

1,4-Bis[3,11-dithiatricyclo[11.3.1.1^{5,9}]octadeca-1(17),5,7,9(18),13,15-hexaen-7-yl]buta-1,3-diyne

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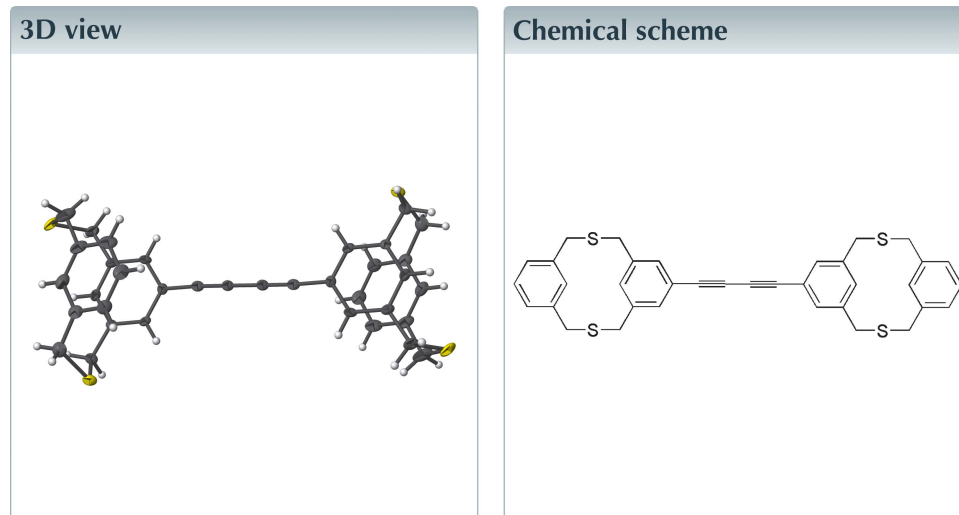
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Structural data: full structural data are available from iucrdata.iucr.org

The complete molecule of the title compound, C₃₆H₃₀S₄ {common name: 1,4-[4-(9,17-dithia[3.3]metacyclophane)]-1,3-butadiyne}, is generated by a crystallographic inversion centre at the mid-point of the central C—C bond [1.367 (5) Å]. Both cyclophane units exist in *cisoid* pseudo-boat–chair chair–boat conformations. In the crystal, the packing is controlled by van der Waals interactions.



Structure description

The synthesis and molecular structure analysis of bridged cyclophanes continue to attract interest in supramolecular chemistry. The understanding of preferred conformations in cyclophanes is of importance in the design of various supramolecular systems. Small-sized cyclophane molecules act as a model to explore the mobility of such cyclophanes due to the presence of a variety of conformational processes including ring-flipping, ring-tilting and *syn–anti* isomerization. Small-sized cyclophane units have been used as a platform to build cofacial bisporphyrins (Tsuge *et al.*, 2012). The [3.3]dithiametacyclophane skeleton have also been used to provide an appropriate platform to arrange two oligomer chains side by side in stacked form because this kind of cyclophane assumes a *syn* structure (Tsuge *et al.*, 2008). On the other hand, [3.3]dithiametacyclophanes consisting of oligothiophene units with extended π -conjugation have shown better fluorescence properties (Tsuge *et al.*, 2008). Thus, the elucidation of the crystal structures of cyclophane derivatives has attracted much attention.

Here, we report the crystal structure of the title compound, possessing extended π -conjugation *via* a 1,3-butadiyne unit (Fig. 1). The complete molecule is generated by a crystallographic inversion centre at the mid-point of the central C—C bond. The C—C single- and triple-bond lengths match the reported values in the literature (Mo *et al.*,

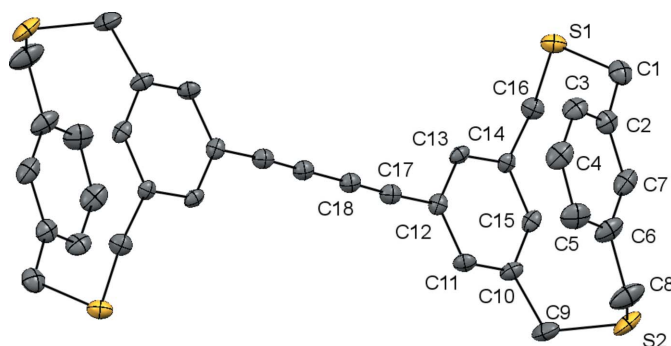


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are generated by the symmetry operation $(-x, -y + 2, -z + 1)$. H atoms have been omitted for clarity.

