

- Hökelek, T., Patir, S., Gülce, A. & Okay, G. (1994). *Acta Cryst.* **C50**, 450–453.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Menziani, M. C., Cocchi, M. & De Benedetti, P. G. (1992). *J. Mol. Struct. (Theochem)*, **256**, 217–229.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Zhao, Y., Beddoes, R. L. & Joule, J. A. (1997). *J. Chem. Res. (S)*, 42–43; (*M*), 401–429.

*Acta Cryst.* (1997). **C53**, 886–888

### 1,4,8,11-Tetrakis(diiodine)-1,4,8,11-tetra-thiacyclotetradecane

ALEXANDER J. BLAKE, WAN-SHEUNG LI, VITO LIPPOLIS AND MARTIN SCHRÖDER

*Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England. E-mail: a.j.blake@nott.ac.uk*

(Received 6 November 1996; accepted 16 January 1997)

#### Abstract

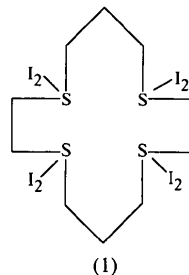
The title compound, C<sub>10</sub>H<sub>20</sub>S<sub>4</sub>4I<sub>2</sub>, [14]aneS<sub>4</sub>4I<sub>2</sub>, possesses crystallographically imposed inversion symmetry and has all four S donor atoms coordinated to diiodine molecules. The principal geometric parameters for the two inequivalent pairs of interactions are S—I 2.803 (2) and 2.880 (2) Å, I—I 2.7894 (8) and 2.7571 (10) Å, and S—I—I 177.71 (5) and 172.50 (4)°. Molecules are linked by S···I and I···I intermolecular contacts to form an infinite three-dimensional lattice.

#### Comment

It is well known that sulfur-containing molecules such as acyclic (Rømming, 1960) and cyclic (Chao & McCullough, 1960) thioethers react with I<sub>2</sub> to give stable charge-transfer complexes in which the sulfur binds the diiodine molecule to give an almost linear S—I—I grouping. Very recently, we and others have reported on the reaction of I<sub>2</sub> with a range of homoleptic thioether macrocycles (Blake, Gould, Radek & Schröder, 1993; Cristiani *et al.*, 1993; Blake *et al.*, 1997*a,b*; Baker, Harris, Dur-

rant, Hughes & Richards, 1995). Although a number of stoichiometries have been observed in the solid state, 1:1 thioether–diiodine adducts appear to be the predominant species in solution regardless of either thioether ring size or the number of S donor atoms in the macrocycle (Blake *et al.*, 1997*a*).

In the present study, we have prepared a new 1:4 stoichiometry in the [14]aneS<sub>4</sub>/I<sub>2</sub> system, namely C<sub>10</sub>H<sub>20</sub>S<sub>4</sub>4I<sub>2</sub>, (1), in addition to the previously known 1:1 and 1:2 adducts (Blake *et al.*, 1997*a*). In the title compound, each of the four S donor atoms coordinates to a diiodine molecule and the resulting adduct exhibits crystallographically imposed inversion symmetry. As seen in related systems (Blake *et al.*, 1997*a*), the asymmetric unit contains geometrically inequivalent S—I—I units, characterized by the parameters: S1—I1 2.803 (2) and S4—I3 2.880 (2) Å, I1—I2 2.7894 (8) and I3—I4 2.7571 (10) Å, and S1—I1—I2 177.71 (5) and S4—I3—I4 172.50 (4)°. The FT-Raman spectrum of the solid adduct shows characteristic ν(I—I) peaks at 166 and 157 cm<sup>-1</sup>, which correspond to the presence of two differently perturbed diiodine molecules (Deplano *et al.*, 1992), as indicated by the two different I—I distances. The pronounced negative correlation between the S—I and I—I distances has been remarked upon previously (Blake *et al.*, 1997*a*). The macrocyclic conformation differs from that seen in the free ligand [14]aneS<sub>4</sub> (DeSimone & Glick, 1976) and in [14]aneS<sub>4</sub>.I<sub>2</sub>, both of which have the same [3434] conformation (Dale, 1973), but also from that observed for [14]aneS<sub>4</sub>.2I<sub>2</sub> (Blake *et al.*, 1997*a*). Although also having a [3434] conformation, the title compound is distinguished from the free ligand by having the S atoms lying along the edges rather than at the corners of the macrocycle (Fig. 1). Bond lengths and angles within the thioether ring correspond closely with literature values for other macrocyclic thioethers (Blake & Schröder, 1990).



