

## 4,7-Diiodo-2,1,3-benzothiadiazole and 7,7'-diiodo-4,4'-bi(2,1,3-benzo- thiadiazole)

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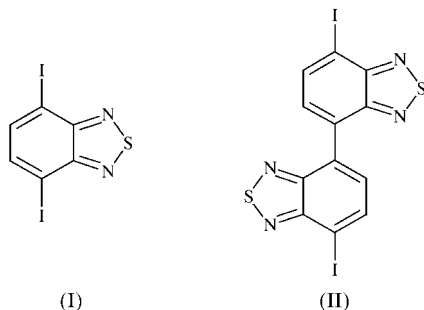
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In the crystal structures of the title compounds, C<sub>6</sub>H<sub>2</sub>I<sub>2</sub>N<sub>2</sub>S, (I), and C<sub>12</sub>H<sub>4</sub>I<sub>2</sub>N<sub>4</sub>S<sub>2</sub>, (II), respectively, a large number of short inter-heteroatom contacts, such as S···N, I···I and N···I, are observed. In (II), which is non-centrosymmetric, two halves of the molecule are related by a crystallographic twofold axis.

### Comment

Compounds containing a 2,1,3-benzothiadiazole ring have received much attention, due to their potential use as fungicides, herbicides, fluorescent materials (Mataka *et al.*, 1982) and organic conductors (Yamashita *et al.*, 1996). We have recently synthesized 4,7-diiodo-2,1,3-benzothiadiazole, (I), and 7,7'-diiodo-4,4'-bi(2,1,3-benzothiadiazole), (II), as important synthetic intermediates for functional materials



with 2,1,3-benzothiadiazole rings. From the viewpoint of crystal engineering, the peripheral S, N and I atoms of (I) and (II) are expected to form short inter-heteroatom contacts, which can result in unique molecular networks (Yamashita & Tomura, 1998). However, only two examples (Mikhno *et al.*, 1973; Ono *et al.*, 1994) of structures containing a 4-halogeno-2,1,3-benzothiadiazole unit were found in the Cambridge

Structural Database (CSD, Version 5.22; Allen & Kennard, 1993). Therefore, we have carried out X-ray analyses of (I) and (II), and report here their molecular and crystal structures.

The non-centrosymmetric space group of (II) is interesting from the standpoint of non-linear optical properties. The molecular structures of (I) and (II) are shown in Figs. 1 and 2, and selected geometric parameters are given in Tables 1 and 3, respectively.

The planar 2,1,3-benzothiadiazole rings of (I) and (II) have almost similar geometries. The geometric parameters of the 1,2,5-thiadiazole rings in (I) and (II) are almost the same as those in 3,4-diphenyl-1,2,5-thiadiazole (Mellini & Merlino, 1976). Considerable shortening of the C1–C6 and C4–C5 bonds in (I) and (II) is observed, and such double-bond fixation suggests quinonoid character for the 2,1,3-benzothiadiazole ring in the two compounds. The angle between the planes of the two 2,1,3-benzothiadiazole rings of (II) is 48.4 (1)°.

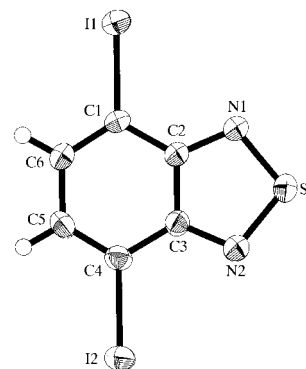


Figure 1

A view of the molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

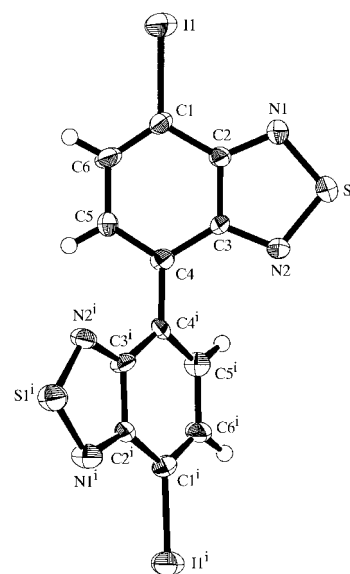
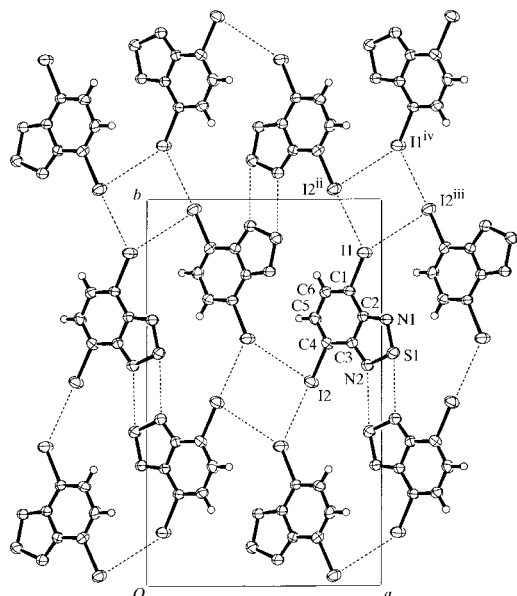


