

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S(1)—C(1)	1.779 (3)	S(1)—C(9)	1.827 (3)
C(1)—C(2)	1.350 (3)	C(1)—C(3)	1.483 (3)
C(2)—C(2')	1.432 (5)	C(3)—C(4)	1.398 (4)
C(3)—C(8)	1.403 (4)	C(4)—C(5)	1.379 (4)
C(5)—C(6)	1.389 (5)	C(6)—C(7)	1.390 (4)
C(7)—C(8)	1.379 (4)	C(9)—C(10)	1.502 (4)
C(10)—C(11)	1.391 (4)	C(10)—C(15)	1.396 (4)
C(11)—C(12)	1.388 (5)	C(12)—C(13)	1.386 (4)
C(13)—C(14)	1.387 (4)	C(13)—C(16)	1.513 (6)
C(14)—C(15)	1.384 (5)		
C(1)—S(1)—C(9)	100.1 (1)	S(1)—C(1)—C(2)	120.0 (2)
S(1)—C(1)—C(3)	117.7 (2)	C(2)—C(1)—C(3)	122.1 (2)
C(1)—C(2)—C(2')	127.3 (3)	C(1)—C(3)—C(4)	120.7 (2)
C(1)—C(3)—C(8)	121.4 (2)	C(4)—C(3)—C(8)	117.9 (2)
C(3)—C(4)—C(5)	121.1 (3)	C(4)—C(5)—C(6)	120.0 (3)
C(5)—C(6)—C(7)	120.0 (3)	C(6)—C(7)—C(8)	119.7 (3)
C(3)—C(8)—C(7)	121.2 (3)	S(1)—C(9)—C(10)	114.1 (2)
C(9)—C(10)—C(11)	121.1 (2)	C(9)—C(10)—C(15)	121.1 (3)
C(11)—C(10)—C(15)	117.7 (3)	C(10)—C(11)—C(12)	121.1 (3)
C(11)—C(12)—C(13)	121.1 (3)	C(12)—C(13)—C(14)	117.9 (3)
C(12)—C(13)—C(16)	121.5 (3)	C(14)—C(13)—C(16)	120.6 (3)
C(13)—C(14)—C(15)	121.5 (3)	C(10)—C(15)—C(14)	120.7 (3)

The structure was solved using direct methods (*SHELXTL-Plus88*; Sheldrick, 1988) and the *UCLA Crystallographic Package* (Strouse, 1981). H atoms were located and included with isotropic temperature factors.

We thank the National Institutes of Health (AI 24779) and the National Science Foundation (grant CHE-90-15849) for support of this research. Funds for the purchase of the Siemens R3m/V diffractometer system were made available from the National Science Foundation under grant CHE-85-14495.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: HH1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). **C51**, 661–663

## Bis(*tert*-butylsulfonyl) Disulfide

FILLMORE FREEMAN, XIAO-BO MA AND JOSEPH W. ZILLER

*Department of Chemistry, University of California, Irvine, California 92717, USA*

ROBERT I. LIN

*Nutrition International Company, 6 Silverfern Drive, Irvine, California 92715, USA*

(Received 4 June 1992; accepted 5 July 1994)

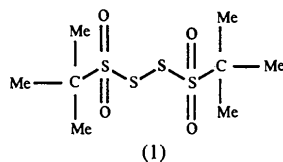
## Abstract

The crystal structure of bis(*tert*-butylsulfonyl) disulfide,  $\text{C}_8\text{H}_{18}\text{O}_4\text{S}_4$ , is described and compared with oxides of other polysulfanes. The  $\text{SO}_2\text{—S}$  bond distance is longer than that of  $\text{S—S}$  and there is considerable double-bond character along the  $\text{S—O}$  bonds.

## Comment

The oxidation of polysulfanes and the structures of the resulting oxides are of considerable interest (Block & Bayer, 1990; Block & Weidner, 1966; Folkins & Harpp, 1993; Freeman, 1984; Freeman & Angeletakis, 1983; Freeman, Ma & Lin, 1993; Oae, 1991). Although the crystal structures of sulfonyl derivatives of disulfides (thiosulfonates; Dawson, Mathieson & Robertson, 1948; Wahl, Bordner, Harpp & Gleason, 1973), two trisulfides [bis(arylsulfonyl) sulfides; Mathieson & Robertson, 1949], one tetrasulfide [bis(methylsulfonyl) disulfide; Sörum & Foss, 1949; Sörum, 1953], and one pentasulfide [bis(arylsulfonyl) trisulfide; Dawson, Mathieson & Robertson, 1948] have been determined, there is a

paucity of structural data concerning the structures of oxides of polysulfanes. This report describes the crystal structure of bis(*tert*-butylsulfonyl) disulfide (1).



