

# (Z)-4,5-Dibromo-3,3,6,6-tetramethyl-2,3,6,7-tetrahydrothiepine-1,1-dione

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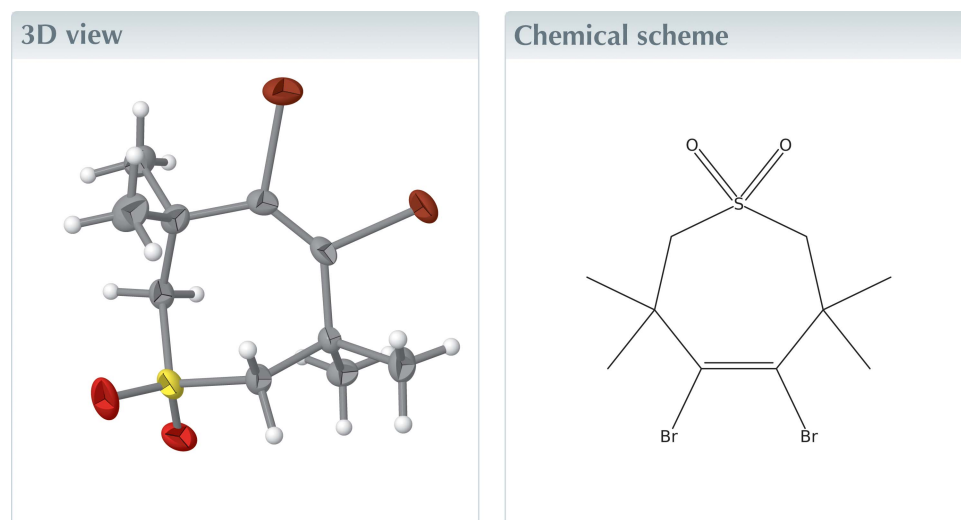
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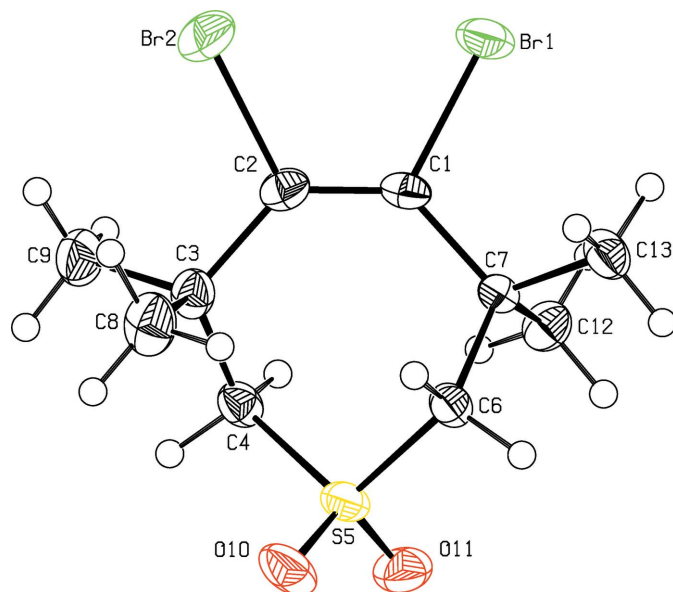
Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

The crystal of the title compound,  $C_{10}H_{16}Br_2O_2S$ , is formed from layers built from centrosymmetric pairs of molecules. The molecule adopts a twist conformation with the carbon atoms next to sulfur above or below the mean plane.