1996). Both cyclophane units exist in *cisoid*, pseudo boat-chair, chair-boat conformations with both substituents positioned on the same side.

No directional interactions beyond normal van der Waals' contacts could be identified in the crystal. The crystal packing is shown in Fig. 2.

Synthesis and crystallization

The title compound was synthesized using Hay coupling as follows. The reaction scheme is shown in Fig. 3. A dichloromethane solution (10 ml) of 6-ethynyl-2,11-dithia[3.3]metacyclophane (40.2 mg, 0.125 mmol) was added dropwise to a solution of tetramethylethylenediamine (TMEDA) (0.80 ml,

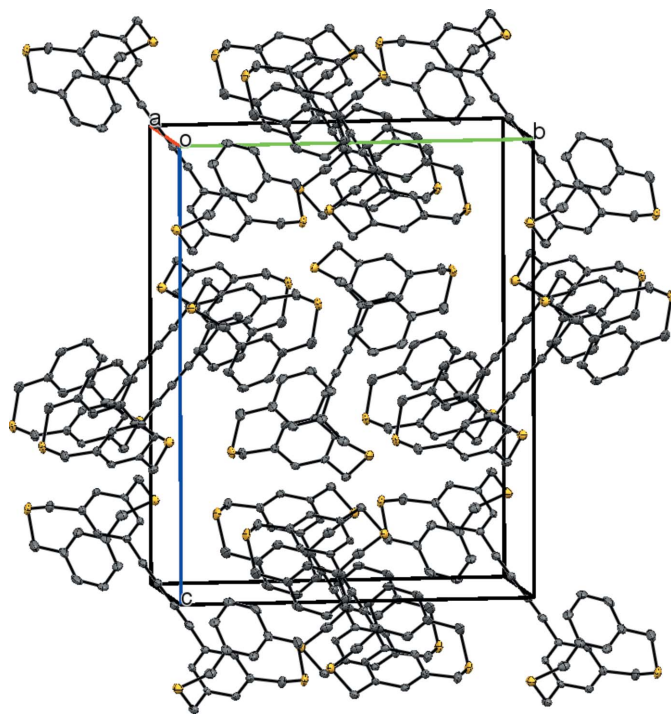


Figure 2

Crystal packing diagram of the title compound, viewed along the *a* axis, with H atoms omitted for clarity.

Table 1

Experimental details.

Crystal data	
Chemical formula	$C_{36}H_{30}S_4$
M_r	590.84
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	90
a, b, c (Å)	8.717 (3), 16.325 (5), 21.043 (7)
V (Å ³)	2994.5 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.34
Crystal size (mm)	0.35 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2009)
T_{min}, T_{max}	0.659, 0.934
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12443, 2641, 2172
R_{int}	0.041
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.130, 1.16
No. of reflections	2641
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.37, -0.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS2014/7* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2008).

5.7 mmol) and CuCl (0.28 g, 2.9 mmol) as a catalyst in dichloromethane (50 ml). The reaction mixture was stirred for 2 h. After the completion of reaction, the resulting mixture was poured into 10% HCl (aq.) and then, the organic layer was washed with water. The resulting organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. The resulting residue was purified by recrystallization and the title compound was obtained as white crystals (33.2 mg, 0.0562 mmol, 39% yield). Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane–hexane solution at room temperature using the slow vapor diffusion technique.

¹H NMR (400 MHz, CDCl₃) 3.75 (s, 8 H, -CH₂-), 3.78 (s, 8 H, -CH₂-), 6.90 (d, 4 H, aryl C-H, $J = 2.5$ Hz), 6.97 (d, 4 H, aryl C-H, $J = 2.5$ Hz), 7.03 (m, 6 H, aryl C-H). EI-MS (75 eV): m/z 590 (M^+). Elemental analysis: C 73.13% (73.18%, calculated), H 5.09% (5.12%, calculated).

