

## 5,5'-Dimethyl-2,2'-dithiodi-1,3,4-thiadiazole

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

$R$  factor = 0.035

$wR$  factor = 0.097

Data-to-parameter ratio = 14.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_6\text{H}_6\text{N}_4\text{S}_4$ , is formed through the thionato S—S bonding of parent 2-mercapto-5-methyl-1,3,4-thiadiazole molecules, following the deprotonation of thiol groups in a mixed solvent. The title compound crystallizes in the monoclinic system, space group  $C2/c$ . The S—S distance is  $2.028(1)\text{ \AA}$ , typical of a single bond. The two 1,3,4-thiadiazole rings in the molecule each remain planar, with a dihedral angle of  $70.5(1)\text{ \AA}$ , and are related by a twofold rotation axis through the middle of the S2—S2 bond. The geometric parameters for the parent ligand are also reported, to demonstrate the influence of deprotonation on the ligand dimensions.

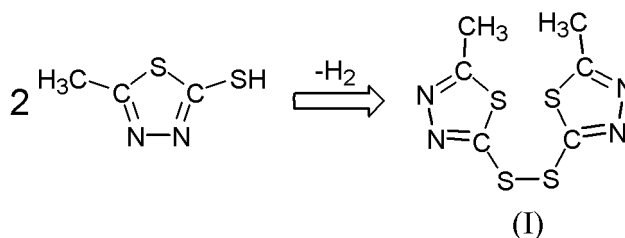
Received 5 June 2002

Accepted 6 August 2002

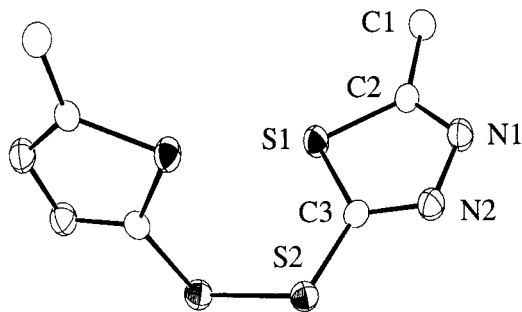
Online 6 September 2002

## Comment

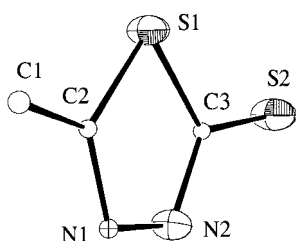
Triazole and its derivative ligands are versatile chelating ligands that can bridge a wide range of metal atoms forming dimers, oligomers, and polymeric chains through multidendate donor atoms (Steel, 1990; Inoue & Kubo, 1976; Maekawa *et al.*, 1999). The combined effects of deprotonation and coordination are found to cause significant changes to the bond lengths and angles in these ligands (Chen *et al.*, 1993; Tandon *et al.*, 1994). In a recent effort to investigate the dependence of optical properties of coinage metal complexes on the molecular structures and metal–metal interactions (Ford *et al.*, 1999; Zhou *et al.*, 2002), the title molecule, (I), was isolated as a dimerized derivative of the parent 1,3,4-triazole, through S—S bonding (see *Scheme* below). In this paper, we report the synthesis and crystal structure of (I).



As shown in Fig. 1, the dimerized structure is formed through the S—S linkage of parent 2-mercapto-5-methyl-1,3,4-thiadiazole moieties, following the deprotonation of thiol groups. The observed S2—S2' distance in the present disulfide structure is  $2.028(1)\text{ \AA}$ , very close to the sum of the atomic radius ( $1.035\text{ \AA}$ ) or single-bond covalent radius ( $1.04\text{ \AA}$ ) of the element. The S—S single-bond character is further confirmed by the associated S2—C3 distance of  $1.764(2)\text{ \AA}$ , which is only slightly smaller than the sum of single-bond radii ( $1.81\text{ \AA}$ ). The S1···S1' non-bonding distance is  $3.666(?)\text{ \AA}$ . The torsion angle of C3—S2—S2'—C3' is  $-84.45(16)^\circ$ . The 2-mercapto-5-



**Figure 1**  
A view of the molecule of (I), shown with 50% probability displacement ellipsoids.



**Figure 2**  
A view of the molecule of (II), shown with 50% probability displacement ellipsoids.

methyl-1,3,4-thiadiazole ring in the molecule remains planar, with an r.m.s deviation of 0.042 Å. The two ring planes make a dihedral angle of 70.5 (1) Å, related by a crystallographic twofold rotation symmetry through the middle of the S—S bond.

