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6,14-Dibromo-2,11-dithia[3.3]paracyclophane

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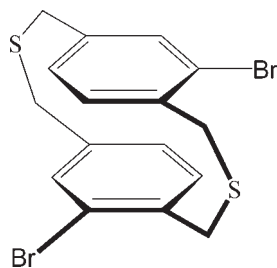
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.041; wR factor = 0.115; data-to-parameter ratio = 18.6.

In the title compound, $\text{C}_{16}\text{H}_{14}\text{Br}_2\text{S}_2$ [systematic name: 1²,5²-dibromo-2,7-dithia-1,5(1,4)-dibenzenaocetaphane], the centroids of the two benzene rings are separated by 3.313 (5) Å. The crystal packing exhibits weak intermolecular $\text{S}\cdots\text{S}$ contacts of 3.538 (2) Å.

Related literature

For the preparation of the title compound, see: Wang *et al.* (2003, 2006). For a related structure, see: Huang *et al.* (2010).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{14}\text{Br}_2\text{S}_2$
 $M_r = 430.21$
 Orthorhombic, $Pbca$
 $a = 9.0563$ (11) Å
 $b = 13.8931$ (17) Å
 $c = 24.641$ (3) Å

$V = 3100.4$ (7) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 5.49$ mm⁻¹
 $T = 298$ K
 $0.26 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.330$, $T_{\max} = 0.610$

21950 measured reflections
 3372 independent reflections
 2150 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.12$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.115$
 $S = 0.99$
 3372 reflections

181 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to Xiang Gao Meng for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2739).

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supplementary materials

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6,14-Dibromo-2,11-dithia[3.3]paracyclophane

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Comment

As a contribution to a structural study of dithia[3.3]paracyclophane derivatives with the bromine substituents (Huang *et al.*, 2010), herewith we present the crystal structure of the title compound (Fig. 1).

The short distance of 3.313 (5) Å between the centroids of two benzene rings is less than the normal packing distance (3.4 Å) between the aromatic rings in organic compounds, thus supporting potential transannular π - π interaction between the rings in the cyclophane unit.

Experimental

The dithiaparacyclophanes were prepared by coupling the corresponding pair of dithiol and dibromide under high dilution conditions (Wang *et al.*, 2003, 2006). A solution with equimolar amounts of the dithiol and the dibromide in degassed THF (500 ml) was added dropwise under N₂ over 12 h to a refluxing solution of K₂CO₃ (5 equiv) in EtOH (1.2 L). After an additional 2 h at the reflux temperature, the mixture was cooled and the solvent were removed. The resulting residue was treated with CH₂Cl₂(300 ml) and water (300 ml).The organic phase was separated, the aqueous extracted with CH₂Cl₂ three times. The combined organic layers were dried over Na₂SO₄, then solvent was removed, and the resulting solid was chromatographed on silica gel using CH₂Cl₂ petroleum ether (1:1, v/v) as eluent.

Refinement

All H atoms were initially located in a difference map, but were constrained to an idealized geometry. Constrained bond lengths and isotropic displacement parameters: (C—H = 0.93 Å) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and (C—H = 0.97 Å) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene, and (C—H = 0.96 Å) and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl.

Figures

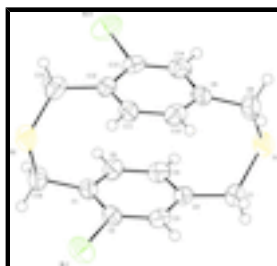


Fig. 1. A view of (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level.

