

Bis(2-bromobenzyl) trisulfide

Suneel. P. Singh,^a Alan. J. Lough^{b*} and Adrian. L. Schwan^a

^aDepartment of Chemistry, University of Guelph, 50 Stone Road East, Guelph, Ontario, Canada N1G 2W1, and ^bDepartment of Chemistry, University of Toronto, 80 St., George Street, Toronto, Ontario, Canada M5S 3H6
Correspondence e-mail: alough@chem.utoronto.ca

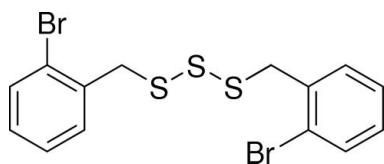
Received 14 January 2009; accepted 14 January 2009

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.034; wR factor = 0.081; data-to-parameter ratio = 20.1.

The title molecule, $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{S}_3$, lies on a crystallographic twofold rotation axis which bisects the S—S—S angle. The dihedral angle between the two symmetry-related benzene rings is $89.91(9)^\circ$. In terms of hybridization principles, the S—C—C angle is slightly larger than expected.

Related literature

For related literature, see: Haoyun *et al.* (2006); De Sousa *et al.* (1990); Johnson *et al.* (1997); Rys *et al.* (2008). For a related synthesis see: Banerji & Kalena (1980); O'Donnell & Schwan (2003). For a related crystal structure, see: Abu-Yousef *et al.* (2006).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{12}\text{Br}_2\text{S}_3$
 $M_r = 436.24$

Orthorhombic, $P2_12_12$
 $a = 12.771(3)$ Å
 $b = 13.030(3)$ Å
 $c = 4.7635(10)$ Å

$V = 792.7(3)$ Å³
 $Z = 2$

Mo $K\alpha$ radiation
 $\mu = 5.49$ mm⁻¹
 $T = 150(1)$ K
 $0.16 \times 0.12 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995)
 $T_{\min} = 0.378$, $T_{\max} = 0.576$

5451 measured reflections
1745 independent reflections
1447 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.081$
 $S = 1.06$
1745 reflections
87 parameters
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.72$ e Å⁻³
Absolute structure: Flack (1983),
659 Friedel pairs
Flack parameter: $-0.024(13)$

Table 1

Selected bond angles ($^\circ$).

S2 ¹ —S1—S2	106.21 (9)	C2—C1—S2	114.0 (3)
------------------------	------------	----------	-----------

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

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research. AJL thanks NSERC Canada for funding.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2135).

References

- Abu-Yousef, I. A., Rys, A. Z. & Harpp, D. N. (2006). *J. Sulfur Chem.* **27**, 15–24.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Banerji, A. & Kalena, G. P. (1980). *Tetrahedron Lett.* **21**, 3003–3004.
Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
De Sousa, J. R., Demuner, A. J., Pinheiro, J. A., Breitaier, E. & Cassels, B. K. (1990). *Phytochemistry*, **29**, 3653–3655.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Haoyun, A., Jenny, Z., Xiaobo, W. & Xiao, X. (2006). *Bioorg. Med. Chem. Lett.* **16**, 4826–4829.
Johnson, L., Williams, L. A. D. & Roberst, E. V. (1997). *Pestic. Sci.* **50**, 228–232.
Nonius (2002). *COLLECT*. Nonius BV, Delft, The Netherlands.
O'Donnell, J. S. & Schwan, A. L. (2003). *Tetrahedron Lett.* **44**, 6293–6296.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet pp. 307–326. New York: Academic Press.
Rys, A. Z., Abu-Yousef, I. A. & Harpp, D. N. (2008). *Tetrahedron Lett.* **49**, 6670–6673.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2009). E65, o361 [doi:10.1107/S1600536809001834]

Bis(2-bromobenzyl) trisulfide

S. P. Singh, A. J. Lough and A. L. Schwan

Comment

Organic sulfides are an attractive class of compounds because of their synthetic and pharmaceutical applications. Dibenzyl trisulfide was isolated from the sub-tropical shrub *Petiveria alliacea L.* (De Sousa *et al.*, 1990; Johnson *et al.*, 1997). Dibenzyl trisulfide derivatives have been synthesized in moderate yield *via* a diimidazolyl sulfide derivative (Banerji & Kalena, 1980). The immunomodulatory activities, molecular mechanism, anti tumor activities and some other biological activities of dibenzyltrisulfide derivatives have been reported (Haoyun *et al.*, 2006).

In the title molecule (Fig. 1), the bond lengths and bond angles are comparable to those observed in a similar compound (Abu-Yousef *et al.*, 2006).