Table 1 lists important bond distances and angles for (I), as well as for the parent 2-mercapto-5-methyl-1,3,4-thiadiazole ligand, which has also been determined [ $C_3H_4N_2S_2$ , (II), space group *Pbca*,  $a = 10.5107$  (6),  $b = 20.398$  (1),  $c = 9.1157$  (5) Å,  $V = 1121.6$  (1) Å<sup>3</sup>,  $R1/wR = 0.0383/0.1307$ ,  $S = 1.152$  (Song *et al.*, 2002)]. To facilitate comparison between dimerized (I) and parent (II), a view of the latter is also shown in Fig. 2. The bond distances in the structure are subjected to small variations upon deprotonation and dimerization. Such an effect was previously observed when the ligand is deprotonated and then coordinated to metal atoms (Chen *et al.*, 1993; Tandon *et al.*, 1994). The N—N distance is slightly lengthened, 1.382 (3) Å in (II), compared to 1.389 (3) Å in (I), an insignificant difference, within  $3\sigma$ , but both are comparable to the single-bond distance of 1.40 Å. Accordingly, the C—N bond distances are slightly shortened from 1.331 (3) Å in (II) to 1.286 (3) Å in (I), sufficiently short to suggest partial double-bond character (Senda *et al.*, 1986; Mathew & Palenik, 1974). The cyclic C—S bond distances are also shortened from 1.742 (2) Å in (II) to 1.712 (2) Å in (I); both are slightly shorter than the value of 1.77 Å for a  $Csp^2$ —S single bond (Mathew & Palenik, 1974). In contrast, the exocyclic C—S bond distances are significantly lengthened from 1.665 (2) Å in (II) with thiols, to 1.764 (2) Å in (I) with disulfur units. The structural effect of deprotonation is evident.

## Experimental

CuBr (0.5 mmol) and  $C_3H_4N_2S_2$  (0.5 mmol) were stirred in a mixed solvent of alcohol (5 ml), acetonitrile (10 ml), and tetrahydropyran (5 ml) at room temperature. Yellow crystals of the title compound were obtained after a few days.

### Crystal data

$C_6H_6N_4S_4$   
 $M_r = 262.39$   
Monoclinic,  $C2/c$   
 $a = 8.5647$  (6) Å  
 $b = 6.9212$  (6) Å  
 $c = 18.2692$  (15) Å  
 $\beta = 98.074$  (1)°  
 $V = 1072.23$  (15) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.625$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 1505 reflections  
 $\theta = 3.8$ – $25.0$ °  
 $\mu = 0.85$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Cube, yellow  
 $0.40 \times 0.40 \times 0.24$  mm

### Data collection

Siemens SMART CCD diffractometer  
 $\omega$  scans  
Absorption correction: empirical  
 $T_{\min} = 0.805$ ,  $T_{\max} = 0.905$   
1847 measured reflections  
948 independent reflections

807 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$   
 $\theta_{\max} = 25.0$ °  
 $h = -10 \rightarrow 7$   
 $k = -8 \rightarrow 4$   
 $l = -21 \rightarrow 18$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.097$   
 $S = 1.04$   
948 reflections  
64 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.4258P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.32$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.28$  e Å<sup>-3</sup>

**Table 1**

Comparison of geometric parameters (Å, °) in (I) and (II).

	(I)	(II)
S1—C2	1.730 (2)	1.742 (2)
S1—C3	1.712 (2)	1.738 (2)
S2—C3	1.764 (2)	1.665 (2)
N1—N2	1.389 (3)	1.382 (3)
N1—C2	1.286 (3)	1.295 (3)
N2—C3	1.287 (3)	1.331 (3)
C1—C2	1.495 (3)	1.479 (3)
C3—S1—C2	86.73 (11)	90.35 (12)
C2—N1—N2	112.9 (2)	109.77 (19)
C3—N2—N1	111.64 (19)	119.09 (18)
N1—C2—C1	123.4 (2)	122.6 (2)
N1—C2—S1	113.74 (18)	113.70 (18)
C1—C2—S1	122.86 (17)	123.62 (19)
N2—C3—S2	118.15 (17)	125.91 (18)
S2—C3—S1	126.53 (14)	127.02 (16)
N2—C3—S1	115.04 (17)	107.07 (17)

The H atoms were placed at geometrically calculated positions, with H-atom parameters constrained.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*.

This work was supported by Innovative Project (No. IP01007) and the Hundred-Talent Program (No. 990168) of the Chinese Academy of Sciences, China.

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