Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

4,5-Diiodo[1,2,5]thiadiazolotetrathiafulvalene

Masaaki Tomura[a]* and Yoshiro Yamashita[b]

[a]Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and [b]Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Correspondence e-mail: tomura@ims.ac.jp

In the crystal structure of the title compound, 5-(4,5-diiodo-1,3-dithiol-2-ylidene)-1,3-diaza-2,4,6-trithiapentalene, $C_6I_2N_2S_5$, a large number of short intermolecular heteroatom contacts, such as S···N, S···S, S···I, N···I and I···I, are observed. The molecules, which are planar within 0.051 Å, stack along the *b* axis in a head-to-head fashion.

Received 21 October 2003
Accepted 1 December 2003
Online 12 December 2003

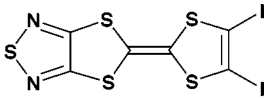
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.019 Å
R factor = 0.099
wR factor = 0.189
Data-to-parameter ratio = 19.9

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

Comment

In recent years, tetrathiafulvalene (TTF) derivatives with a fused 1,2,5-thiadiazole ring have received much attention as component molecules for conducting organic solids (Tomura *et al.*, 1993; Underhill *et al.*, 1993; Naito *et al.*, 1996; Tomura & Yamashita, 1997; 2003). The heteroatom intermolecular S···N and S···S contacts are of special intertest in these structures as they may increase the dimensionality of aggregation in the solid state (Yamashita & Tomura, 1998).



(I)

Introduction of I atoms as substituents in the TTF framework is expected to enhance intermolecular interactions through N···I, S···I and I···I heteroatom contacts. Imakubo *et al.* (1998, 2002) reported supramolecular conductors and superconductors involving diiodo-diselenadithiafulvalene derivatives. Some cation radical salts derived from diiodo–TTF derivatives show a metallic conductivity (Kuwatani *et al.*, 1997; Iyoda *et al.*, 2001). We report here the molecular and crystal structure of an unsymmetrical TTF derivative, the title compound (I), which contains a fused 1,2,5-thiadiazole ring and two iodo substituents at the other end of the molecule.

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The molecule of (I) is planar within 0.0506 Å. The angle between the least-squares planes of the two 1,3-dithiole rings is 2.9 (6)°. The geometric parameters of the 1,2,5-thiadiazole ring in (I)

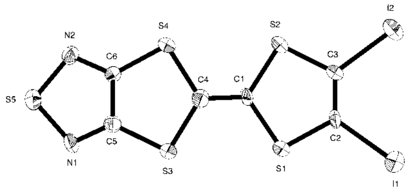


Figure 1
The molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

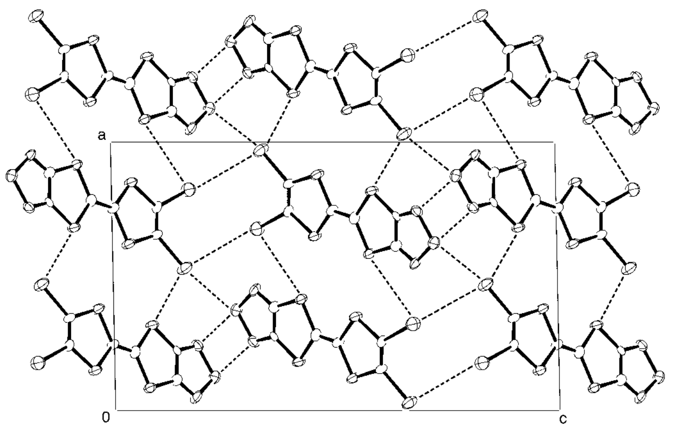


Figure 2
Packing diagram of (I), viewed along the *b* axis. Dashed lines indicate the short intermolecular S···N, S···I and I···I contacts.

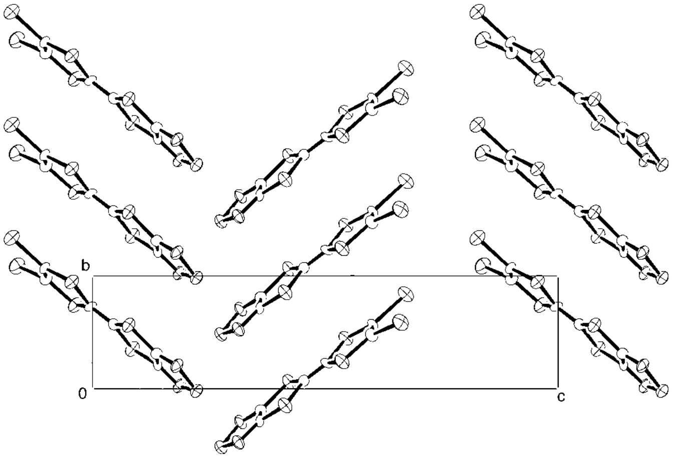


Figure 3
Packing diagram of (I), viewed along the *a* axis.

are almost the same as those reported for 3,4-diphenyl-1,2,5-thiadiazole (Mellini & Merlino, 1976).