The C1—S2 bond length of 1.827 (3) Å in compound (1) is slightly longer than the sum (1.81 Å) of the covalent single bond radii for sulfur and carbon. Although both values are close to S—S bond lengths (2.05 Å) in organic disulfanes (*RSSR*, Oae, 1985; Steudel, 1975), the S1—S2 bond distance of 2.136 (1) Å is longer than the S1—S1' bond length of 2.016 (1) Å. These bond distances are similar to those in thiosulfonates (Noordik & Vos, 1967; Wahl, Bordner, Harpp & Gleason, 1973) and in bis(dimethylsulfonyl) disulfide (Sörum, 1953). Introduction of an O atom to sulfur causes a lengthening and weakening of the neighboring S—S bonds and a strengthening of the S—O bond (Steudel, 1975). The range of covalent S—O double bonds is 1.40–1.49 Å which is consistent with the observed S2—O1 [1.443 (2) Å] and the S2—O2 [1.433 (2) Å] bond distances in (1), thus indicating considerable double-bond character in the S—O bonds. The O1—S2—O2 bond angle of 119.9 (1)° is close to the values of 117 (4) and 120° observed in bis(phenylsulfonyl) sulfide (Mathieson & Robertson, 1949) and bis(dimethylsulfonyl) disulfide (Sörum, 1953), respectively. The S1—S2—O1, S1—S2—O2 and S2—S1—S1' bond angles are 102.4 (1), 109.3 (1) and 103.8 (1)°, respectively, in (1).

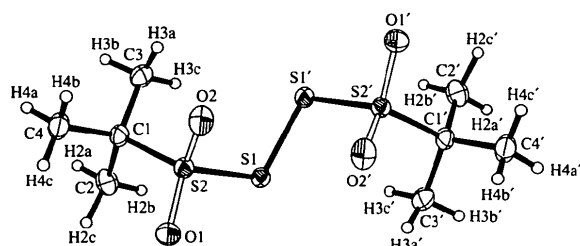


Fig. 1. ORTEPII (Johnson, 1976) plot of the molecular structure and atom numbering of (1). The displacement ellipsoids are drawn at the 50% probability level.

## Experimental

The crystal was prepared by the trifluoroperoxyacetic acid (4.76 mmol) oxidation of *tert*-butyltrisulfide (2.38 mmol) in dichloromethane at 268 K for 5 h. Recrystallization was from 4:1 hexane/diethyl ether.

## Crystal data

C<sub>8</sub>H<sub>18</sub>O<sub>4</sub>S<sub>4</sub>  
*M<sub>r</sub>* = 306.5  
 Monoclinic  
 C2/c  
*a* = 12.392 (2) Å  
*b* = 5.6940 (11) Å  
*c* = 19.951 (3) Å  
 $\beta$  = 98.13 (13)°  
*V* = 1393.5 (4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.46 Mg m<sup>-3</sup>

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 30 reflections  
 $\theta$  = 10.0–15.0°  
 $\mu$  = 0.651 mm<sup>-1</sup>  
*T* = 153 K  
 Plate  
 0.43 × 0.30 × 0.17 mm  
 Colorless

## Data collection

Siemens P3 diffractometer  
 $\theta$ – $2\theta$  scans  
 Absorption correction: none  
 1858 measured reflections  
 1502 independent reflections  
 1398 observed reflections  
 [|*F<sub>o</sub>*| > 2.0 $\sigma$ (|*F<sub>o</sub>*|)]  
*R<sub>int</sub>* = 0.011

$\theta_{\max}$  = 27.5°  
*h* = 0 → 16  
*k* = 0 → 7  
*l* = –25 → 25  
 2 standard reflections monitored every 98 reflections  
 intensity decay: none

## Refinement

Refinement on *F*  
*R* = 0.041  
*wR* = 0.045  
*S* = 1.40  
 1398 reflections  
 109 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(|F_o|) + 0.0004(|F_o|)^2]$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
S1	0.4572 (1)	0.2414 (1)	0.2031 (1)	0.0221 (2)
S2	0.5386 (1)	0.4964 (1)	0.1498 (1)	0.0191 (2)
O1	0.4544 (1)	0.5663 (4)	0.0960 (1)	0.0330 (6)
O2	0.5888 (2)	0.6682 (3)	0.1968 (1)	0.0294 (6)
C1	0.6441 (2)	0.3365 (4)	0.1133 (1)	0.0208 (7)
C2	0.5886 (3)	0.1542 (5)	0.0643 (1)	0.0302 (8)
C3	0.7216 (2)	0.2263 (6)	0.1709 (1)	0.0299 (8)
C4	0.7025 (2)	0.5235 (5)	0.0764 (2)	0.0298 (8)

Table 2. Selected geometric parameters (Å, °)