## Structure description

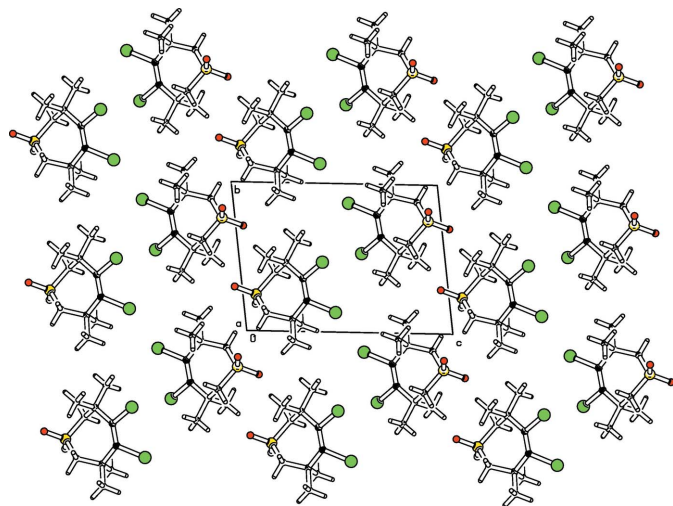
As part of our studies on the reactivity of angle-strained compounds (Krämer *et al.*, 2009; Detert 2011), the addition of bromine appeared to be a challenging project (Chiappe *et al.*, 2002; Detert *et al.* 1992). Whereas the addition of bromine to alkynes generally leads *via* bridged bromonium ions to *trans*-dibromoalkenes, the bromination of cyclooctyne gives *cis*-1,2-dibromocyclooctene (Wittig & Dorsch, 1968). While this can proceed *via* isomerization of the initially formed *trans* isomer, the addition of bromine to cycloheptynes avoids cationic intermediates (Herges *et al.* 2005). The title compound (Fig. 1) was obtained within these studies *via* addition of bromine to tetramethylthiacycloheptyne-*S,S*-dioxide (Krebs *et al.* 1979). Two identical, non-symmetrical molecules comprise the unit cell. The conformation of the seven-membered ring is similar to a twist form. The atoms C7, C1, C3, S5 are nearly coplanar with the largest deviation from planarity at C1 [0.056 (3) Å]. The atoms vicinal to sulfur adopt positions below [−0.789 (3) Å, C4] and above [0.785 (3) Å, C6] this plane. The tetrasubstituted olefin is twisted, torsion angle C7–C1–C2–C3 is −13.7 (6)° and Br1–C1–C2–Br2 at −15.3 (3)° is even larger. Two molecules are connected by a center of inversion, the packing appears as a layer structure (Fig. 2). Layers are parallel to the *a* axis, the minimal distance between bromine atoms (Br1···Br1') of different layers is 3.4168 (6) Å.



**Figure 1**  
View of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

### Synthesis and crystallization

The title compound  $C_{10}H_{16}O_2Br_2S$  was prepared from the cyclic alkyne (Krebs *et al.*, 1979; Krebs & Colberg 1980) by addition of bromine at 203 K according to the procedure given by Herges *et al.* (2005). After evaporation of the solvent, the oily compound crystallized after standing for 15 years at ambient temperature.



**Figure 2**  
Partial packing diagram. View along the *a*-axis.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{16}Br_2O_2S$
$M_r$	360.11
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	193
$a, b, c$ (Å)	5.9685 (4), 8.9642 (6), 12.4927 (9)
$\alpha, \beta, \gamma$ (°)	94.804 (6), 102.448 (5), 99.356 (5)
$V$ (Å <sup>3</sup> )	639.09 (8)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	6.49
Crystal size (mm)	0.67 × 0.39 × 0.08
Data collection	
Diffractometer	Stoe <i>IPDS 2T</i>
Absorption correction	Integration ( <i>X-RED</i> ; Stoe <i>et al.</i> , 2019)
$T_{min}, T_{max}$	0.088, 0.553
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	8129, 3038, 2686
$R_{int}$	0.023
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.663
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.089, 1.14
No. of reflections	3038
No. of parameters	140
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	1.28, -0.89

Computer programs: *X-AREA* *WinXpose*, *Recipe* and *Integrate* (Stoe & Cie, 2019), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *PLATON* (Spek, 2020).