Refinement

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

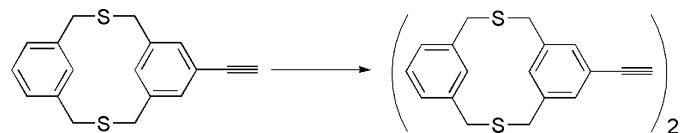


Figure 3

The reaction scheme for the synthesis of the title compound.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161378 [doi:10.1107/S241431461601378X]

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Crystal data

C₃₆H₃₀S₄

$M_r = 590.84$

Orthorhombic, *Pbca*

$a = 8.717$ (3) Å

$b = 16.325$ (5) Å

$c = 21.043$ (7) Å

$V = 2994.5$ (17) Å³

$Z = 4$

$F(000) = 1240$

$D_x = 1.311$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 12443 reflections

$\theta = 1.9$ – 25.0°

$\mu = 0.34$ mm⁻¹

$T = 90$ K

Prism, yellow

$0.35 \times 0.25 \times 0.20$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine focus sealed tube

Graphite monochromator

Detector resolution: 8.333 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

$T_{\min} = 0.659$, $T_{\max} = 0.934$

12443 measured reflections

2641 independent reflections

2172 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -10 \rightarrow 6$

$k = -19 \rightarrow 19$

$l = -24 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.130$

$S = 1.16$

2641 reflections

181 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 2.2214P]$

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

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7566 (3)	0.93934 (17)	0.63894 (13)	0.0272 (6)
H1A	0.8431	0.9633	0.6167	0.033*
H1B	0.7974	0.9048	0.6724	0.033*
C2	0.6688 (3)	0.88566 (16)	0.59271 (12)	0.0232 (6)
C3	0.6204 (3)	0.91543 (16)	0.53423 (12)	0.0253 (6)
H3	0.6481	0.968	0.5216	0.03*
C4	0.5310 (3)	0.86717 (17)	0.49439 (13)	0.0291 (7)
H4	0.4995	0.8875	0.4552	0.035*
C5	0.4883 (4)	0.78859 (17)	0.51288 (13)	0.0315 (7)
H5	0.4252	0.7573	0.4868	0.038*
C6	0.5397 (4)	0.75665 (16)	0.57031 (12)	0.0297 (7)
C7	0.6325 (3)	0.80538 (16)	0.60904 (13)	0.0271 (6)
H7	0.6709	0.7836	0.6467	0.033*
C8	0.4951 (4)	0.66958 (17)	0.58834 (14)	0.0413 (8)
H8B	0.5769	0.6334	0.5746	0.05*
H8A	0.4043	0.6551	0.5642	0.05*
C9	0.2692 (3)	0.69461 (16)	0.68376 (13)	0.0285 (6)
H9A	0.1963	0.6704	0.6544	0.034*
H9B	0.2345	0.6827	0.7266	0.034*
C10	0.2712 (3)	0.78628 (15)	0.67415 (11)	0.0205 (6)
C11	0.1831 (3)	0.82242 (15)	0.62706 (11)	0.0194 (5)
H11	0.113	0.791	0.6044	0.023*
C12	0.1990 (3)	0.90631 (15)	0.61345 (11)	0.0169 (5)
C13	0.3051 (3)	0.95296 (15)	0.64694 (11)	0.0170 (5)
H13	0.3166	1.0083	0.6375	0.02*
C14	0.3943 (3)	0.91761 (14)	0.69438 (11)	0.0155 (5)
C15	0.3743 (3)	0.83492 (15)	0.70824 (11)	0.0189 (5)
H15	0.4309	0.8115	0.741	0.023*
C16	0.5167 (3)	0.96678 (16)	0.72801 (12)	0.0211 (6)
H16A	0.5767	0.93	0.7543	0.025*
H16B	0.4671	1.0059	0.756	0.025*
C17	0.1119 (3)	0.94410 (15)	0.56359 (12)	0.0190 (5)
C18	0.0414 (3)	0.97970 (15)	0.52266 (12)	0.0188 (5)
S1	0.64610 (8)	1.02199 (4)	0.67558 (3)	0.0240 (2)
S2	0.45632 (10)	0.64782 (4)	0.67156 (4)	0.0328 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0255 (14)	0.0334 (16)	0.0228 (14)	−0.0002 (12)	0.0054 (12)	0.0026 (12)
C2	0.0259 (14)	0.0251 (14)	0.0185 (13)	0.0024 (11)	0.0088 (11)	−0.0026 (11)
C3	0.0330 (15)	0.0248 (14)	0.0181 (14)	−0.0005 (12)	0.0082 (12)	0.0037 (11)
C4	0.0437 (17)	0.0301 (15)	0.0135 (13)	0.0048 (13)	0.0064 (12)	−0.0001 (11)
C5	0.0440 (17)	0.0298 (16)	0.0207 (14)	−0.0020 (13)	0.0086 (13)	−0.0119 (12)
C6	0.0493 (18)	0.0196 (14)	0.0204 (14)	0.0041 (13)	0.0115 (13)	−0.0041 (11)

