Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

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

Xingxun Zhu and Ming Hu*

Key Laboratory of Pesticides and Chemical Biology of the Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China
Correspondence e-mail: zhuxingxun1986@sina.com

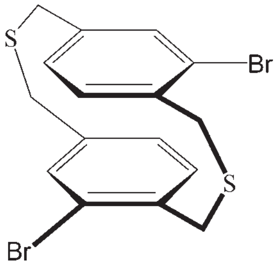
Received 30 June 2010; accepted 20 July 2010

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.041; wR factor = 0.115; data-to-parameter ratio = 18.6.

In the title compound, $C_{16}H_{14}Br_2S_2$ [systematic name: 1^2,5^2-dibromo-2,7-dithia-1,5(1,4)-dibenzenaoctaphane], the centroids of the two benzene rings are separated by 3.313 (5) Å. The crystal packing exhibits weak intermolecular S···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

$C_{16}H_{14}Br_2S_2$
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) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 5.49 mm^{-1}
T = 298 K
0.26 × 0.20 × 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_{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
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −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).

References

Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Huang, S. & Wang, Q. (2010). *Acta Cryst.* E**66**, o1993.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, W.-L., Xu, J. & Lai, Y.-H. (2003). *Org. Lett.* **5**, 2765–2768.
Wang, W.-L., Xu, J., Sun, Z., Zhang, X., Lu, Y. & Lai, Y.-H. (2006). *Macromolecules*, **39**, 7277–7285.

supporting information

Acta Cryst. (2010). E**66**, o2123   [https://doi.org/10.1107/S1600536810028874]

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

Xingxun Zhu and Ming Hu

S1. Comment

As a contribution to a structural study of dithia[3.3]paracyclophane derivatives with the bromine sustituents (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.

S2. 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 N_2 over 12 h to a refluxing solution of K_2CO_3 (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 CH_2Cl_2(300 ml) and water (300 ml).The organic phase was separated, the aqueous extracted with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4, then solvent was removed, and the resulting solid was chromatographed on silica gel using CH_2Cl_2 petroleum ether (1:1, *v*/*v*) as eluent.

S3. 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_{iso}(H) =1.2U_{eq}(C) for aromatic H atoms, and (C—H =0.97 Å) and U_{iso}(H) =1.2U_{eq}(C) for methylene, and (C—H =0.96 Å) and U_{iso}(H)=1.5U_{eq}(C) for methyl.

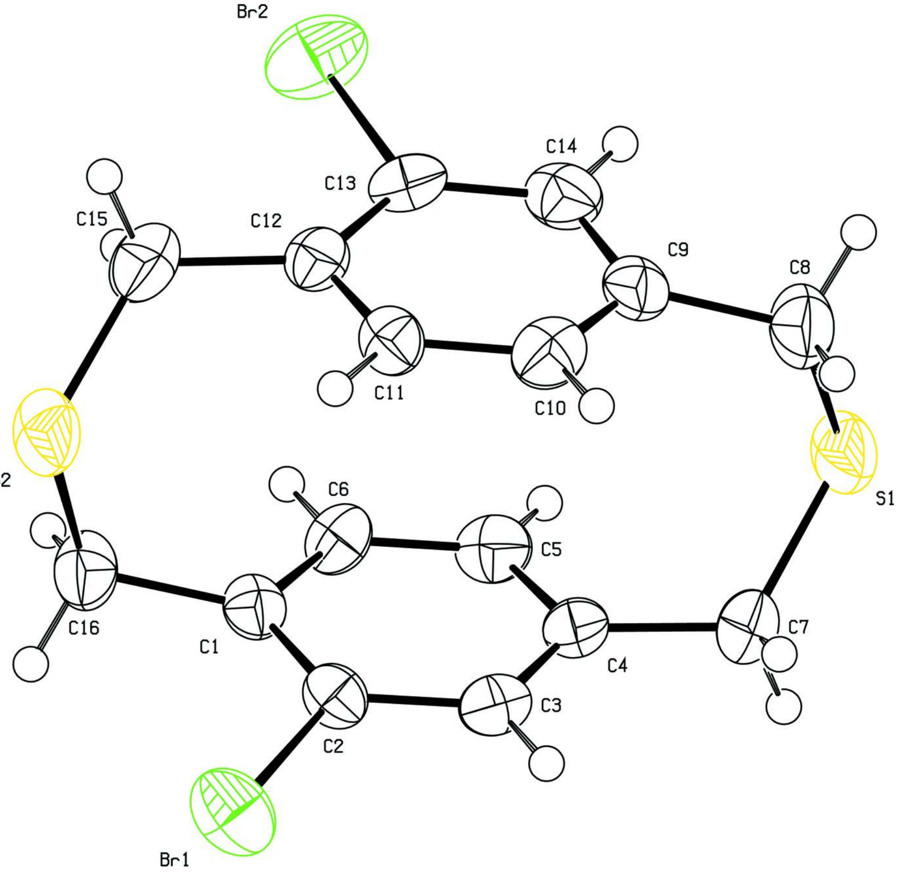


Figure 1

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

1^2,5^2-dibromo-2,7-dithia-1,5(1,4)-dibenzenaoctaphane

Crystal data

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

Data collection

Bruker SMART APEX diffractometer	21950 measured reflections
Radiation source: fine-focus sealed tube	3372 independent reflections
Graphite monochromator	2150 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.12$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{\max} = 27.0°$, $\theta_{\min} = 1.7°$
	$h = -10\rightarrow11$
	$k = -17\rightarrow17$
$T_{\min} = 0.330$, $T_{\max} = 0.610$	$l = -31\rightarrow31$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.115$
$S = 0.99$
3372 reflections
181 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.93$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ 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.

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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
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 (Å^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)
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, º)

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)