Whereas adducts with 1:1 stoichiometry tend to have extended structures dominated by infinite one-dimensional chains comprising alternating macrocycle and I<sub>2</sub> molecules linked by S···I contacts, those with higher proportions of diiodine tend to adopt more complex three-dimensional motifs. Molecules of (1) are linked by both I···I and S···I intermolecular contacts to form an infinite three-dimensional lattice. The I···I

contacts (dotted lines in Fig. 2) are between terminal and S-bound I atoms [I2...I3<sup>i</sup> 3.926 (2) and I1...I4<sup>ii</sup> 3.879 (2) Å; symmetry codes: (i) 2 - x, -y, 3 - z, (ii) 1 + x, y, -1 + z] and link molecules into infinite two-dimensional sheets. S4...I2<sup>iii</sup> [symmetry code: (iii) -1 + x, 1 + y, z] contacts of 3.844 (3) Å, shown as dashed lines in Fig. 2, link these sheets to form the three-dimensional infinite lattice. These features have also been seen in an adduct formed between 1,4,7,10,13-pentathiacyclopentadecane and diiodine (Blake *et al.*, 1997b).

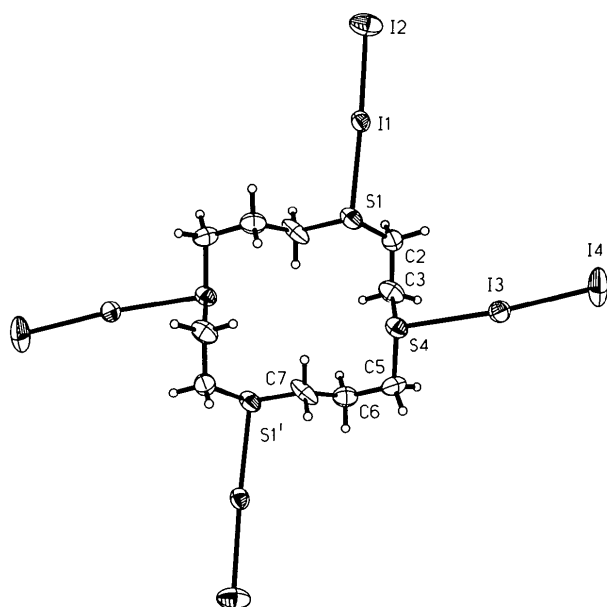


Fig. 1. A view of a molecule of (1) with the atom-numbering scheme. Displacement ellipsoids enclose 70% probability surfaces and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) 1 - x, 1 - y, 2 - z.]

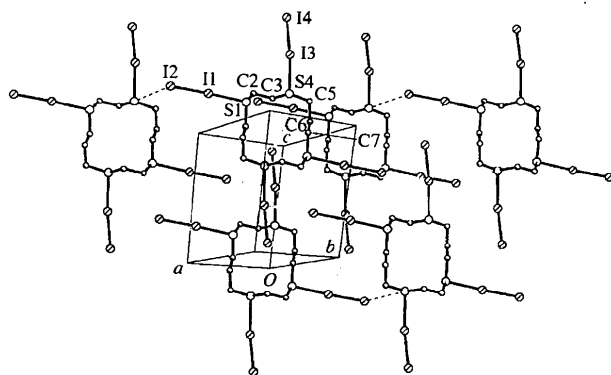


Fig. 2. A diagram showing the intermolecular contacts between C<sub>10</sub>H<sub>20</sub>S<sub>4</sub>.4I<sub>2</sub> units. I...I and S...I contacts are shown as dotted and dashed lines, respectively.

## Experimental

The title compound was prepared from a dichloromethane solution containing 1,4,8,11-tetrathiacyclopentadecane and diiodine in a 1:4 molar ratio. After 24 h, crystals of diffraction quality were obtained in quantitative yield. Microanalysis calculated for C<sub>10</sub>H<sub>20</sub>I<sub>8</sub>S<sub>4</sub>: C 9.35, H 1.57, S 9.98%; found C 9.43, H 1.52, S 9.78%. FT-Raman spectrum (5000–50 cm<sup>-1</sup>): ν(I—I) 166, 157 cm<sup>-1</sup>.