Fig. 2 shows a packing diagram of (I), viewed along the *b* axis. Numerous short intermolecular heteroatom contacts, *viz*. S···N, S···S, S···I, N···I and I···I, within the sum of the corresponding van der Waals radii (Pauling, 1960) are observed in the crystal structure (Table 2). The S···N, S···I and I···I distances are 2.4, 4.2–7.2 and 8.5% shorter than the sum of the corresponding van der Waals radii, respectively. Although the N···I contacts are 3.0–6.1% shorter than the sum of the van der Waals radii, they are longer than the typical N···I distance (Desiraju & Harlow, 1989; Xu *et al.*, 1994; Walsh *et al.*, 2001), and the corresponding C—I···N angles are in the range 135.4 (4) to 148.4 (5)°.

The molecules form a herringbone-type stacking along the *b* axis, where the distance between the molecular planes is 3.592 Å (Fig. 3). The shortest intermolecular S···S contact [3.596 (6) Å] involves the S atoms of adjacent molecules in the stack.

Unsymmetrical TTF derivatives with a fused heterocycle tend to stack in a head-to-tail fashion (Tomura & Yamashita, 2001). In the stacking of (I), however, the molecules overlap head-to-head with each other.

Experimental

The title compound, (I), was synthesized by the reaction of [1,2,5]-thiadiazolo-1,3-dithiol-2-one (Tomura & Yamashita, 1997) with 4,5-diiodo-1,3-dithiole-2-thione (Gompper *et al.*, 1994). To a solution of [1,2,5]thiadiazolo-1,3-dithiol-2-one (211 mg, 1.20 mmol) and 4,5-diiodo-1,3-dithiole-2-thione (463 mg, 1.20 mmol) in toluene (10 ml), trimethyl phosphite (1490 mg, 12.00 mmol) was added, and the reaction mixture was refluxed for 2 h. After the mixture was cooled for 6 h at 277 K, the resulting dark yellow precipitate was collected to give 345 mg (56% yield) of (I). Physical data for (I): m.p. 513–515 K; MS (EI): *m*/*z* 514 (M^+). Yellow crystals of (I) suitable for X-ray analysis were grown from a dichloromethane solution.

Crystal data

$C_6I_2N_2S_5$
M_r = 514.18
Monoclinic, $P2_1/n$
a = 12.180 (5) Å
b = 4.8825 (17) Å
c = 20.083 (8) Å
β = 91.152 (9)°
V = 1194.1 (8) Å^3
Z = 4
D_x = 2.860 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 3488 reflections
θ = 3.0–27.5°
μ = 6.11 mm^{-1}
T = 296 (2) K
Needle, yellow
0.50 × 0.08 × 0.03 mm

Data collection

Rigaku Mercury CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min}$ = 0.146, $T_{\max}$ = 0.836
11499 measured reflections
2709 independent reflections
2256 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.078
$\theta_{\max}$ = 27.5°
h = −15 → 14
k = −6 → 4
l = −25 → 25

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.099
$wR(F^2)$ = 0.189
S = 1.31
2709 reflections
136 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 25.5736P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 1.79 e Å^{-3}
$\Delta\rho_{\min}$ = −1.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—C2	2.083 (13)	S4—C6	1.734 (13)
I2—C3	2.054 (13)	S5—N1	1.641 (12)
S1—C1	1.771 (14)	S5—N2	1.648 (13)
S1—C2	1.739 (13)	N1—C5	1.288 (17)
S2—C1	1.758 (13)	N2—C6	1.324 (17)
S2—C3	1.756 (14)	C1—C4	1.309 (18)
S3—C4	1.754 (14)	C2—C3	1.327 (19)
S3—C5	1.761 (14)	C5—C6	1.417 (18)
S4—C4	1.796 (14)		
C2—S1—C1	94.9 (6)	C2—C3—S2	117.1 (10)
C1—S2—C3	95.3 (6)	C2—C3—I2	126.4 (10)
C4—S3—C5	95.1 (6)	S2—C3—I2	116.5 (7)
C6—S4—C4	93.5 (6)	C1—C4—S3	123.3 (11)
N2—S5—N1	99.1 (6)	C1—C4—S4	120.0 (11)
C5—N1—S5	106.1 (10)	S3—C4—S4	116.7 (8)
C6—N2—S5	105.7 (9)	N1—C5—C6	115.7 (12)
C4—C1—S2	124.3 (11)	N1—C5—S3	128.8 (11)
C4—C1—S1	121.6 (11)	C6—C5—S3	115.5 (10)
S2—C1—S1	114.0 (7)	N2—C6—C5	113.4 (12)
C3—C2—S1	118.6 (10)	N2—C6—S4	127.4 (10)
C3—C2—I1	125.8 (10)	C5—C6—S4	119.2 (10)
S1—C2—I1	115.5 (7)		

