

## 2,2'-Spirobi(1,3-benzodithiole)

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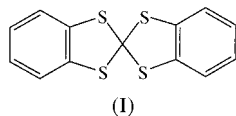
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The X-ray structure analysis of 2,2'-spirobi(1,3-benzodithiole),  $C_{13}H_8S_4$ , has been performed. The molecule has crystallographic twofold rotation symmetry, the axis passing through the spiro-C atom. The four S atoms are arranged around the spiro-C atom in two almost orthogonal  $CS_2$  planes. However, because of large bending of the two five-membered rings, close contact is present between two connected C atoms on the benzo group of each 1,3-benzodithiole ring and one S atom on the other 1,3-benzodithiole ring.

### Comment

In the title compound, (I), the  $S1-C1$ ,  $S1-C2$ ,  $S2-C1$ ,  $S2-C7$ ,  $S1^i-C1$ ,  $S1^i-C2^i$ ,  $S2^i-C1$  and  $S2^i-C7^i$  bond distances [symmetry code: (i)  $y, x, 1-z$ ] are in the range 1.77–1.84 Å, which are near to the values reported so far (1.80–1.81 Å; Sutton, 1958, 1965). The  $C1-S1-C2$ ,  $C1-S2-C7$ ,  $C1-S1^i-C2^i$  and  $C1-S2^i-C7^i$  bond angles are in the range 94–96° and slightly smaller than the normal values (97–99°; Sutton, 1958, 1965). The  $S1-C1-S2$  and  $S1^i-C1-S2^i$  planes make a dihedral angle of 93.8 (1)°. The five-membered  $C1-S1-C2-C7-C2$  and  $C1-S1^i-C2^i-C7^i-C2^i$  rings have an envelope-like conformation, as seen from the dihedral angles between



the  $C1/S1/S2$  and  $S1/S2/C7/C2$  planes [35.0 (1)°], resulting in a dihedral angle of 79.2 (1)° between the two benzene rings. As the result of large bending of the two five-membered rings,  $C2$  and  $C2^i$  or  $C7$  and  $C7^i$  atom on the benzo group of one 1,3-benzodithiole ring and the  $S2$  or  $S2^i$  atom on the other 1,3-benzodithiole ring become closer to each other. In particular, the closest contact can be seen between  $S2$  and  $C2^i$  atoms

[3.58 (1) Å]. The contact distance is near to the sum of van der Waals' radii of C (1.75 Å) and S atoms (1.85 Å; Pauling, 1960).

The  $^1H$  NMR spectrum of (I) in  $DMF-d_7$  showed each of two kinds of signals due to the *ortho*-protons ( $H3/H3^i$  and  $H6/H6^i$ ) at  $\delta$  7.26 (2H, *dd*,  $J = 2.57, 3.33$  Hz) and 7.46 (2H, *dd*,  $J = 2.57, 3.33$  Hz), and to the *meta*-protons ( $H4/H4^i$  and  $H5/H5^i$ ) at  $\delta$  7.27 (2H, *t*,  $J = 3.33$  Hz) and 7.44 (2H, *t*,  $J = 3.33$  Hz) on the benzo groups. The different chemical shifts between  $H3/H3^i$  and  $H6/H6^i$  protons and between  $H4/H4^i$  and  $H5/H5^i$  protons are caused by the magnetic anisotropy due to the sulfur lone pairs in close proximity to  $H3/H3^i$  and  $H4/H4^i$  protons, as seen from the crystal structure. On the other hand, only three kinds of signals (138.22, 129.01 and 124.64 p.p.m.) due to the benzo C atoms were observed together with the spiro-carbon signal (90.01 p.p.m.) in the  $^{13}C$  NMR spectrum. This result clearly suggests that also in solution the five-membered rings maintain an envelope-like conformation without rapid flipping on the NMR time-scale (Horn *et al.*, 1993; Setaka *et al.*, 1999).

### Experimental

The title compound was first obtained as a by-product (<5% yield) in the thermal decomposition of 2-(*n*-amyloxybenzo)-1,3-dithiole (Nakayama, 1975). In order to improve the yield, the following method was now used. 2-Methylthio-1,3-benzodithiolium tetrafluoroborate was reacted with an equimolar amount of benzene-1,2-dithiol in the presence of a catalytic amount of *p*-toluenesulfonic acid in 1,2-dichloroethane at 356 K for 3 h. The crude product was purified by silica-gel column chromatography with an eluent of *n*-hexane/*n*-benzene ( $v/v = 3:1$ ), followed by recrystallization from benzene/*n*-hexane to give colourless crystals of (I) (m.p. 393 K) in 23% yield.