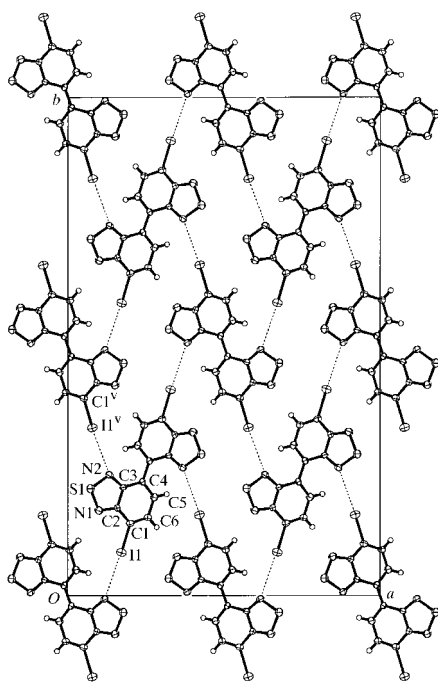
Figure 2

A view of the molecular structure of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, z$ ].

Fig. 3 shows the packing diagram for (I) viewed along the  $c$  axis. The molecules stack along the  $c$  axis. Short S $\cdots$ N inter-heteroatom contacts (Table 2) are found between the two 1,2,5-thiadiazole rings. The S $\cdots$ N distance is 7.7% shorter than the sum of the corresponding van der Waals radii (Pauling, 1960). Short I $\cdots$ I contacts within the sum of the van der Waals radii are also observed, as shown in Table 2. Four I atoms [I1, I2<sup>ii</sup>, I2<sup>iii</sup> and I1<sup>iv</sup> in Fig. 3; symmetry codes: (ii)  $\frac{3}{2} - x$ ,



**Figure 3**  
Packing diagram for (I) viewed along the  $c$  axis. Dotted lines show the short S $\cdots$ N and I $\cdots$ I contacts [symmetry codes: (ii)  $\frac{3}{2} - x, y + \frac{1}{2}, 1 - z$ ; (iii)  $x + \frac{1}{2}, \frac{3}{2} - y, z + 1$ ; (iv)  $2 - x, 2 - y, 2 - z$ ].



**Figure 4**  
Packing diagram for (II) viewed along the  $c$  axis. Dotted lines show the short N $\cdots$ I contacts [3.333 (8) Å for N2 $\cdots$ I1<sup>v</sup> and 174.2 (4) $^\circ$  for N2 $\cdots$ I1<sup>v</sup>-C1<sup>v</sup>; symmetry code: (v)  $\frac{1}{4} - x, y + \frac{1}{4}, z + \frac{1}{4}$ ].

$y + \frac{1}{2}, 1 - z$ ; (iii)  $x + \frac{1}{2}, \frac{3}{2} - y, z + 1$ ; (iv)  $2 - x, 2 - y, 2 - z$ ] form a planar I<sub>4</sub> square cluster with short I $\cdots$ I contacts.

Fig. 4 shows the packing diagram for (II) viewed along the  $c$  axis. The molecules form mono-stacks along the  $c$  axis, and the interstack distance and intermolecular I $\cdots$ I distance within the stack are 3.596 (5) and 3.942 (3) Å, respectively. In contrast with (I), short N $\cdots$ I contacts are observed [3.333 (8) Å] and are nearly linear [174.2 (4) $^\circ$ ], as shown in Fig. 4. Although slightly longer than the typical N $\cdots$ I distance, these N $\cdots$ I contacts may control the crystal packing of (II) (Desiraju & Harlow, 1989; Xu *et al.*, 1994; Walsh *et al.*, 2001).

Studies on the construction of new molecular architectures using compounds (I) and (II) are now in progress.

## Experimental

The title compounds were synthesized according to the literature method of Suzuki (1994) for (I) and the method of Fukushima *et al.* (1999) for (II). Pale-yellow crystals of (I) and (II) suitable for X-ray analysis were grown from an ethyl acetate and a dichloromethane solution, respectively.

### Compound (I)

#### Crystal data

C<sub>6</sub>H<sub>2</sub>I<sub>2</sub>N<sub>2</sub>S  
*M<sub>r</sub>* = 387.96  
 Monoclinic,  $P2_1/a$   
*a* = 11.0515 (17) Å  
*b* = 18.2104 (12) Å  
*c* = 4.3441 (11) Å  
 $\beta$  = 90.47 (2) $^\circ$   
*V* = 874.2 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.948 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 14.7–15.0 $^\circ$   
 $\mu$  = 7.37 mm<sup>-1</sup>  
*T* = 296 (2) K  
 Plate, pale yellow  
 0.5 × 0.3 × 0.1 mm

#### Data collection

Rigaku AFC-7R diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.109, *T<sub>max</sub>* = 0.479  
 2110 measured reflections  
 2014 independent reflections  
 1763 reflections with  $I > 2\sigma(I)$