Table 2
Contact distances (Å).

I1···N1$^{\mathrm{i}}$	3.564 (12)	I2···S5$^{\mathrm{iii}}$	3.670 (4)
I1···S3$^{\mathrm{i}}$	3.786 (4)	I2···S4$^{\mathrm{iv}}$	3.666 (4)
I1···I2$^{\mathrm{ii}}$	3.934 (2)	S3···S5$^{\mathrm{v}}$	3.596 (6)
I2···N1$^{\mathrm{iii}}$	3.473 (12)	S5···N2$^{\mathrm{vi}}$	3.269 (13)
I2···N2$^{\mathrm{iv}}$	3.590 (12)		

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

The largest positive and negative features of the final difference map were found near the I atoms. The crystals showed rather weak diffracting ability, with a steep decrease of intensities towards higher angles; this accounts for the rather low precision of the structure.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Desiraju, G. R. & Harlow, R. L. (1989). *J. Am. Chem. Soc.* **111**, 6757–6764.

Gompper, R., Hansel, J.-G., Hock, J., Polborn, K., Dormann, E. & Winter, H. (1994). *Phosphorus Sulfur Silicon Relat. Elem.* **95–96**, 521–525.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Imakubo, T., Maruyama, T., Sawa, H. & Kobayashi, K. (1998). *Chem. Commun.* pp. 2021–2022.

Imakubo, T., Tajima, N., Tamura, M., Kato, R., Nishio, Y. & Kajita, K. (2002). *J. Mater. Chem.* **12**, 159–161.

Iyoda, M., Kuwatani, Y., Ogura, E., Hara, K., Suzuki, H., Takano, T., Takeda, K., Takano, J., Ugawa, K., Yoshida, M., Matsuyama, H., Nishikawa, H., Ikemoto, I., Kato, T., Yoneyama, N., Nishijo, J., Miyazaki, A. & Enoki, T. (2001). *Heterocycles*, **54**, 833–843.

Kuwatani, Y., Ogura, E., Nishikawa, H., Ikemoto, I. & Iyoda, M. (1997). *Chem. Lett.* pp. 817–818.

Mellini, M. & Merlino, S. (1976). *Acta Cryst.* B**32**, 1074–1078.

Molecular Structure Corporation & Rigaku (2000). *TEXSAN*. Version 1.11. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, 3–9–12 Akishima, Tokyo, Japan.

Molecular Structure Corporation & Rigaku (2001). *CrystalClear*. Version 1.3. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, 3–9–12 Akishima, Tokyo, Japan.

Naito, T., Kobayashi, A., Kobayashi, H. & Underhill, A. E. (1996). *Chem. Commun.* pp. 521–522.

Pauling, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell University Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Tomura, M., Tanaka, S. & Yamashita, Y. (1993). *Heterocycles*, **35**, 69–72.

Tomura, M. & Yamashita, Y. (1997). *Synth. Met.* **86**, 1871–1872.

Tomura, M. & Yamashita, Y. (2001). *Acta Cryst.* E**57**, o307–o308.

Tomura, M. & Yamashita, Y. (2003). *Acta Cryst.* E**59**, o145–o147.

Underhill, A. E., Hawkins, I., Edge, S. & Wilkes, S. B. (1993). *Synth. Met.* **56**, 1914–1919.

Walsh, R. B., Padgett, C. W., Metrangolo, P., Resnati, G., Hanks, T. W. & Pennington, W. T. (2001). *Cryst. Growth Des.* **1**, 165–175.

Xu, K., Ho, D. M. & Pascal, R. A. Jr (1994). *J. Am. Chem. Soc.* **116**, 105–111.

Yamashita, Y. & Tomura, M. (1998). *J. Mater. Chem.* **8**, 1933–1944.