



Crystal structure of 2-(3-bromophenyl)-1,3-dithiane

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Received 4 February 2015; accepted 10 February 2015

Edited by P. C. Healy, Griffith University, Australia

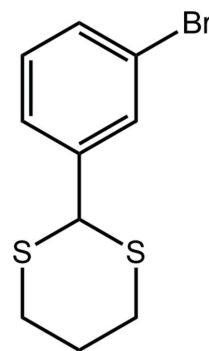
In the title compound, C₁₀H₁₁BrS₂, the 1,3-dithiane ring has a chair conformation with the 1,4-disposed C atoms being above and below the remaining four atoms. The bromobenzene ring occupies an equatorial position and forms a dihedral angle of 86.38 (12)° with the least-squares plane through the 1,3-dithiane ring. Thus, to a first approximation the molecule has mirror symmetry with the mirror containing the bromobenzene ring and the 1,4-disposed C atoms of the 1,3-dithiane ring. In the crystal, molecules associate *via* weak methylene–bromobenzene C–H...π and π–π [Cg...Cg = 3.7770 (14) Å for centrosymmetrically related bromobenzene rings] interactions, forming supramolecular layers parallel to [101̄]; these stack with no specific intermolecular interactions between them.

Keywords: crystal structure; 1,3-dithiane; conformation; C–H...π interactions; π–π interactions.

CCDC reference: 1048592

1. Related literature

For the original synthesis and characterization of the title compound, see: Ballesteros *et al.* (2005). For the structure of the unsubstituted parent compound which is virtually superimposable on the title compound, see: Kalf & Romers (1966).



2. Experimental

2.1. Crystal data

C ₁₀ H ₁₁ BrS ₂	<i>V</i> = 1114.86 (9) Å ³
<i>M_r</i> = 275.22	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.9821 (4) Å	<i>μ</i> = 4.01 mm ⁻¹
<i>b</i> = 11.3871 (5) Å	<i>T</i> = 296 K
<i>c</i> = 11.0550 (5) Å	0.33 × 0.28 × 0.16 mm
<i>β</i> = 99.604 (3)°	

2.2. Data collection

Bruker APEXII CCD diffractometer	7307 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2060 independent reflections
<i>T</i> _{min} = 0.374, <i>T</i> _{max} = 0.745	1820 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.029

2.3. Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.031	118 parameters
<i>wR</i> (<i>F</i> ²) = 0.082	H-atom parameters constrained
<i>S</i> = 1.06	Δρ _{max} = 0.54 e Å ⁻³
2060 reflections	Δρ _{min} = -0.65 e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C5–C10 ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C2–H2b...Cg1 ¹	0.97	2.83	3.668 (4)	146

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SIR2014* (Burla *et al.*, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *MarvinSketch* (ChemAxon, 2010) and *pubCIF* (Westrip, 2010).

Acknowledgements

We thank Professor Regina H. A. Santos from IQSC–USP for the X-ray data collection. The Brazilian agencies CNPq (305626/2013-2 to JZS, 306121/2013-2 to IC and 308320/2010-7

to HAS), FAPESP (2012/00424-2 and 2013/21925-2) and CAPES are acknowledged for financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HG5429).

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supporting information

Acta Cryst. (2015). E71, o179–o180 [doi:10.1107/S2056989015002832]

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S1. Experimental

A solution of 3-bromobenzaldehyde (0.037 mol, 1 equiv.) in chloroform (20 ml) was combined with an equimolar amount of propane-1,3-dithiol (3.7 ml, 0.037 mol) at room temperature. The solution was stirred for 1 h at this temperature, then cooled to -20 °C after which BF₃ etherate (0.46 ml, 0.0037 mol, 0.1 equiv.) was added drop-wise. The reaction solution was allowed to warm to room temperature and stirred overnight. After this time, the solution was washed three times each with water, 10% aqueous KOH, then water followed by drying over MgSO₄. Evaporation of the solvent furnishes a pure product as colourless crystals in 90% yield. To obtain crystals suitable for X-ray analysis, the product was crystallized from CH₃OH. The spectroscopic data matched those reported in the literature (Ballesteros *et al.*, 2005).

