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2,3,10,11-Tetrathiatricyclo[10.4.0.0^{4,9}]-hexadeca-4,6,8,12,14,16-hexaene (precession camera *versus* CCD)

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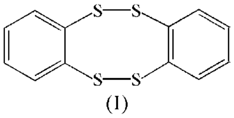
The title compound, $C_{12}H_8S_4$, has crystallographic $\overline{1}$ symmetry, the benzene groups thus being *anti* with respect to the plane of the four S atoms. The S—S and C—S bond lengths of the sulfur–carbon eight-membered ring were found to be similar to those in other structures containing such sulfur–carbon rings. There is evidence for π–π interactions between the aromatic rings of neighboring molecules, linking them into sheets.

Comment

Bis(*o*-phenylene) tetrasulfide, (I), was synthesized in 1961 as part of a study of organic disulfides and related compounds (Field *et al.*, 1961). Two forms are possible, *viz.* a rigid *anti* form with the benzene rings on opposite sides of the plane of the S atoms and a *syn* form with the rings on the same side. The *syn* form may also exist in a conformation with the rings mutually perpendicular. Because of these interesting possibilities and attendant questions concerning the nature of the C—S bonding, a single-crystal X-ray study was undertaken.



(I)

A crystal was grown from a carbon disulfide solution. Using photographic film and Buerger precession camera techniques, 591 independent reflections were recorded with Mo $K\alpha$ radiation. On the basis of the method of Howells *et al.* (1950) and statistics proposed by Karle & Hauptman (1953), Hauptman & Karle (1953) and Karle (1961), the space group indicated was $P1$ (Mitchell & Lippert, 1965; in this short communication, the compound was incorrectly called bis(*o*-phenylene disulfide). It is now known that, although these tests are necessary, neither is sufficient. Mitchell and Lippert were unable to solve this triclinic structure in the early 1960s. Direct methods for solution of the phase problem were in their initial stages and the necessary resources for a structure solution were not readily available. Coordinates for the S atoms were found from a Patterson map, but the structure remained incomplete (Mitchell, 1965). Using the corrected observed $F_{\rm obs}$ of Mitchell (1965), the structure has now been solved in space group $P\overline{1}$ using *SHELXTL* (Sheldrick, 2000). This structure was refined to $R1 = 0.1083$, but with bond lengths and angles unacceptable by today's standards. Since more accurate measurement and data reduction methods are now available, it was decided that the crystalline structure of (I) should be redetermined as described in the experimental and refinement sections.

The structure is the *anti* form (Fig. 1) with the parallel benzene rings on opposite sides of the planar sulfur group. The S—S and S—C bond lengths (Table 1) are similar to those found in seven other sulfur–carbon eight-membered rings, where the average S—S and S—C bond lengths are 2.06 and 1.78 Å, respectively (Kopf *et al.*, 1979; Lakshmikantham *et al.*, 1987; Chivers *et al.*, 1998; Ogawa *et al.*, 1999; Kimura *et al.*, 2002; Joshi *et al.*, 2003; Sugimoto *et al.*, 2005). The average bond length from X-ray and neutron diffraction studies of all organic disulfide bonds is 2.048 (26) Å (Allen *et al.*, 1987), and the average length of a disulfide bridge in macromolecular structures is 2.03 Å (Engh & Huber, 1991). For comparison, the S—S distance ranges from 2.035 to 2.060 Å in the various allotropes of sulfur (Gallacher & Pinkerton, 1993; Rettig & Trotter, 1987; Templeton *et al.*, 1976; Goldsmith & Strouse, 1977).

A packing diagram of (I) is shown in Fig. 2. No hydrogen bonds are discernible, as all the S$\cdots$H distances are greater than 3 Å. There is evidence of face-to-face π–π stacking interactions between the benzene rings of neighboring molecules (Hunter & Sanders, 1990; Steed & Atwood, 2000). According to the Hunter–Sanders model (Hunter & Sanders, 1990), the aromatic rings in the face-to-face mode should have an interplanar separation of about 3.4–3.6 Å and be slightly offset from one another. A direct face-to-face mode between the aromatic rings would result in a repulsion instead of an attraction between the two rings. The ring at (x, y, z), part of the molecule centered across (0, 0, 0), is parallel to the two rings at $(-x, -y, 1 - z)$ and $(1 - x, 1 - y, 1 - z)$, which lie in the molecules centered at $(0, 0, \frac{1}{2})$ and $(1 - x, 1 - y, 1 - z)$. The interplanar spacings are 3.418 (2) and 3.442 (2) Å, with ring-centroid separations of 3.768 (2) and 3.769 (2) Å, corre-

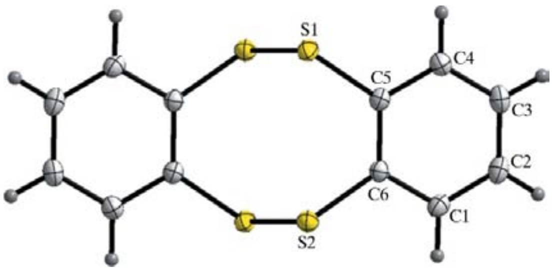


Figure 1
A molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

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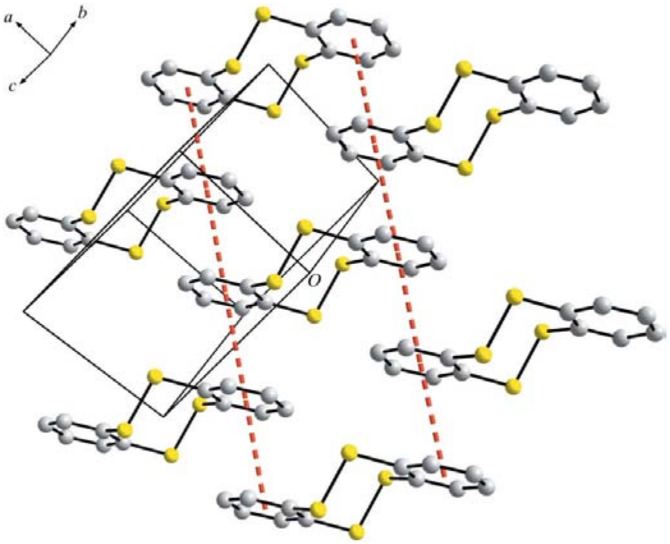