S1—S2	2.136 (1)	S1—S1'	2.016 (1)
S2—O1	1.443 (2)	S2—O2	1.433 (2)
S2—C1	1.827 (3)	C1—C2	1.522 (4)
C1—C3	1.526 (3)	C1—C4	1.533 (4)
S2—S1—S1	103.8 (1)	S1—S2—O1	102.4 (1)
S1—S2—O2	109.3 (1)	O1—S2—O2	119.9 (1)
S1—S2—C1	106.0 (1)	O1—S2—C1	108.9 (1)
O2—S2—C1	109.4 (1)	S2—C1—C2	108.2 (2)
S2—C1—C3	108.3 (2)	C2—C1—C3	112.5 (2)
S2—C1—C4	105.0 (2)	C2—C1—C4	111.5 (2)
C3—C1—C4	110.9 (2)		

The determination of the Laue symmetry, crystal class, unit-cell parameters and crystal orientation matrix was by previously described techniques (Churchill, Lashewycz & Rotella, 1977). All data were corrected for Lorentz and polarization effects and placed on an absolute scale. Any reflection with  $I(\text{net}) < 0$  was assigned the value  $|F_o| = 0$ . The systematic extinctions observed were  $hkl$  for  $h + k = 2n + 1$  and  $h0l$  for  $l = 2n + 1$ ; the diffraction symmetry was  $2/m$ . The two possible monoclinic space groups were  $Cc$  [ $C_2^4$ ; No. 9] and  $C2/c$  [ $C_2^6$ ; No. 15]; the centrosymmetric space group  $C2/c$  was determined to be the correct choice.

The structure was solved via an automatic Patterson routine (SHELXTL-Plus88; Sheldrick, 1988) and refined by full-matrix least-squares techniques. The molecule is located about a twofold rotation axis (1/2,  $y$ , 1/4). H atoms were located from a difference Fourier synthesis and refined with isotropic temperature factors. All crystallographic calculations were performed using either the UCI-modified version of the UCLA Crystallographic Computing Package (Strouse, 1981) or SHELXTL-Plus. Molecular graphics were drawn with ORTEPII (Johnson, 1976).

Acknowledgement is made to the National Science Foundation for support of this research (CHE-90-15849) and for the purchase of the Siemens R3m/V diffractometer system (CHE-85-14495).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HH1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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 Acta Cryst. (1995). **C51**, 663–666

## [Aib<sup>5,6</sup>-D-Ala<sup>8</sup>]-Cyclolinopeptide A, Grown from a Benzene/Acetonitrile Mixture

MICHELE SAVIANO,\* FILOMENA ROSSI, MARTA FILIZOLA, BENEDETTO DI BLASIO AND CARLO PEDONE

Centro di Studio di Biocristallografia del CNR, Università di Napoli Federico II, Dipartimento di Chimica, via Mezzocannone 4, 80134 Napoli, Italy

(Received 7 February 1994; accepted 13 June 1994)

### Abstract

*cyclo*-(Prolyl-prolyl-phenylalanyl-phenylalanyl- $\alpha$ -aminoisobutyryl- $\alpha$ -aminoisobutyryl-isoleucyl-D-alanyl-valyl) ([Aib<sup>5,6</sup>-D-Ala<sup>8</sup>]-cyclolinopeptide A), grown from benzene/acetonitrile mixture, crystallizes with one acetonitrile and two water molecules. The molecular structure is almost identical to that obtained from methanol/water. The dimension of the solvent channels found in these structures is reduced in the present one, but the intramolecular hydrogen-bond pattern is preserved. The Pro<sup>1</sup>-Pro<sup>2</sup> peptide unit is *cis* ( $\omega = 8^\circ$ ); all others are *trans*.

### Comment

Cyclolinopeptide A (CLA), a homodetic nonapeptide of sequence *cyclo*-(Pro<sup>1</sup>-Pro<sup>2</sup>-Phe<sup>3</sup>-Phe<sup>4</sup>-Leu<sup>5</sup>-Ile<sup>6</sup>-Ile<sup>7</sup>-Leu<sup>8</sup>-Val<sup>9</sup>), isolated from linseed (Kaufmann & Tobshirbel, 1959), belongs to a class of cyclic peptides well known for their competitive inhibitory activity towards the cholate uptake in hepatocytes (Kessler, Klein, Müller, Wagner, Bats, Ziegler & Frimmer, 1986; Di Blasio, Rossi, Benedetti, Pavone, Pedone, Temussi, Zanotti & Tancredi, 1989). Various synthetic analogues were synthesized and characterized in our laboratories (Zanotti, Tancredi, Rossi, Benedetti, Pedone & Temussi, 1989; Di Blasio, Rossi, Benedetti, Pavone, Saviano, Pedone, Zanotti & Tancredi, 1992; Zanotti, Maione, Rossi, Saviano, Pedone & Tancredi, 1993; Rossi, Saviano, Di Blasio, Zanotti, Maione, Tancredi & Pedone, 1994) in order to investigate the structure-activity relationships of CLA. Recently, the conformational analysis of one of these analogues, [Aib<sup>5,6</sup>-D-Ala<sup>8</sup>]-cyclolinopeptide A (CLAIB) grown from a methanol/water mixture,