S2. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.95–0.98 Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

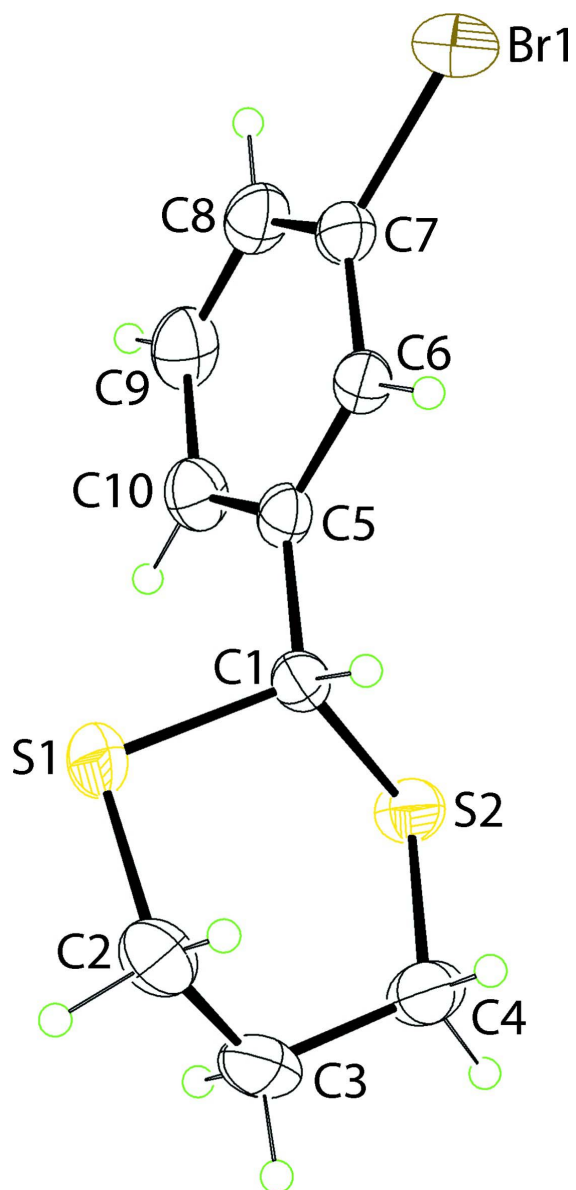
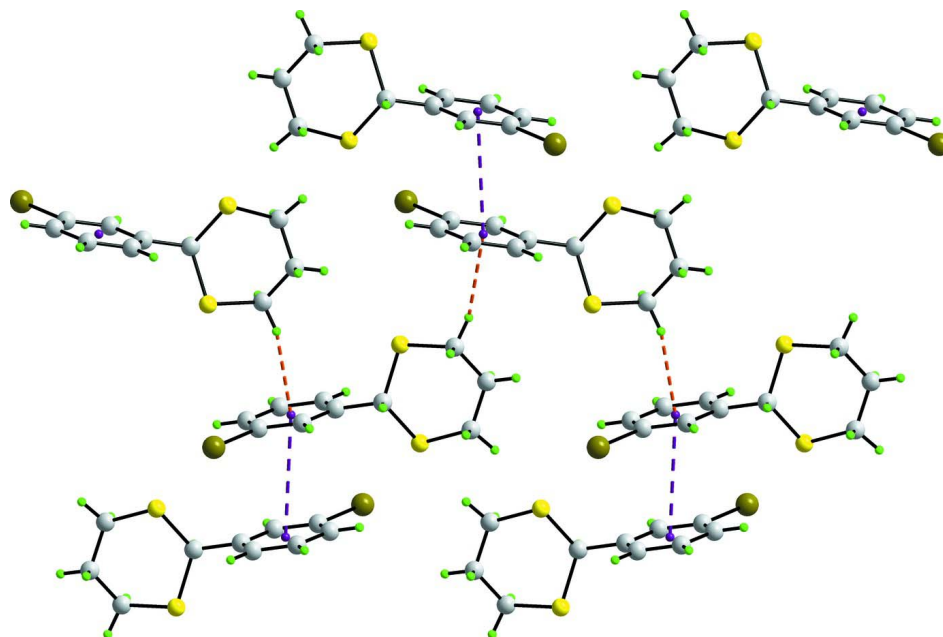
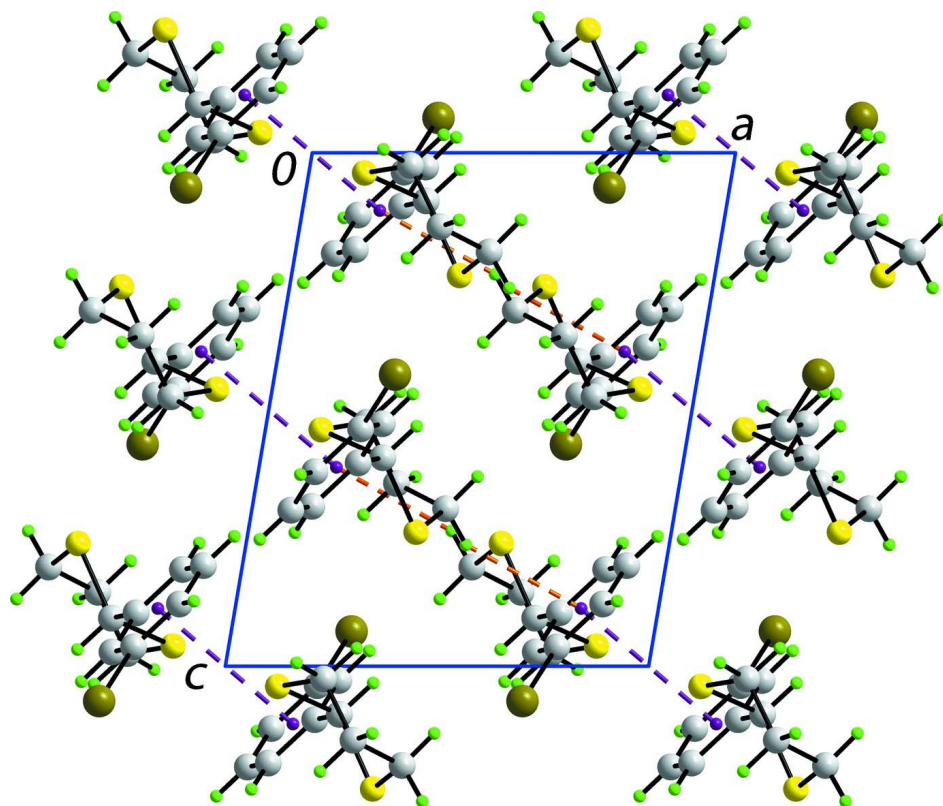