Figure 2
Part of the crystal structure of (I), showing the formation of a π-stacked sheet. For the sake of clarity, H atoms have been omitted.

sponding to centroid offsets of 1.585 (2) and 1.535 (2) Å, respectively. Propagation of these two π-stacking interactions links the molecules into sheets parallel to $(1\overline{1}0)$ (Fig. 2). We also note the similarity to the packing of graphite (Nelson & Riley, 1945; Franklin, 1951; Pauling, 1966).

Experimental

The synthesis of (I) has been described in detail by Field *et al.* (1961). A sample of (I) retained from the 1961 synthesis was still available. Prismatic crystals were obtained by slow evaporation of a carbon disulfide solution in a glass vial.

Crystal data

$C_{12}H_8S_4$
$M_r = 280.42$
Triclinic, $P\overline{1}$
$a = 7.0875$ (2) Å
$b = 7.2827$ (2) Å
$c = 7.2971$ (2) Å
$\alpha = 114.534$ (1)°
$\beta = 95.685$ (1)°
$\gamma = 116.754$ (1)°
$V = 286.37$ (1) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.79$ mm^{-1}
$T = 140$ (1) K
0.38 × 0.34 × 0.22 mm

Data collection

Bruker SMART 6000 CCD area detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.76$, $T_{max} = 0.84$
4521 measured reflections
1649 independent reflections
1565 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.067$
$S = 1.07$
1649 reflections
89 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Crystals of (I) are triclinic and the structure was solved and refined in the $P\overline{1}$ space group. All H atoms were located in difference maps and their parameters were then refined, leading to C—H distances in the range 0.948 (19)–1.011 (19) Å.

Table 1
Selected bond lengths (Å).

S1—C5	1.7748 (10)	S2—C6	1.7734 (10)
S1—S2^{i}	2.0655 (4)		

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3134). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Brandenburg, K. (2006). *DIAMOND*. Version 3.1d. Crystal Impact GbR, Bonn, Germany.
Bruker (1997). *SAINT* (Version 6.0) and *SMART* (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.
Chivers, T., Parvez, M., Vargas-Baca, I. & Schatte, G. (1998). *Can. J. Chem.* **76**, 1093–1101.
Engh, R. A. & Huber, R. (1991). *Acta Cryst.* A**47**, 392–400.
Field, L., Stephens, W. D. & Lippert, E. L. Jr (1961). *J. Org. Chem.* **26**, 4782–4783.
Franklin, R. E. (1951). *Acta Cryst.* **4**, 253–261.
Gallacher, A. C. & Pinkerton, A. A. (1993). *Acta Cryst.* C**49**, 125–126.
Goldsmith, L. M. & Strouse, C. E. (1977). *J. Am. Chem. Soc.* **99**, 7580–7589.
Hauptman, H. & Karle, J. (1953). *Acta Cryst.* **6**, 136–141.
Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210–214.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Joshi, H. K., Cooney, J. A., Inscore, F. E., Gruhn, N. E., Lichtenberger, D. L. & Enemark, J. H. (2003). *Proc. Natl Acad. Sci. USA*, **100**, 3719–3724.
Karle, I. L. (1961). *Acta Cryst.* **14**, 497–502.
Karle, J. & Hauptman, H. (1953). *Acta Cryst.* **6**, 131–135.
Kimura, T., Mizusawa, S., Yoneshima, A., Ito, S., Tsujimura, K., Yamashita, T., Kawai, Y., Ogawa, S. & Sato, R. (2002). *Bull. Chem. Soc. Jpn*, **75**, 2647–2653.
Kopf, J., Von Deuten, K., Nakhdjavan, B. & Klar, G. (1979). *Z. Naturforsch. Teil B*, **34**, 48–51.
Lakshmikantham, M. V., Raasch, M. S., Cava, M. P., Bott, S. G. & Atwood, J. L. (1987). *J. Org. Chem.* **52**, 1874–1877.
Mitchell, D. J. (1965). Thesis, Doctor of Philosophy in Chemistry, Vanderbilt University, Nashville, Tennessee, USA.
Mitchell, D. J. & Lippert, E. L. (1965). *Acta Cryst.* **18**, 559–560.
Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc. London*, **57**, 477–486.
Ogawa, S., Sugawara, M., Kawai, Y., Niizuma, S., Kimura, T. & Sato, R. (1999). *Tetrahedron Lett.* **40**, 9101–9106.
Pauling, L. (1966). *Proc. Natl Acad. Sci. USA*, **56**, 1646–1652.
Rettig, S. J. & Trotter, J. (1987). *Acta Cryst.* C**43**, 2260–2262.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Steed, J. W. & Atwood, J. L. (2000). *Supramolecular Chemistry*. Chichester, England: John Wiley & Sons.
Sugimoto, H., Tarumizu, M., Tanaka, K., Miyake, H. & Tsukube, H. (2005). *Dalton Trans.* pp. 3558–3565.
Templeton, L. K., Templeton, D. H. & Zalkin, A. (1976). *Inorg. Chem.* **15**, 199–2001.