C7	0.0377 (16)	0.0246 (14)	0.0191 (13)	0.0087 (12)	0.0079 (12)	0.0033 (11)
C8	0.072 (2)	0.0209 (15)	0.0308 (17)	0.0021 (15)	0.0123 (17)	-0.0049 (13)
C9	0.0409 (16)	0.0160 (14)	0.0287 (15)	-0.0041 (12)	-0.0035 (13)	0.0040 (11)
C10	0.0288 (14)	0.0144 (12)	0.0182 (13)	-0.0007 (11)	0.0017 (11)	-0.0011 (10)
C11	0.0252 (13)	0.0170 (12)	0.0161 (12)	-0.0032 (11)	-0.0015 (10)	-0.0047 (10)
C12	0.0200 (12)	0.0194 (12)	0.0113 (12)	0.0025 (10)	0.0010 (10)	0.0002 (10)
C13	0.0234 (13)	0.0129 (12)	0.0148 (12)	0.0019 (10)	0.0037 (11)	-0.0021 (9)
C14	0.0185 (12)	0.0157 (12)	0.0124 (12)	0.0021 (10)	0.0021 (10)	-0.0045 (9)
C15	0.0256 (13)	0.0186 (13)	0.0126 (12)	0.0044 (10)	-0.0004 (10)	0.0025 (10)
C16	0.0241 (13)	0.0239 (14)	0.0154 (13)	-0.0017 (11)	0.0006 (11)	-0.0035 (10)
C17	0.0223 (13)	0.0197 (13)	0.0151 (13)	-0.0014 (11)	0.0030 (11)	-0.0029 (10)
C18	0.0217 (13)	0.0190 (13)	0.0156 (12)	-0.0005 (10)	0.0006 (10)	-0.0026 (10)
S1	0.0276 (4)	0.0220 (4)	0.0224 (4)	-0.0074 (3)	0.0002 (3)	-0.0014 (3)
S2	0.0526 (5)	0.0131 (4)	0.0327 (4)	0.0065 (3)	0.0014 (4)	0.0054 (3)

Geometric parameters (Å, °)

C1—C2	1.517 (4)	C9—S2	1.820 (3)
C1—S1	1.828 (3)	C9—H9A	0.97
C1—H1A	0.97	C9—H9B	0.97
C1—H1B	0.97	C10—C11	1.386 (4)
C2—C3	1.389 (4)	C10—C15	1.397 (4)
C2—C7	1.391 (4)	C11—C12	1.406 (3)
C3—C4	1.390 (4)	C11—H11	0.93
C3—H3	0.93	C12—C13	1.390 (3)
C4—C5	1.391 (4)	C12—C17	1.434 (3)
C4—H4	0.93	C13—C14	1.390 (4)
C5—C6	1.390 (4)	C13—H13	0.93
C5—H5	0.93	C14—C15	1.392 (3)
C6—C7	1.397 (4)	C14—C16	1.511 (3)
C6—C8	1.522 (4)	C15—H15	0.93
C7—H7	0.93	C16—S1	1.817 (3)
C8—S2	1.818 (3)	C16—H16A	0.97
C8—H8B	0.97	C16—H16B	0.97
C8—H8A	0.97	C17—C18	1.207 (4)
C9—C10	1.510 (3)	C18—C18 ⁱ	1.367 (5)
C2—C1—S1	115.54 (19)	S2—C9—H9A	109.0
C2—C1—H1A	108.4	C10—C9—H9B	109.0
S1—C1—H1A	108.4	S2—C9—H9B	109.0
C2—C1—H1B	108.4	H9A—C9—H9B	107.8
S1—C1—H1B	108.4	C11—C10—C15	118.8 (2)
H1A—C1—H1B	107.5	C11—C10—C9	120.7 (2)
C3—C2—C7	118.7 (3)	C15—C10—C9	120.2 (2)
C3—C2—C1	121.3 (2)	C10—C11—C12	120.4 (2)
C7—C2—C1	120.0 (2)	C10—C11—H11	119.8
C2—C3—C4	120.4 (3)	C12—C11—H11	119.8
C2—C3—H3	119.8	C13—C12—C11	119.7 (2)