#### Crystal data

$C_{13}H_8S_4$   
 $M_r = 292.45$   
Tetragonal,  $P4_12_12$   
 $a = 6.287$  (6) Å  
 $c = 31.93$  (1) Å  
 $V = 1261.9$  (8) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.539$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 10.4$ – $11.9^\circ$   
 $\mu = 0.723$  mm<sup>-1</sup>  
 $T = 293.2$  K  
Prismatic, colorless  
 $0.20 \times 0.20 \times 0.10$  mm

#### Data collection

Rigaku AFC-7R diffractometer  
 $\omega$ - $2\theta$  scans  
934 measured reflections  
934 independent reflections  
755 reflections with  $F^2 > 2\sigma(F^2)$   
 $\theta_{\max} = 27.33^\circ$

$h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 5$   
 $l = 0 \rightarrow 41$   
3 standard reflections  
every 150 reflections  
intensity decay: 0.70%

#### Refinement

Refinement on  $F$   
 $R = 0.0347$   
 $wR = 0.0453$   
 $S = 1.325$   
803 reflections [ $I > 0.7\sigma(I)$ ]  
77 parameters

H-atom parameters not refined  
 $w = 1/[\sigma^2(F_o) + 0.00040|F_o|^2]$   
 $(\Delta/\sigma)_{\max} = 0.039$   
 $\Delta\rho_{\max} = 0.17$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.17$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

S1—C1	1.821 (3)	C2—C7	1.407 (5)
S1—C2	1.77 (1)	C3—C4	1.404 (9)
S2—C1	1.843 (3)	C4—C5	1.388 (6)
S2—C7	1.768 (10)	C5—C6	1.380 (8)
C2—C3	1.391 (8)	C6—C7	1.391 (8)
C1—S1—C2	94.7 (2)	S1—C2—C7	116.5 (3)
C1—S2—C7	95.2 (2)	C3—C2—C7	120.1 (4)
S1—C1—S1 <sup>i</sup>	112.5 (3)	C2—C3—C4	118.7 (5)
S1—C1—S2	107.24 (8)	C3—C4—C5	120.5 (4)
S1—C1—S2 <sup>i</sup>	108.0 (2)	C4—C5—C6	121.2 (4)
S1—C1 <sup>i</sup> —S2	107.2 (4)	C5—C6—C7	119.0 (5)
S1—C1 <sup>i</sup> —S2 <sup>i</sup>	108.0 (1)	S2—C7—C2	115.2 (3)
S2—C1—S2 <sup>i</sup>	114.0 (4)	S2—C7—C6	124.2 (4)
S1—C2—C3	123.3 (4)	C2—C7—C6	120.6 (4)
S1—C1—S1 <sup>i</sup> —C2 <sup>i</sup>	150.1 (1)	C1—S1 <sup>i</sup> —C2 <sup>i</sup> —C3 <sup>i</sup>	159.9 (4)
S1—C1—S2—C7	-31.0 (2)	C1—S1 <sup>i</sup> —C2 <sup>i</sup> —C7 <sup>i</sup>	-21.3 (3)
S1—C1—S2 <sup>i</sup> —C7 <sup>i</sup>	-152.5 (2)	C1—S2—C7—C2	18.7 (3)
S1—C2—C3—C4	176.7 (3)	C1—S2—C7—C6	-162.9 (3)
S1—C2—C7—S2	1.7 (4)	C1—S2 <sup>i</sup> —C7 <sup>i</sup> —C2 <sup>i</sup>	18.7 (3)
S1—C2—C7—C6	-176.8 (3)	C1—S2 <sup>i</sup> —C7 <sup>i</sup> —C6 <sup>i</sup>	-162.9 (3)
S2—C1—S1—C2	31.5 (2)	C2—C3—C4—C5	0.1 (6)
S2—C1—S1 <sup>i</sup> —C2 <sup>i</sup>	-91.8 (2)	C2—C7—C6—C5	0.0 (6)
S2—C1—S2 <sup>i</sup> —C7 <sup>i</sup>	88.4 (4)	C3—C2—C7—C6	2.0 (5)
S2—C7—C2—C3	-179.5 (3)	C3—C4—C5—C6	2.0 (6)
S2—C7—C6—C5	-178.3 (3)	C4—C3—C2—C7	-2.0 (6)
C1—S1—C2—C3	159.9 (3)	C4—C5—C6—C7	-2.0 (6)
C1—S1—C2—C7	-21.3 (3)		

Symmetry code: (i)  $y, x, 1 - z$ .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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