Experimental

The N-protected amino acid derivative (1) (Fig. 2) was synthesized by following the described procedure for its benzyl analog (O'Donnell & Schwan, 2003). Compound (1) was reacted with trifluoroacetic acid (20 equiv.) at 273 K for 2 hr to give amino acid derivative (2). The title compound (3) was prepared by stirring (2) in dichloromethane at room temperature in 20% yield and was crystallized by slow evaporation of a dichloromethane/methanol (9:1, *v/v*) solution. It should be noted that compound (2) in dichloromethane on standing at room temperature for several days also gave compound (3).

Refinement

H atoms bonded to C atoms were placed in calculated positions with C—H = 0.95 - 0.99 Å and were included in a riding-model approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

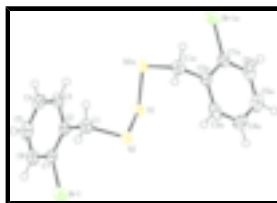


Fig. 1. The molecular structure of title compound. All non-H atoms are represented by 30% probability displacement ellipsoids. Atoms labeled with the suffix 'a' are related by the symmetry operator $(-x + 1, -y, z)$.



Fig. 2. The reaction scheme for the formation of the title compound.

Bis(2-bromobenzyl) trisulfide

Crystal data

$C_{14}H_{12}Br_2S_3$

$M_r = 436.24$

Orthorhombic, $P2_12_12$

Hall symbol: P 2 2ab

$a = 12.771 (3) \text{ \AA}$

$b = 13.030 (3) \text{ \AA}$

$c = 4.7635 (10) \text{ \AA}$

$V = 792.7 (3) \text{ \AA}^3$

$Z = 2$

$F_{000} = 428$

$D_x = 1.828 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5451 reflections

$\theta = 3.1\text{--}27.5^\circ$

$\mu = 5.49 \text{ mm}^{-1}$

$T = 150 (1) \text{ K}$

Block, colourless

$0.16 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 9 pixels mm^{-1}

$T = 150(1) \text{ K}$

φ scans and ω scans with κ offsets

Absorption correction: multi-scan
(SORTAV; Blessing, 1995)

$T_{\min} = 0.378$, $T_{\max} = 0.576$

5451 measured reflections

1745 independent reflections

1447 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 3.1^\circ$

$h = -16 \rightarrow 16$

$k = -16 \rightarrow 16$

$l = -6 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.081$

$S = 1.06$

1745 reflections

87 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.72 \text{ e \AA}^{-3}$

Extinction correction: none

Absolute structure: Flack (1983), 659 Friedel pairs

Flack parameter: $-0.024 (13)$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.42247 (3)	0.38038 (3)	0.13013 (11)	0.04922 (17)
S1	0.5000	0.0000	0.2536 (3)	0.0305 (3)
S2	0.53734 (6)	0.11976 (7)	-0.0036 (2)	0.0319 (2)
C1	0.4113 (3)	0.1583 (3)	-0.1526 (8)	0.0311 (8)
H1A	0.4221	0.2196	-0.2718	0.037*
H1B	0.3853	0.1024	-0.2750	0.037*
C2	0.3293 (3)	0.1822 (3)	0.0620 (7)	0.0271 (8)
C3	0.2529 (3)	0.1057 (3)	0.1324 (8)	0.0356 (9)
H3A	0.2544	0.0412	0.0395	0.043*
C4	0.1784 (3)	0.1239 (3)	0.3296 (8)	0.0369 (9)
H4A	0.1282	0.0724	0.3722	0.044*
C5	0.1750 (3)	0.2175 (3)	0.4693 (9)	0.0433 (11)
H5A	0.1232	0.2294	0.6086	0.052*
C6	0.2470 (3)	0.2930 (3)	0.4058 (8)	0.0367 (10)
H6A	0.2446	0.3572	0.5002	0.044*
C7	0.3222 (3)	0.2750 (3)	0.2054 (8)	0.0283 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0469 (2)	0.0294 (2)	0.0713 (3)	-0.00040 (19)	-0.0036 (2)	0.0041 (2)
S1	0.0356 (7)	0.0339 (7)	0.0219 (6)	0.0098 (6)	0.000	0.000
S2	0.0286 (4)	0.0303 (4)	0.0369 (5)	0.0012 (4)	0.0002 (4)	-0.0007 (5)
C1	0.0356 (19)	0.0353 (18)	0.0224 (18)	0.0040 (16)	-0.0018 (16)	0.0010 (15)
C2	0.0272 (18)	0.0307 (19)	0.023 (2)	0.0053 (15)	-0.0051 (13)	0.0018 (15)
C3	0.043 (2)	0.037 (2)	0.027 (2)	0.0185 (18)	-0.015 (2)	-0.007 (2)
C4	0.0286 (19)	0.044 (2)	0.038 (2)	-0.0044 (18)	-0.0051 (16)	0.010 (2)
C5	0.033 (2)	0.063 (3)	0.033 (2)	0.016 (2)	0.0022 (18)	0.004 (2)
C6	0.038 (2)	0.041 (2)	0.031 (2)	0.0149 (19)	-0.0079 (19)	-0.0082 (18)
C7	0.0277 (19)	0.0294 (18)	0.028 (2)	0.0042 (14)	-0.0081 (15)	0.0033 (15)