*R<sub>int</sub>* = 0.018  
 $\theta_{\text{max}}$  = 27.5 $^\circ$   
 $h = 0 \rightarrow 14$   
 $k = 0 \rightarrow 23$   
 $l = -5 \rightarrow 5$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 0.2%

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.055$   
*S* = 0.96  
 2014 reflections  
 101 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0270P)^2 + 2.4993P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 (Sheldrick, 1997)  
 Extinction coefficient: 0.00185 (18)

### Compound (II)

#### Crystal data

C<sub>12</sub>H<sub>4</sub>I<sub>2</sub>N<sub>4</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 522.11  
 Orthorhombic,  $Fdd2$   
*a* = 20.892 (14) Å  
*b* = 33.376 (21) Å  
*c* = 3.9422 (25) Å  
*V* = 2749 (3) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 2.523 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation  
 Cell parameters from 3274 reflections  
 $\theta = 3.1\text{--}27.5^\circ$   
 $\mu = 4.87 \text{ mm}^{-1}$   
*T* = 296 (2) K  
 Needle, pale yellow  
 0.60 × 0.04 × 0.04 mm

**Table 1**  
Selected geometric parameters (Å, °) for (I).

I1—C1	2.068 (3)	C1—C6	1.363 (5)
I2—C4	2.080 (4)	C1—C2	1.415 (5)
S1—N1	1.616 (3)	C2—C3	1.439 (5)
S1—N2	1.615 (3)	C3—C4	1.427 (5)
N1—C2	1.347 (4)	C4—C5	1.355 (5)
N2—C3	1.342 (4)	C5—C6	1.421 (5)
N1—S1—N2	101.00 (16)	N2—C3—C4	126.6 (3)
C2—N1—S1	106.5 (2)	N2—C3—C2	113.3 (3)
C3—N2—S1	106.4 (2)	C4—C3—C2	120.1 (3)
C6—C1—C2	118.7 (3)	C5—C4—C3	118.4 (3)
N1—C2—C1	127.8 (3)	C4—C5—C6	121.5 (3)
N1—C2—C3	112.8 (3)	C1—C6—C5	121.9 (3)
C1—C2—C3	119.4 (3)		

**Table 2**  
Inter-heteroatom contacts (Å) for (I).

S1...N2 <sup>i</sup>	3.093 (3)	I1...I2 <sup>iii</sup>	4.138 (1)
N2...S1 <sup>i</sup>	3.093 (3)	I1...I2 <sup>iv</sup>	4.196 (1)
I1...I2 <sup>ii</sup>	3.789 (1)		

Symmetry codes: (i)  $2 - x, 1 - y, 2 - z$ ; (ii)  $\frac{3}{2} - x, \frac{1}{2} + y, 1 - z$ ; (iii)  $\frac{1}{2} + x, \frac{3}{2} - y, 1 + z$ ; (iv)  $\frac{3}{2} - x, \frac{1}{2} + y, 2 - z$ .

**Data collection**

Rigaku Mercury CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (REQAB; Jacobson, 1998)  
 $T_{\min} = 0.132, T_{\max} = 0.829$   
 6500 measured reflections

1438 independent reflections  
 1394 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -26 \rightarrow 22$   
 $k = -36 \rightarrow 42$   
 $l = -5 \rightarrow 4$

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.152$   
 $S = 1.21$   
 1438 reflections  
 92 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 102.9652P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.98 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.07 \text{ e } \text{Å}^{-3}$   
 Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient: 0.0012 (2)  
 Absolute structure: Flack (1983);  
 563 Friedel pairs  
 Flack parameter =  $-0.01 (8)$

**Table 3**  
Selected geometric parameters (Å, °) for (II).

I1—C1	2.065 (9)	C1—C2	1.446 (14)
S1—N1	1.599 (9)	C2—C3	1.445 (13)
S1—N2	1.616 (9)	C3—C4	1.423 (13)
N1—C2	1.331 (13)	C4—C5	1.376 (14)
N2—C3	1.337 (13)	C4—C4 <sup>i</sup>	1.462 (18)
C1—C6	1.332 (16)	C5—C6	1.417 (15)
N1—S1—N2	100.3 (4)	N2—C3—C2	111.9 (9)
C2—N1—S1	107.3 (7)	N2—C3—C4	127.1 (9)
C3—N2—S1	107.2 (7)	C2—C3—C4	121.0 (9)
C6—C1—C2	117.1 (9)	C5—C4—C3	116.4 (9)
N1—C2—C3	113.2 (9)	C5—C4—C4 <sup>i</sup>	121.5 (10)
N1—C2—C1	127.3 (9)	C3—C4—C4 <sup>i</sup>	122.1 (10)
C3—C2—C1	119.5 (9)	C4—C5—C6	122.2 (10)

Symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, z$ .

All H atoms in compounds (I) and (II) were placed in geometrically calculated positions, with C—H = 0.93 Å, and refined using a riding model.

For compound (I), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). For compound (II), data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku Corporation, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1368). Services for accessing these data are described at the back of the journal.

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