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syn-6,15-Dihydroxy-2,11-dithia[3.3]metacyclophane ethyl acetate monosolvate

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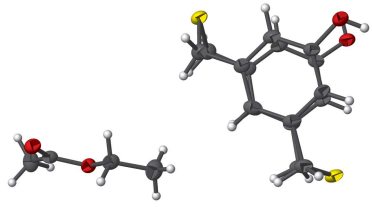
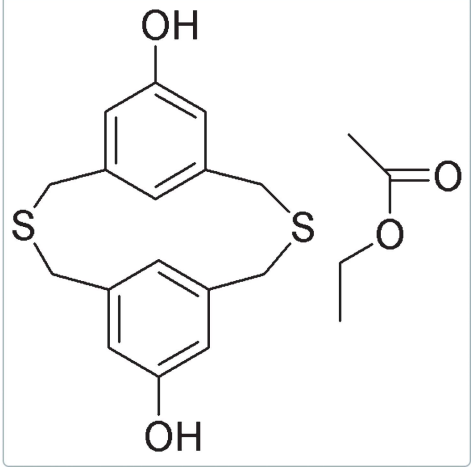
The title compound, $C_{16}H_{16}O_2S_2{\cdot}C_4H_8O_2$, is a cyclophane derivative, which was crystallized from an ethylacetate/methanol solvent system. The metacyclophane moiety exists with the benzene rings in the *syn* orientation, and with a pseudo chair–chair conformation for the dithia 12-membered ring. Both hydroxy groups are positioned on same side of this ring. In the crystal, the cyclophane and the lattice solvent are linked by O—H···O hydrogen bonds.

3D view



Chemical scheme



Structure description

The synthesis and molecular structure analysis of short-bridged cyclophanes continues to attract interest in supramolecular chemistry. The understanding of the preferred conformations of cyclophane is of importance in the design of various supramolecular systems. Small-sized cyclophane molecules act as a model to explore the flexibility 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 has also been used to provide an appropriate platform to arrange two oligomer chains side by side in a stacked arrangement, because this kind of cyclophane assumes a *syn* structure (Tsuge *et al.*, 2008).

We have compared the conformation of the title compound (Fig. 1) with other cyclophanes having different substitutions at C5/C13 in the benzene rings. The title compound has OH groups at the C5/C13 positions and exists in a *syn*, pseudo chair-chair conformation, with both hydroxy groups positioned on the same side of the core 12-membered dithia ring. When methyl groups substitute the C5/C13 positions, the *anti*,

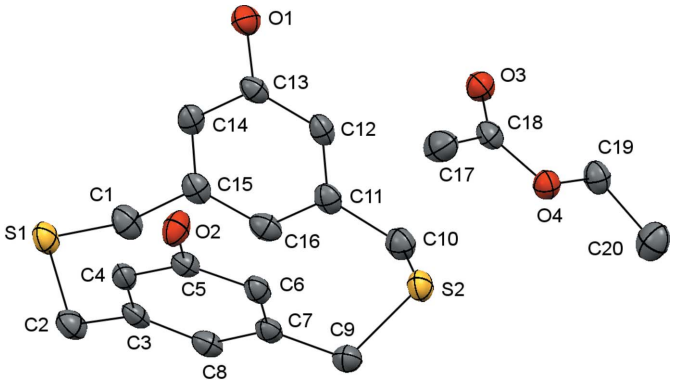


Figure 1
Molecular configuration and atom-numbering scheme for the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

pseudo boat-chair conformation is stabilized (Chan *et al.*, 1977). Unsubstituted cyclophane exists in a *syn*, pseudo chair–chair conformation (Anker *et al.*, 1979), and when cyano group are bonded at C5/C13 positions the *syn*, pseudo boat-boat conformation is obtained (Bodwell *et al.*, 1997).

The crystal structure (Fig. 2) features O—H···O hydrogen bonds (Table 1) involving the hydroxy groups belonging to the cyclophane, and the carbonyl functionality of the ethyl acetate solvent.