supplementary materials

Geometric parameters (Å, °)

Br1—C7	1.911 (3)	C3—C4	1.358 (5)
S1—S2 ⁱ	2.0403 (13)	C3—H3A	0.9500
S1—S2	2.0403 (13)	C4—C5	1.389 (5)
S2—C1	1.829 (3)	C4—H4A	0.9500
C1—C2	1.496 (5)	C5—C6	1.380 (6)
C1—H1A	0.9900	C5—H5A	0.9500
C1—H1B	0.9900	C6—C7	1.374 (5)
C2—C7	1.392 (5)	C6—H6A	0.9500
C2—C3	1.435 (5)		
S2 ⁱ —S1—S2	106.21 (9)	C2—C3—H3A	119.5
C1—S2—S1	103.71 (12)	C3—C4—C5	120.5 (4)
C2—C1—S2	114.0 (3)	C3—C4—H4A	119.8
C2—C1—H1A	108.7	C5—C4—H4A	119.8
S2—C1—H1A	108.7	C6—C5—C4	120.0 (4)
C2—C1—H1B	108.7	C6—C5—H5A	120.0
S2—C1—H1B	108.7	C4—C5—H5A	120.0
H1A—C1—H1B	107.6	C7—C6—C5	119.8 (4)
C7—C2—C3	116.4 (3)	C7—C6—H6A	120.1
C7—C2—C1	124.2 (3)	C5—C6—H6A	120.1
C3—C2—C1	119.4 (3)	C6—C7—C2	122.3 (3)
C4—C3—C2	121.1 (4)	C6—C7—Br1	118.4 (3)
C4—C3—H3A	119.5	C2—C7—Br1	119.2 (3)

Symmetry codes: (i) $-x+1, -y, z$.

Fig. 1

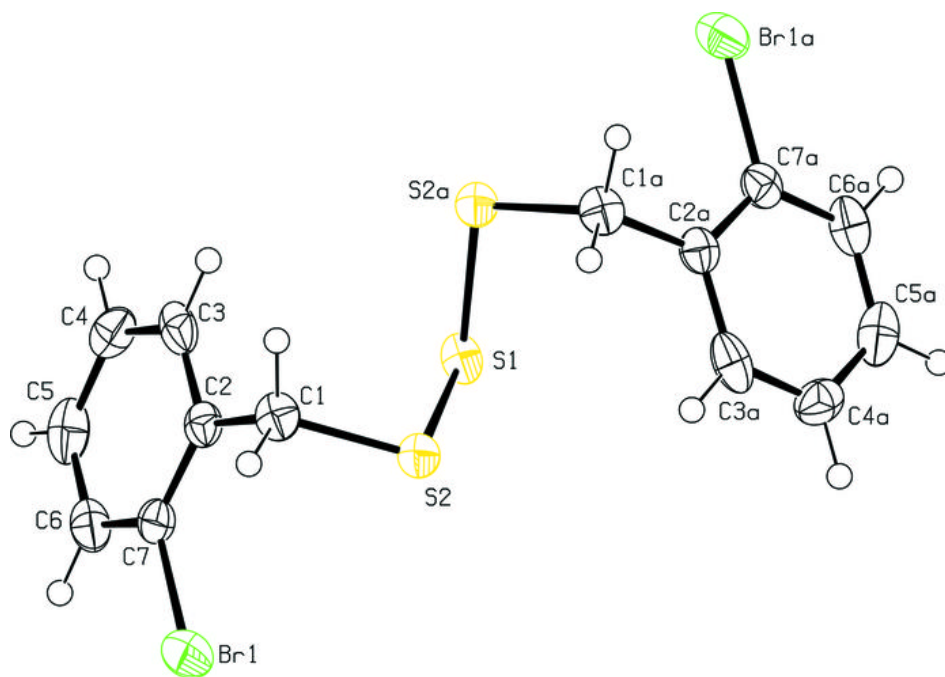


Fig. 2