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

### References

- Chiappe, C., De Rubertis, A., Detert, H., Lenoir, D., Wannere, C. S. & Schleyer, P. von R. (2002). *Chem. Eur. J.* **8**, 967–978.
- Detert, H. (2011). *Targets in Heterocyclic Systems*, vol. 15, edited by O. A. Attanasi & D. Spinelli, pp. 1–49. Rome: Italian Society of Chemistry.
- Detert, H., Anthony-Mayer, C. & Meier, H. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 791–792.
- Herges, R., Papafilippopoulos, A., Hess, K., Chiappe, C., Lenoir, D. & Detert, H. (2005). *Angew. Chem. Int. Ed.* **44**, 2–6.
- Krämer, G., Detert, H. & Meier, H. (2009). *Tetrahedron Lett.* **50**, 4810–4812.
- Krebs, A. & Colberg, H. (1980). *Chem. Ber.* **113**, 2007–2014.
- Krebs, A., Colberg, H., Höpfner, U., Kimling, H. & Odenthal, J. (1979). *Heterocycles*, **12**, 1153–1156.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Stoe & Cie (2019). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Wittig, G. & Dorsch, H.-L. (1968). *Justus Liebigs Ann. Chem.* **711**, 46–54.

## full crystallographic data

*IUCrData* (2023). 8, x230042 [https://doi.org/10.1107/S2414314623000421]

**(Z)-4,5-Dibromo-3,3,6,6-tetramethyl-2,3,6,7-tetrahydrothiepine-1,1-dione**

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**(Z)-4,5-Dibromo-3,3,6,6-tetramethyl-2,3,6,7-tetrahydrothiepine-1,1-dione***Crystal data*

$C_{10}H_{16}Br_2O_2S$	$Z = 2$
$M_r = 360.11$	$F(000) = 356$
Triclinic, $P\bar{1}$	$D_x = 1.871 \text{ Mg m}^{-3}$
$a = 5.9685 (4) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 8.9642 (6) \text{ \AA}$	Cell parameters from 18448 reflections
$c = 12.4927 (9) \text{ \AA}$	$\theta = 2.7\text{--}28.4^\circ$
$\alpha = 94.804 (6)^\circ$	$\mu = 6.49 \text{ mm}^{-1}$
$\beta = 102.448 (5)^\circ$	$T = 193 \text{ K}$
$\gamma = 99.356 (5)^\circ$	Plate, colourless
$V = 639.09 (8) \text{ \AA}^3$	$0.67 \times 0.39 \times 0.08 \text{ mm}$

*Data collection*

Stoe IPDS 2T	8129 measured reflections
diffractometer	3038 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	2686 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels $\text{mm}^{-1}$	$R_{\text{int}} = 0.023$
rotation method, $\omega$ scans	$\theta_{\text{max}} = 28.1^\circ$ , $\theta_{\text{min}} = 2.7^\circ$
Absorption correction: integration (XRED; Stoe et al., 2019)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.088$ , $T_{\text{max}} = 0.553$	$k = -11 \rightarrow 11$
	$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 1.4492P]$
$wR(F^2) = 0.089$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3038 reflections	$\Delta\rho_{\text{max}} = 1.28 \text{ e \AA}^{-3}$
140 parameters	$\Delta\rho_{\text{min}} = -0.89 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

*Special details*

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

**Refinement.** Hydrogen atoms attached to carbons were placed at calculated positions and were refined in the riding-model approximation with C–H = 0.95 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ .

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.15368 (7)	0.46873 (4)	0.40230 (3)	0.03826 (12)
Br2	0.21628 (8)	0.13145 (5)	0.44057 (3)	0.04584 (13)
C1	0.2846 (5)	0.3563 (4)	0.3004 (2)	0.0251 (6)
C2	0.2791 (5)	0.2074 (4)	0.3085 (3)	0.0265 (6)
C3	0.3191 (6)	0.0802 (4)	0.2281 (3)	0.0281 (7)
C4	0.2643 (5)	0.1158 (4)	0.1074 (3)	0.0266 (6)
H4A	0.115877	0.154728	0.094409	0.032*
H4B	0.235588	0.018273	0.058883	0.032*
S5	0.46965 (15)	0.24522 (9)	0.06328 (7)	0.02945 (18)
C6	0.5605 (5)	0.3987 (3)	0.1695 (3)	0.0254 (6)
H6A	0.674923	0.368072	0.229620	0.031*
H6B	0.645465	0.484410	0.140356	0.031*
C7	0.3767 (5)	0.4610 (3)	0.2221 (3)	0.0226 (6)
C8	0.5636 (6)	0.0428 (5)	0.2667 (4)	0.0401 (9)
H8A	0.586667	-0.036909	0.213729	0.060*
H8B	0.578609	0.006994	0.339500	0.060*
H8C	0.681643	0.134537	0.271694	0.060*
C9	0.1385 (7)	-0.0676 (4)	0.2226 (4)	0.0396 (8)
H9A	0.155064	-0.144330	0.165629	0.059*
H9B	-0.019675	-0.045063	0.204374	0.059*
H9C	0.165983	-0.106587	0.294348	0.059*
O10	0.6724 (5)	0.1800 (3)	0.0569 (3)	0.0434 (7)
O11	0.3486 (5)	0.2945 (3)	-0.0361 (2)	0.0416 (6)
C12	0.1749 (6)	0.4981 (4)	0.1357 (3)	0.0300 (7)
H12A	0.238109	0.561693	0.085059	0.045*
H12B	0.078319	0.553061	0.172897	0.045*
H12C	0.079307	0.403256	0.093870	0.045*
C13	0.5228 (6)	0.6125 (4)	0.2895 (3)	0.0315 (7)
H13A	0.593338	0.675014	0.240333	0.047*
H13B	0.646160	0.589899	0.348092	0.047*
H13C	0.420881	0.668146	0.322457	0.047*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0480 (2)	0.0446 (2)	0.03061 (19)	0.01935 (16)	0.02005 (15)	0.00268 (15)
Br2	0.0666 (3)	0.0435 (2)	0.0296 (2)	0.00595 (19)	0.01546 (18)	0.01398 (16)
C1	0.0262 (14)	0.0332 (16)	0.0169 (13)	0.0094 (12)	0.0058 (11)	0.0003 (12)
C2	0.0254 (15)	0.0331 (16)	0.0230 (15)	0.0073 (12)	0.0064 (12)	0.0086 (13)
C3	0.0255 (15)	0.0251 (15)	0.0356 (18)	0.0066 (12)	0.0088 (13)	0.0062 (13)
C4	0.0242 (14)	0.0244 (15)	0.0296 (16)	0.0013 (12)	0.0075 (12)	-0.0034 (12)
S5	0.0316 (4)	0.0281 (4)	0.0289 (4)	-0.0004 (3)	0.0151 (3)	-0.0049 (3)
C6	0.0250 (14)	0.0226 (14)	0.0285 (16)	0.0033 (11)	0.0083 (12)	-0.0011 (12)
C7	0.0267 (14)	0.0217 (14)	0.0209 (14)	0.0066 (11)	0.0079 (11)	0.0008 (11)
C8	0.0314 (18)	0.0378 (19)	0.055 (2)	0.0150 (15)	0.0094 (16)	0.0136 (17)

C9	0.041 (2)	0.0278 (17)	0.052 (2)	0.0009 (15)	0.0191 (17)	0.0054 (16)
O10	0.0377 (14)	0.0372 (14)	0.0587 (18)	0.0019 (11)	0.0290 (13)	-0.0124 (12)
O11	0.0546 (16)	0.0428 (15)	0.0247 (12)	-0.0024 (12)	0.0133 (11)	0.0007 (11)
C12	0.0280 (16)	0.0327 (17)	0.0300 (17)	0.0070 (13)	0.0052 (13)	0.0087 (13)
C13	0.0373 (18)	0.0261 (16)	0.0291 (17)	0.0066 (13)	0.0053 (14)	-0.0034 (13)