Figure 1

The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level.

**Figure 2**

A view of the supramolecular layer parallel to $[10\bar{1}]$ mediated by $C-H\cdots\pi$ and $\pi-\pi$ interactions shown as orange and purple dashed lines, respectively.

**Figure 3**

A view in projection down the b axis of the unit-cell contents. The $C-H\cdots\pi$ and $\pi-\pi$ interactions shown as orange and purple dashed lines, respectively.

2-(3-Bromophenyl)-1,3-dithiane

Crystal data

C₁₀H₁₁BrS₂ $M_r = 275.22$ Monoclinic, $P2_1/c$ $a = 8.9821$ (4) Å $b = 11.3871$ (5) Å $c = 11.0550$ (5) Å $\beta = 99.604$ (3)° $V = 1114.86$ (9) Å³ $Z = 4$ $F(000) = 552$ $D_x = 1.640$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4286 reflections

 $\theta = 2.6$ – 25.4 ° $\mu = 4.01$ mm⁻¹ $T = 296$ K

Prism, colourless

 $0.33 \times 0.28 \times 0.16$ mm

Data collection

Bruker APEXII CCD

diffractometer

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.374$, $T_{\max} = 0.745$

7307 measured reflections

2060 independent reflections

1820 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.029$ $\theta_{\max} = 25.4$ °, $\theta_{\min} = 2.3$ ° $h = -9 \rightarrow 10$ $k = -13 \rightarrow 12$ $l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.031$ $wR(F^2) = 0.082$ $S = 1.06$