### Crystal data

C<sub>10</sub>H<sub>20</sub>S<sub>4</sub>.4I<sub>2</sub>  
*M<sub>r</sub>* = 1283.70  
 Triclinic  
*P* $\bar{1}$   
*a* = 8.3549 (11) Å  
*b* = 9.1092 (14) Å  
*c* = 10.290 (2) Å  
 $\alpha$  = 64.196 (16)°  
 $\beta$  = 77.525 (14)°  
 $\gamma$  = 82.951 (11)°  
*V* = 688.04 (19) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 3.098 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 21 reflections  
 $\theta$  = 13.4–14.9°  
 $\mu$  = 9.316 mm<sup>-1</sup>  
*T* = 150.0 (2) K  
 Plate  
 0.20 × 0.17 × 0.04 mm  
 Dark red

### Data collection

Stoe Stadi-4 four-circle diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction:  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min}$  = 0.247,  $T_{\max}$  = 0.689  
 2419 measured reflections  
 2419 independent reflections

2133 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max}$  = 25.05°  
 $h$  = -9 → 9  
 $k$  = -9 → 10  
 $l$  = 0 → 12  
 3 standard reflections  
 frequency: 60 min  
 intensity variation: ±3%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)]$  = 0.0312  
 $wR(F^2)$  = 0.0689  
 $S$  = 1.156  
 2418 reflections  
 101 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 4.6P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$  = 0.021  
 $\Delta\rho_{\max}$  = 0.93 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.85 e Å<sup>-3</sup>  
 Extinction correction: SHELXL96  
 Extinction coefficient: 0.00011 (17)  
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—I1	2.803 (2)	S4—I3	2.880 (2)
I1—I2	2.7894 (8)	I3—I4	2.7571 (10)
S1—I1—I2	177.71 (5)	S4—I3—I4	172.50 (4)
C7'—S1—C2—C3	-66.7 (7)	S4—C5—C6—C7	-53.9 (8)
I1—S1—C2—C3	-169.4 (6)	C5—C6—C7—S1'	175.9 (5)
S1—C2—C3—S4	-49.9 (8)	C7'—S1—I1—I2	25.3 (12)
C2—C3—S4—C5	179.4 (6)	C2—S1—I1—I2	128.4 (11)
C2—C3—S4—I3	-75.6 (6)	C5—S4—I3—I4	109.9 (4)
C3—S4—C5—C6	-70.1 (6)	C3—S4—I3—I4	8.8 (5)
I3—S4—C5—C6	-168.4 (5)		

Symmetry code: (i) 1 - x, 1 - y, 2 - z.

H atoms were placed geometrically and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Azimuthal scans were used to derive absorption corrections as the crystal was cut from a larger aggregated mass and the faces could not be indexed satisfactorily. The scans obtained were of high quality, having excellent agreement for  $\psi$  angles 180° apart and similar  $T_{\text{min}}/T_{\text{max}}$  for each scan. Poor agreement with the expected absorption correction range is attributed to the high value of  $\mu$  combined with the large relative uncertainty in measuring the thin plate dimension.

Data collection: *STADI-4* (Stoe & Cie, 1995a). Cell refinement: *STADI-4*. Data reduction: *X-RED* (Stoe & Cie, 1995b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL96*.

The authors thank EPSRC for provision of a four-circle diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1440). Services for accessing these data are described at the back of the journal.