1²,5²-dibromo-2,7-dithia-1,5(1,4)-dibenzenaocaphane

Crystal data

$C_{16}H_{14}Br_2S_2$	$F(000) = 1696$
$M_r = 430.21$	$D_x = 1.839 \text{ Mg m}^{-3}$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P\ 2ac\ 2ab$	Cell parameters from 5026 reflections
$a = 9.0563 (11) \text{ \AA}$	$\theta = 2.8\text{--}25.5^\circ$
$b = 13.8931 (17) \text{ \AA}$	$\mu = 5.49 \text{ mm}^{-1}$
$c = 24.641 (3) \text{ \AA}$	$T = 298 \text{ K}$
$V = 3100.4 (7) \text{ \AA}^3$	Block, colourless
$Z = 8$	$0.26 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEX diffractometer	3372 independent reflections
Radiation source: fine-focus sealed tube graphite	2150 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.12$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 1.7^\circ$
$T_{\text{min}} = 0.330$, $T_{\text{max}} = 0.610$	$h = -10 \rightarrow 11$
21950 measured reflections	$k = -17 \rightarrow 17$
	$l = -31 \rightarrow 31$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.115$	H-atom parameters constrained
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$
3372 reflections	where $P = (F_o^2 + 2F_c^2)/3$
181 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.93 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

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.

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	-0.01106 (5)	0.31316 (4)	0.233829 (17)	0.05380 (18)
Br2	-0.18330 (6)	0.72155 (4)	0.04515 (2)	0.0638 (2)
C1	-0.0858 (4)	0.4030 (3)	0.13260 (15)	0.0325 (9)
C2	0.0281 (4)	0.3739 (3)	0.16606 (15)	0.0324 (9)
C3	0.1766 (4)	0.3880 (3)	0.15182 (16)	0.0364 (9)
H3	0.2509	0.3694	0.1757	0.044*
C4	0.2127 (4)	0.4289 (3)	0.10301 (17)	0.0364 (9)
C5	0.0981 (4)	0.4501 (3)	0.06696 (15)	0.0397 (10)
H5	0.1197	0.4726	0.0323	0.048*
C6	-0.0453 (4)	0.4379 (3)	0.08239 (15)	0.0366 (9)
H6	-0.1194	0.4540	0.0579	0.044*
C7	0.3717 (4)	0.4516 (3)	0.0900 (2)	0.0507 (11)
H7A	0.4112	0.3984	0.0690	0.061*
H7B	0.4260	0.4536	0.1239	0.061*
C8	0.3707 (5)	0.6542 (3)	0.1030 (2)	0.0527 (12)
H8A	0.4314	0.6433	0.1348	0.063*
H8B	0.3986	0.7160	0.0878	0.063*
C9	0.2122 (4)	0.6589 (3)	0.12027 (16)	0.0380 (10)
C10	0.1679 (4)	0.6251 (3)	0.16986 (17)	0.0420 (10)
H10	0.2385	0.6104	0.1960	0.050*
C11	0.0198 (4)	0.6126 (3)	0.18176 (16)	0.0353 (9)
H11	-0.0071	0.5876	0.2153	0.042*
C12	-0.0886 (4)	0.6365 (3)	0.14498 (15)	0.0342 (9)
C13	-0.0416 (5)	0.6791 (3)	0.09759 (17)	0.0379 (10)
C14	0.1044 (5)	0.6900 (3)	0.08435 (17)	0.0432 (10)
H14	0.1310	0.7181	0.0515	0.052*
C15	-0.2488 (4)	0.6110 (3)	0.15519 (18)	0.0492 (11)
H15A	-0.2963	0.6022	0.1203	0.059*
H15B	-0.2955	0.6659	0.1725	0.059*
C16	-0.2467 (4)	0.4062 (3)	0.15006 (17)	0.0435 (10)
H16A	-0.2715	0.3461	0.1679	0.052*
H16B	-0.3084	0.4120	0.1181	0.052*
S1	0.41002 (13)	0.56115 (8)	0.05360 (5)	0.0539 (3)
S2	-0.28742 (12)	0.50583 (8)	0.19606 (5)	0.0497 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0655 (3)	0.0599 (3)	0.0360 (3)	-0.0119 (2)	-0.0004 (2)	0.0092 (2)

