	0.7546(6)	1.0230(2)	0.051(2)	0.034(3)	0.031(2)	0.002(2)	0.016(2)	0.003(2)
C(5)	4e	0.0958(2)	0.7835(7)	1.1650(2)	0.042(2)	0.057(3)	0.031(2)	−0.003(2)	0.019(2)	0.000(2)
C(6)	4e	0.0978(3)	0.6185(7)	1.2110(2)	0.073(3)	0.068(4)	0.047(3)	−0.007(3)	0.026(3)	0.010(3)
C(7)	4e	0.1445(3)	0.6343(9)	1.2899(3)	0.085(4)	0.109(5)	0.047(3)	0.002(3)	0.028(3)	0.027(3)
C(8)	4e	0.1878(3)	0.812(1)	1.3202(3)	0.072(3)	0.127(5)	0.033(3)	−0.005(4)	0.012(3)	0.000(3)
C(9)	4e	0.1846(3)	0.9753(8)	1.2732(3)	0.088(4)	0.084(4)	0.047(3)	−0.019(3)	0.017(3)	−0.018(3)
C(10)	4e	0.1383(3)	0.9630(7)	1.1939(2)	0.073(3)	0.062(4)	0.041(3)	−0.017(3)	0.013(2)	−0.007(3)
C(11)	4e	0.1416(2)	1.0858(6)	0.7241(2)	0.048(3)	0.043(3)	0.035(2)	−0.001(2)	0.018(2)	0.010(2)
C(12)	4e	0.0428(3)	1.3204(8)	0.6224(2)	0.047(3)	0.058(3)	0.036(2)	0.003(2)	0.019(2)	0.011(2)
C(13)	4e	0.0559(3)	1.5104(8)	0.6565(2)	0.058(3)	0.066(4)	0.051(3)	0.001(3)	0.018(2)	0.015(3)
C(14)	4e	−0.0062(3)	1.6592(8)	0.6280(3)	0.081(4)	0.070(4)	0.075(4)	0.016(3)	0.030(3)	0.027(3)
C(15)	4e	−0.0799(3)	1.617(1)	0.5642(3)	0.068(4)	0.109(5)	0.085(5)	0.034(4)	0.037(4)	0.057(4)
C(16)	4e	−0.0925(3)	1.428(1)	0.5302(3)	0.056(3)	0.133(6)	0.050(3)	0.006(4)	0.010(3)	0.032(4)
C(17)	4e	−0.0311(3)	1.2749(8)	0.5592(2)	0.060(3)	0.087(4)	0.040(3)	−0.008(3)	0.019(2)	0.005(3)

Acknowledgment. We would like to thank the Shaanxi Normal University for research grants.

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