## References

- Baker, P. K., Harris, S. D., Durrant, M. C., Hughes, D. L. & Richards, R. L. (1995). *Acta Cryst.* **C51**, 697–700.
- Blake, A. J., Cristiani, F., Demartin, F., Devillanova, F. A., Garau, A., Gould, R. O., Isaia, F., Lippolis, V., Parsons, S., Radek, C. & Schröder, M. (1997a). *J. Chem. Soc. Dalton Trans.* In the press.
- Blake, A. J., Demartin, F., Devillanova, F. A., Garau, A., Gilby, L. M., Gould, R. O., Lippolis, V., Parsons, S., Radek, C. & Schröder, M. (1997b). *J. Chem. Soc. Dalton Trans.* Submitted.
- Blake, A. J., Gould, R. O., Radek, C. & Schröder, M. (1993). *J. Chem. Soc. Chem. Commun.* pp. 1191–1193.
- Blake, A. J. & Schröder, M. (1990). *Chemistry of Thioether Macrocyclic Complexes. Advances in Inorganic Chemistry*, Vol. 35, edited by A. G. Sykes, pp. 1–80, and references therein. Orlando, Florida: Academic Press.
- Chao, G. Y. & McCulloch, J. D. (1960). *Acta Cryst.* **13**, 727–732.
- Cristiani, F., Demartin, F., Devillanova, F. A., Isaia, F., Garau, A., Lippolis, V. & Verani, G. (1993). *Heteroatom Chem.* **4**, 571–578.
- Dale, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.
- Deplano, P., Devillanova, F. A., Ferraro, J. R., Isaia, F., Lippolis, V. & Mercuri, M. L. (1992). *Appl. Spectrosc.* **46**, 1625–1629.
- DeSimone, R. E. & Glick, M. D. (1976). *J. Am. Chem. Soc.* **98**, 762–767.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rømming, C. (1960). *Acta Chem. Scand.* **14**, 2145–2151.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1994). *SHELXTL/PC. Structure Determination Programs*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1996). *SHELXL96. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Stoe & Cie (1995a). *STADI-4. Data Collection Program for Windows*. Version 1.04. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1995b). *X-RED. Data Reduction Program for Windows*. Version 1.04. Stoe & Cie, Darmstadt, Germany.
- Acta Cryst.* (1997). **C53**, 888–890

## 2,6-Diacetylpyridinebis(*p*-methoxyaniline),† a Terdentate *NNN* Donor Ligand

PAUL R. MEEHAN, ELMER C. ALYEA AND GEORGE FERGUSON

*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: paul@xray.chembio.uoguelph.ca*

(Received 15 January 1997; accepted 3 February 1997)

### Abstract

The title compound, C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>, is a terdentate *NNN* donor ligand. The molecule lies about a crystallographic mirror plane which passes through a C and an N atom of the substituted pyridine ring. The orientation of the exocyclic N atoms in the solid is not what is required for complex formation with metal centres.

### Comment

The commercially available *NNN* donor ligand terpyridine is of considerable interest as a planar terdentate ligand, however, its synthesis is laborious and expensive (McWhinnie & Miller, 1969). Our interest in the generation of cheaper alternative terdentate ligands derived from 2,6-diacetylpyridine has been well documented (Alyea & Merrell, 1974; Alyea, Ecott & Merrell, 1982). Complexation of these ligands with transition metal salts of general formula *MX*<sub>2</sub> has produced five- and six-coordinate species of types *MX*<sub>2</sub>*L* (*M* = Ni, Cd; *X* = Cl) and [*ML*<sub>2</sub>]*X*<sub>2</sub> (*M* = Ni, Cd; *X* = ClO<sub>4</sub><sup>−</sup>) (Alyea & Merrell, 1974; Alyea, 1983).

The Schiff base condensation of 2,6-diacetylpyridine produced the title compound, (I). The molecule (Fig. 1) lies about a mirror plane which passes through the N1 and C4 atoms. The bond lengths within the ligand are as expected. The double-bond nature of C5—N2 is shown by the bond length of 1.274 (5) Å; the N1—C2 bond length is longer, as expected, at 1.343 (4) Å. The *sp*<sup>2</sup> nature of the C5 atom is also established by the planarity of the C2, N2, C5, C6 moiety [deviations from −0.003 (1) to 0.007 (4) Å]. The interplanar angle which the C2, N2, C5, C6 plane makes with that defined by N1, C2—C5 is 1.98 (10)°. The interplanar angle between the C2, C5, C6, N2 and N2, C11—C16 planes is 57.20 (15)°. The *p*-methoxy group adopts the usual conformation and lies in the plane of its aromatic ring [torsion angle C13—C14—O1—C17 0.3 (6)°].

† Alternative name: 2,6-bis[1-(4-methoxyphenylimino)ethyl]pyridine.