2060 reflections

118 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 0.6522P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.54$ e Å⁻³ $\Delta\rho_{\min} = -0.65$ e Å⁻³

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.71577 (4)	1.19362 (3)	1.06788 (3)	0.06773 (15)
S1	0.60308 (9)	0.70880 (7)	0.76097 (6)	0.0565 (2)
S2	0.86833 (7)	0.65738 (6)	0.96061 (6)	0.04880 (19)
C1	0.7115 (3)	0.7543 (2)	0.9063 (2)	0.0373 (5)
H1	0.6439	0.7542	0.9674	0.045*
C2	0.5426 (4)	0.5670 (3)	0.8068 (3)	0.0657 (8)
H2A	0.4799	0.5784	0.8692	0.079*
H2B	0.4805	0.5306	0.7366	0.079*
C3	0.6689 (4)	0.4839 (3)	0.8560 (3)	0.0649 (8)
H3A	0.6262	0.4076	0.8690	0.078*
H3B	0.7342	0.4746	0.7950	0.078*

C4	0.7631 (3)	0.5247 (3)	0.9752 (3)	0.0587 (7)
H4A	0.8331	0.4628	1.0065	0.070*
H4B	0.6969	0.5378	1.0349	0.070*
C5	0.7677 (2)	0.8778 (2)	0.8960 (2)	0.0377 (5)
C6	0.7265 (3)	0.9638 (2)	0.9723 (2)	0.0382 (5)
H6	0.6661	0.9450	1.0301	0.046*
C7	0.7754 (3)	1.0778 (2)	0.9623 (2)	0.0432 (6)
C8	0.8665 (3)	1.1081 (3)	0.8788 (2)	0.0526 (7)
H8	0.8994	1.1851	0.8733	0.063*
C9	0.9078 (3)	1.0224 (3)	0.8039 (2)	0.0575 (7)
H9	0.9692	1.0417	0.7469	0.069*
C10	0.8598 (3)	0.9074 (3)	0.8115 (2)	0.0496 (6)
H10	0.8892	0.8503	0.7602	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0883 (3)	0.0415 (2)	0.0730 (2)	0.00622 (14)	0.01259 (18)	-0.00728 (13)
S1	0.0631 (5)	0.0554 (4)	0.0434 (4)	-0.0065 (3)	-0.0132 (3)	0.0005 (3)
S2	0.0406 (3)	0.0434 (4)	0.0579 (4)	0.0002 (3)	-0.0047 (3)	0.0017 (3)
C1	0.0393 (12)	0.0381 (13)	0.0343 (12)	0.0000 (10)	0.0053 (9)	-0.0026 (10)
C2	0.0624 (18)	0.0590 (19)	0.0669 (18)	-0.0188 (15)	-0.0145 (15)	-0.0067 (15)
C3	0.075 (2)	0.0415 (16)	0.073 (2)	-0.0107 (14)	-0.0016 (16)	-0.0100 (14)
C4	0.0611 (18)	0.0409 (15)	0.0682 (18)	-0.0039 (13)	-0.0062 (14)	0.0077 (13)
C5	0.0353 (12)	0.0419 (13)	0.0339 (11)	-0.0019 (10)	-0.0002 (9)	0.0037 (10)
C6	0.0390 (12)	0.0402 (13)	0.0348 (11)	-0.0006 (10)	0.0043 (9)	0.0028 (10)
C7	0.0449 (14)	0.0395 (13)	0.0412 (13)	-0.0015 (10)	-0.0041 (10)	0.0014 (10)
C8	0.0559 (16)	0.0479 (16)	0.0507 (15)	-0.0157 (13)	-0.0007 (12)	0.0100 (12)
C9	0.0554 (17)	0.072 (2)	0.0476 (15)	-0.0166 (14)	0.0153 (13)	0.0098 (14)
C10	0.0502 (15)	0.0592 (17)	0.0414 (13)	-0.0046 (13)	0.0130 (11)	-0.0015 (12)