C4—C3—H3	119.8	C13—C12—C17	119.2 (2)
C3—C4—C5	120.3 (3)	C11—C12—C17	121.0 (2)
C3—C4—H4	119.9	C14—C13—C12	120.6 (2)
C5—C4—H4	119.9	C14—C13—H13	119.7
C6—C5—C4	120.2 (3)	C12—C13—H13	119.7
C6—C5—H5	119.9	C13—C14—C15	118.9 (2)
C4—C5—H5	119.9	C13—C14—C16	120.7 (2)
C5—C6—C7	118.7 (3)	C15—C14—C16	120.4 (2)
C5—C6—C8	119.0 (3)	C14—C15—C10	121.6 (2)
C7—C6—C8	122.3 (3)	C14—C15—H15	119.2
C2—C7—C6	121.6 (3)	C10—C15—H15	119.2
C2—C7—H7	119.2	C14—C16—S1	114.68 (17)
C6—C7—H7	119.2	C14—C16—H16A	108.6
C6—C8—S2	118.0 (2)	S1—C16—H16A	108.6
C6—C8—H8B	107.8	C14—C16—H16B	108.6
S2—C8—H8B	107.8	S1—C16—H16B	108.6
C6—C8—H8A	107.8	H16A—C16—H16B	107.6
S2—C8—H8A	107.8	C18—C17—C12	176.7 (3)
H8B—C8—H8A	107.1	C17—C18—C18 ⁱ	178.6 (3)
C10—C9—S2	112.7 (2)	C16—S1—C1	102.53 (13)
C10—C9—H9A	109.0	C8—S2—C9	102.74 (15)
S1—C1—C2—C3	69.6 (3)	C9—C10—C11—C12	-172.5 (2)
S1—C1—C2—C7	-109.1 (3)	C10—C11—C12—C13	0.7 (4)
C7—C2—C3—C4	3.2 (4)	C10—C11—C12—C17	178.1 (2)
C1—C2—C3—C4	-175.5 (2)	C11—C12—C13—C14	-0.8 (4)
C2—C3—C4—C5	0.3 (4)	C17—C12—C13—C14	-178.3 (2)
C3—C4—C5—C6	-2.4 (4)	C12—C13—C14—C15	-0.7 (3)
C4—C5—C6—C7	0.9 (4)	C12—C13—C14—C16	176.1 (2)
C4—C5—C6—C8	-178.2 (3)	C13—C14—C15—C10	2.4 (4)
C3—C2—C7—C6	-4.8 (4)	C16—C14—C15—C10	-174.4 (2)
C1—C2—C7—C6	174.0 (2)	C11—C10—C15—C14	-2.5 (4)
C5—C6—C7—C2	2.7 (4)	C9—C10—C15—C14	171.0 (2)
C8—C6—C7—C2	-178.2 (3)	C13—C14—C16—S1	-49.5 (3)
C5—C6—C8—S2	-143.7 (3)	C15—C14—C16—S1	127.3 (2)
C7—C6—C8—S2	37.2 (4)	C14—C16—S1—C1	-69.7 (2)
S2—C9—C10—C11	118.5 (2)	C2—C1—S1—C16	69.8 (2)
S2—C9—C10—C15	-54.8 (3)	C6—C8—S2—C9	74.4 (3)
C15—C10—C11—C12	0.9 (4)	C10—C9—S2—C8	-62.9 (2)

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