supplementary materials

Br2	0.0722 (4)	0.0703 (4)	0.0490 (3)	0.0220 (3)	-0.0132 (2)	0.0041 (3)
C1	0.034 (2)	0.030 (2)	0.033 (2)	-0.0036 (17)	0.0022 (16)	-0.0072 (17)
C2	0.037 (2)	0.033 (2)	0.0276 (19)	-0.0034 (17)	0.0013 (16)	0.0008 (16)
C3	0.039 (2)	0.032 (2)	0.038 (2)	0.0051 (18)	-0.0051 (18)	-0.0020 (18)
C4	0.035 (2)	0.028 (2)	0.046 (2)	0.0032 (18)	0.0047 (17)	-0.0039 (18)
C5	0.050 (3)	0.039 (2)	0.030 (2)	0.006 (2)	0.0070 (18)	-0.0010 (18)
C6	0.032 (2)	0.043 (2)	0.035 (2)	0.0051 (19)	-0.0032 (17)	-0.0034 (19)
C7	0.034 (2)	0.046 (3)	0.072 (3)	0.004 (2)	0.014 (2)	0.002 (2)
C8	0.040 (3)	0.051 (3)	0.067 (3)	-0.006 (2)	0.016 (2)	-0.010 (2)
C9	0.039 (2)	0.027 (2)	0.047 (2)	-0.0050 (18)	0.0051 (19)	-0.0080 (18)
C10	0.042 (3)	0.041 (2)	0.042 (2)	0.003 (2)	-0.0049 (19)	-0.009 (2)
C11	0.039 (2)	0.036 (2)	0.031 (2)	-0.0020 (18)	0.0074 (17)	-0.0042 (17)
C12	0.036 (2)	0.033 (2)	0.034 (2)	0.0043 (18)	0.0072 (17)	-0.0033 (17)
C13	0.045 (2)	0.031 (2)	0.038 (2)	0.0117 (19)	-0.0023 (18)	-0.0021 (18)
C14	0.055 (3)	0.034 (2)	0.040 (2)	0.002 (2)	0.011 (2)	-0.0012 (19)
C15	0.038 (2)	0.054 (3)	0.056 (3)	0.010 (2)	0.007 (2)	-0.004 (2)
C16	0.033 (2)	0.048 (3)	0.049 (2)	-0.005 (2)	0.002 (2)	-0.006 (2)
S1	0.0477 (7)	0.0482 (7)	0.0658 (8)	-0.0043 (6)	0.0279 (6)	-0.0069 (6)
S2	0.0453 (7)	0.0557 (7)	0.0481 (6)	-0.0039 (6)	0.0205 (5)	-0.0097 (6)

Geometric parameters (Å, °)

Br1—C2	1.905 (4)	C8—H8A	0.9700
Br2—C13	1.914 (4)	C8—H8B	0.9700
C1—C6	1.379 (5)	C9—C10	1.369 (6)
C1—C2	1.381 (5)	C9—C14	1.387 (6)
C1—C16	1.519 (5)	C10—C11	1.384 (5)
C2—C3	1.403 (5)	C10—H10	0.9300
C3—C4	1.370 (5)	C11—C12	1.377 (5)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.398 (5)	C12—C13	1.377 (5)
C4—C7	1.508 (5)	C12—C15	1.514 (6)
C5—C6	1.364 (5)	C13—C14	1.370 (6)
C5—H5	0.9300	C14—H14	0.9300
C6—H6	0.9300	C15—S2	1.809 (5)
C7—S1	1.800 (4)	C15—H15A	0.9700
C7—H7A	0.9700	C15—H15B	0.9700
C7—H7B	0.9700	C16—S2	1.827 (4)
C8—C9	1.498 (6)	C16—H16A	0.9700
C8—S1	1.811 (4)	C16—H16B	0.9700
C6—C1—C2	116.1 (3)	C10—C9—C8	121.3 (4)
C6—C1—C16	119.9 (4)	C14—C9—C8	120.5 (4)
C2—C1—C16	123.8 (3)	C9—C10—C11	121.1 (4)
C1—C2—C3	121.7 (3)	C9—C10—H10	119.5
C1—C2—Br1	120.9 (3)	C11—C10—H10	119.5
C3—C2—Br1	117.4 (3)	C12—C11—C10	121.4 (4)
C4—C3—C2	120.4 (4)	C12—C11—H11	119.3
C4—C3—H3	119.8	C10—C11—H11	119.3
C2—C3—H3	119.8	C11—C12—C13	116.2 (3)