*Geometric parameters (Å, °)*

Br1—C1	1.927 (3)	C6—H6B	0.9900
Br2—C2	1.923 (3)	C7—C12	1.536 (4)
C1—C2	1.343 (5)	C7—C13	1.556 (4)
C1—C7	1.536 (4)	C8—H8A	0.9800
C2—C3	1.538 (5)	C8—H8B	0.9800
C3—C8	1.535 (5)	C8—H8C	0.9800
C3—C4	1.543 (5)	C9—H9A	0.9800
C3—C9	1.552 (5)	C9—H9B	0.9800
C4—S5	1.758 (3)	C9—H9C	0.9800
C4—H4A	0.9900	C12—H12A	0.9800
C4—H4B	0.9900	C12—H12B	0.9800
S5—O11	1.438 (3)	C12—H12C	0.9800
S5—O10	1.441 (3)	C13—H13A	0.9800
S5—C6	1.758 (3)	C13—H13B	0.9800
C6—C7	1.547 (4)	C13—H13C	0.9800
C6—H6A	0.9900		
C2—C1—C7	132.0 (3)	C1—C7—C12	111.0 (3)
C2—C1—Br1	117.5 (2)	C1—C7—C6	112.8 (2)
C7—C1—Br1	110.4 (2)	C12—C7—C6	112.6 (3)
C1—C2—C3	130.6 (3)	C1—C7—C13	109.7 (3)
C1—C2—Br2	118.0 (2)	C12—C7—C13	108.7 (3)
C3—C2—Br2	111.4 (2)	C6—C7—C13	101.5 (2)
C8—C3—C2	110.8 (3)	C3—C8—H8A	109.5
C8—C3—C4	113.7 (3)	C3—C8—H8B	109.5
C2—C3—C4	112.0 (3)	H8A—C8—H8B	109.5
C8—C3—C9	107.6 (3)	C3—C8—H8C	109.5
C2—C3—C9	110.2 (3)	H8A—C8—H8C	109.5
C4—C3—C9	102.1 (3)	H8B—C8—H8C	109.5
C3—C4—S5	119.1 (2)	C3—C9—H9A	109.5
C3—C4—H4A	107.5	C3—C9—H9B	109.5
S5—C4—H4A	107.5	H9A—C9—H9B	109.5
C3—C4—H4B	107.5	C3—C9—H9C	109.5
S5—C4—H4B	107.5	H9A—C9—H9C	109.5
H4A—C4—H4B	107.0	H9B—C9—H9C	109.5
O11—S5—O10	116.84 (18)	C7—C12—H12A	109.5
O11—S5—C4	107.11 (16)	C7—C12—H12B	109.5
O10—S5—C4	110.42 (17)	H12A—C12—H12B	109.5
O11—S5—C6	109.96 (16)	C7—C12—H12C	109.5
O10—S5—C6	106.90 (16)	H12A—C12—H12C	109.5

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C4—S5—C6	105.01 (15)	H12B—C12—H12C	109.5
C7—C6—S5	119.5 (2)	C7—C13—H13A	109.5
C7—C6—H6A	107.4	C7—C13—H13B	109.5
S5—C6—H6A	107.4	H13A—C13—H13B	109.5
C7—C6—H6B	107.4	C7—C13—H13C	109.5
S5—C6—H6B	107.4	H13A—C13—H13C	109.5
H6A—C6—H6B	107.0	H13B—C13—H13C	109.5
C7—C1—C2—C3	-13.7 (6)	C3—C4—S5—O10	70.2 (3)
Br1—C1—C2—C3	165.7 (3)	C3—C4—S5—C6	-44.7 (3)
C7—C1—C2—Br2	165.3 (3)	O11—S5—C6—C7	71.3 (3)
Br1—C1—C2—Br2	-15.3 (3)	O10—S5—C6—C7	-161.0 (3)
C1—C2—C3—C8	102.4 (4)	C4—S5—C6—C7	-43.7 (3)
Br2—C2—C3—C8	-76.6 (3)	C2—C1—C7—C12	105.5 (4)
C1—C2—C3—C4	-25.7 (5)	Br1—C1—C7—C12	-73.9 (3)
Br2—C2—C3—C4	155.3 (2)	C2—C1—C7—C6	-21.9 (5)
C1—C2—C3—C9	-138.6 (4)	Br1—C1—C7—C6	158.6 (2)
Br2—C2—C3—C9	42.4 (3)	C2—C1—C7—C13	-134.3 (4)
C8—C3—C4—S5	-48.3 (4)	Br1—C1—C7—C13	46.3 (3)
C2—C3—C4—S5	78.3 (3)	S5—C6—C7—C1	74.8 (3)
C9—C3—C4—S5	-163.9 (2)	S5—C6—C7—C12	-51.8 (3)
C3—C4—S5—O11	-161.6 (2)	S5—C6—C7—C13	-167.8 (2)

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