Geometric parameters (Å, °)

Br1—C7	1.897 (3)	C4—H4A	0.9700
S1—C2	1.803 (3)	C4—H4B	0.9700
S1—C1	1.810 (2)	C5—C6	1.383 (3)
S2—C4	1.803 (3)	C5—C10	1.389 (4)
S2—C1	1.811 (2)	C6—C7	1.381 (3)
C1—C5	1.505 (3)	C6—H6	0.9300
C1—H1	0.9800	C7—C8	1.375 (4)
C2—C3	1.507 (4)	C8—C9	1.371 (4)
C2—H2A	0.9700	C8—H8	0.9300
C2—H2B	0.9700	C9—C10	1.385 (4)
C3—C4	1.515 (4)	C9—H9	0.9300
C3—H3A	0.9700	C10—H10	0.9300
C3—H3B	0.9700		
C2—S1—C1	98.61 (12)	S2—C4—H4A	108.8

C4—S2—C1	98.59 (13)	C3—C4—H4B	108.8
C5—C1—S1	109.74 (15)	S2—C4—H4B	108.8
C5—C1—S2	110.01 (16)	H4A—C4—H4B	107.7
S1—C1—S2	113.16 (13)	C6—C5—C10	119.2 (2)
C5—C1—H1	107.9	C6—C5—C1	119.3 (2)
S1—C1—H1	107.9	C10—C5—C1	121.5 (2)
S2—C1—H1	107.9	C7—C6—C5	119.7 (2)
C3—C2—S1	114.8 (2)	C7—C6—H6	120.1
C3—C2—H2A	108.6	C5—C6—H6	120.1
S1—C2—H2A	108.6	C8—C7—C6	121.5 (3)
C3—C2—H2B	108.6	C8—C7—Br1	120.0 (2)
S1—C2—H2B	108.6	C6—C7—Br1	118.53 (19)
H2A—C2—H2B	107.5	C9—C8—C7	118.6 (3)
C4—C3—C2	113.5 (3)	C9—C8—H8	120.7
C4—C3—H3A	108.9	C7—C8—H8	120.7
C2—C3—H3A	108.9	C8—C9—C10	121.2 (3)
C4—C3—H3B	108.9	C8—C9—H9	119.4
C2—C3—H3B	108.9	C10—C9—H9	119.4
H3A—C3—H3B	107.7	C9—C10—C5	119.8 (3)
C3—C4—S2	113.8 (2)	C9—C10—H10	120.1
C3—C4—H4A	108.8	C5—C10—H10	120.1
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C2—S1—C1—C5	-175.91 (19)	S2—C1—C5—C10	66.0 (3)
C2—S1—C1—S2	60.79 (17)	C10—C5—C6—C7	0.9 (3)
C4—S2—C1—C5	175.20 (17)	C1—C5—C6—C7	-179.0 (2)
C4—S2—C1—S1	-61.65 (17)	C5—C6—C7—C8	-0.9 (4)
C1—S1—C2—C3	-58.8 (3)	C5—C6—C7—Br1	179.66 (17)
S1—C2—C3—C4	65.2 (4)	C6—C7—C8—C9	0.5 (4)
C2—C3—C4—S2	-65.7 (4)	Br1—C7—C8—C9	179.9 (2)
C1—S2—C4—C3	60.0 (3)	C7—C8—C9—C10	-0.2 (4)
S1—C1—C5—C6	120.8 (2)	C8—C9—C10—C5	0.3 (4)
S2—C1—C5—C6	-114.1 (2)	C6—C5—C10—C9	-0.7 (4)
S1—C1—C5—C10	-59.1 (3)	C1—C5—C10—C9	179.3 (2)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C5—C10 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C2—H2b \cdots Cg1 ⁱ	0.97	2.83	3.668 (4)	146

Symmetry code: (i) $-x+1, y-1/2, -z+3/2$.