C3—C4—C5	117.9 (4)	C11—C12—C15	121.2 (4)
C3—C4—C7	120.1 (4)	C13—C12—C15	122.5 (4)
C5—C4—C7	122.0 (4)	C14—C13—C12	123.2 (4)
C6—C5—C4	120.3 (4)	C14—C13—Br2	116.9 (3)
C6—C5—H5	119.9	C12—C13—Br2	119.8 (3)
C4—C5—H5	119.9	C13—C14—C9	119.5 (4)
C5—C6—C1	123.2 (4)	C13—C14—H14	120.2
C5—C6—H6	118.4	C9—C14—H14	120.2
C1—C6—H6	118.4	C12—C15—S2	117.8 (3)
C4—C7—S1	117.8 (3)	C12—C15—H15A	107.9
C4—C7—H7A	107.9	S2—C15—H15A	107.9
S1—C7—H7A	107.9	C12—C15—H15B	107.9
C4—C7—H7B	107.9	S2—C15—H15B	107.9
S1—C7—H7B	107.9	H15A—C15—H15B	107.2
H7A—C7—H7B	107.2	C1—C16—S2	113.0 (3)
C9—C8—S1	114.2 (3)	C1—C16—H16A	109.0
C9—C8—H8A	108.7	S2—C16—H16A	109.0
S1—C8—H8A	108.7	C1—C16—H16B	109.0
C9—C8—H8B	108.7	S2—C16—H16B	109.0
S1—C8—H8B	108.7	H16A—C16—H16B	107.8
H8A—C8—H8B	107.6	C7—S1—C8	103.3 (2)
C10—C9—C14	118.0 (4)	C15—S2—C16	103.2 (2)
C6—C1—C2—C3	6.1 (5)	C9—C10—C11—C12	-2.1 (6)
C16—C1—C2—C3	-168.6 (4)	C10—C11—C12—C13	-4.2 (6)
C6—C1—C2—Br1	-174.1 (3)	C10—C11—C12—C15	172.1 (4)
C16—C1—C2—Br1	11.2 (5)	C11—C12—C13—C14	6.0 (6)
C1—C2—C3—C4	-1.9 (6)	C15—C12—C13—C14	-170.3 (4)
Br1—C2—C3—C4	178.3 (3)	C11—C12—C13—Br2	-176.7 (3)
C2—C3—C4—C5	-4.0 (6)	C15—C12—C13—Br2	7.0 (5)
C2—C3—C4—C7	174.8 (4)	C12—C13—C14—C9	-1.4 (6)
C3—C4—C5—C6	5.7 (6)	Br2—C13—C14—C9	-178.8 (3)
C7—C4—C5—C6	-173.1 (4)	C10—C9—C14—C13	-5.1 (6)
C4—C5—C6—C1	-1.4 (6)	C8—C9—C14—C13	169.4 (4)
C2—C1—C6—C5	-4.4 (5)	C11—C12—C15—S2	-28.6 (5)
C16—C1—C6—C5	170.4 (4)	C13—C12—C15—S2	147.5 (3)
C3—C4—C7—S1	-141.7 (3)	C6—C1—C16—S2	-100.7 (4)
C5—C4—C7—S1	37.1 (5)	C2—C1—C16—S2	73.7 (5)
S1—C8—C9—C10	104.9 (4)	C4—C7—S1—C8	70.3 (4)
S1—C8—C9—C14	-69.4 (5)	C9—C8—S1—C7	-64.4 (4)
C14—C9—C10—C11	6.8 (6)	C12—C15—S2—C16	-74.8 (3)
C8—C9—C10—C11	-167.6 (4)	C1—C16—S2—C15	62.9 (3)

Fig. 1