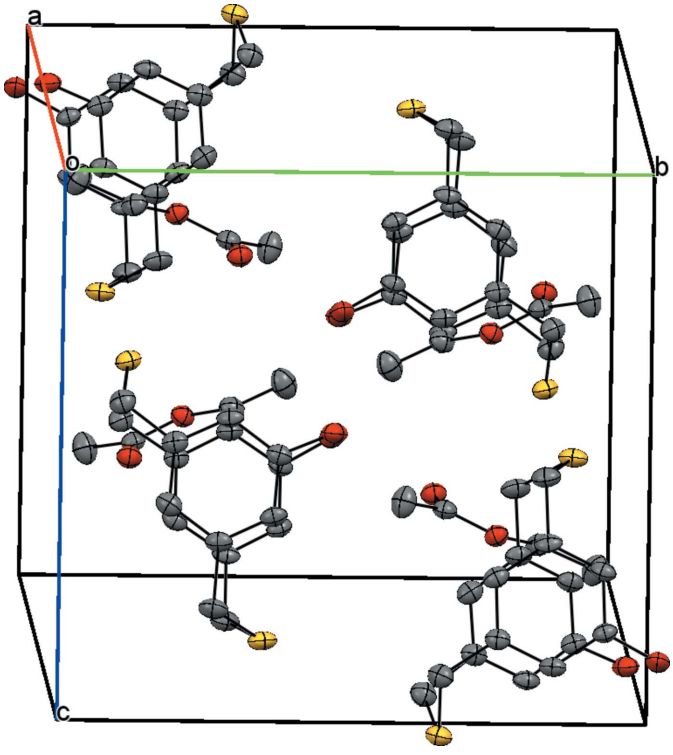


Figure 2
Crystal packing diagram of the title compound, viewed along the *a* axis, with H atoms omitted for clarity.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O2^{i}	0.82	1.91	2.732 (3)	176
O2—H2*O*···O3^{ii}	0.82	1.84	2.656 (3)	172

Symmetry codes: (i) $-x+2, -y, -z$; (ii) $x, y-1, z$.

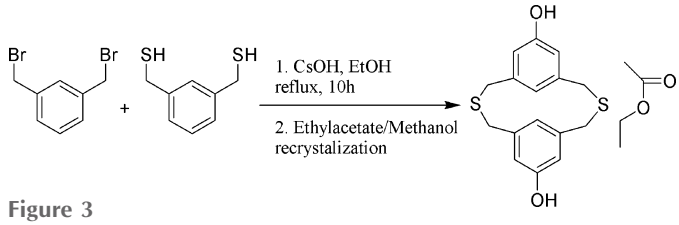


Figure 3
Reaction scheme for the synthesis of the title compound.

Synthesis and crystallization

The synthesis of the title compound is shown in Fig. 3. An ethanol solution (100 ml) of 3,5-bis(bromomethyl)phenol (2 mmol) and 3,5-bis(mercaptomethyl)phenol (2 mmol) was added dropwise to a solution of CsOH (5 mmol) as an alkaline catalyst in ethanol (250 ml). The reaction mixture was refluxed for 10 h. After completion of the reaction, the resulting mixture was cooled to room temperature, poured into ice-cold water, and extracted with dichloromethane. The organic layer was washed with water. The resulting organic layer was dried

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{16}O_2S_2{\cdot}C_4H_8O_2$
M_r	392.51
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, *b*, *c* (Å)	12.1691 (9), 13.1263 (10), 12.2750 (9)
β (°)	99.818 (1)
V (Å^3)	1932.0 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.30
Crystal size (mm)	0.40 × 0.40 × 0.40
Data collection	
Diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.770, 0.886
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18213, 3400, 2628
R_{int}	0.055
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.100, 1.00
No. of reflections	3400
No. of parameters	239
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.04, −0.21

Computer programs: *APEX2* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008).

over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting residue was purified on column chromatography (silica gel), and the title cyclophane was obtained as a white powder. Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate–methanol solution at room temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{16}H_{16}O_2S_2{\cdot}C_4H_8O_2$
M_r = 392.51
Monoclinic, $P2_1/n$
a = 12.1691 (9) Å
b = 13.1263 (10) Å
c = 12.2750 (9) Å
β = 99.818 (1)°
V = 1932.0 (2) Å^3
Z = 4
$F(000)$ = 832
D_x = 1.349 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3174 reflections
θ = 2.2–24.1°
μ = 0.30 mm^{-1}
T = 120 K
Prism, colorless
0.40 × 0.40 × 0.40 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 16.6666 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.770, T_{max} = 0.886
18213 measured reflections
3400 independent reflections
2628 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 25.0°, θ_{min} = 2.2°
h = −14→14
k = −15→15
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.100
S = 1.00
3400 reflections
239 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
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 1.921P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.04 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8223 (2)	0.2151 (2)	0.3808 (2)	0.0318 (6)
H1A	0.7478	0.2052	0.3971	0.038*
H1B	0.8456	0.2835	0.4043	0.038*

C2	1.0536 (2)	0.1794 (2)	0.4633 (2)	0.0316 (6)
H2A	1.0528	0.2497	0.4875	0.038*
H2B	1.107	0.1429	0.5171	0.038*
C3	1.0928 (2)	0.1765 (2)	0.35338 (19)	0.0251 (6)
C4	1.1255 (2)	0.0850 (2)	0.3124 (2)	0.0251 (6)
H4	1.1277	0.0259	0.3544	0.03*
C5	1.1548 (2)	0.0824 (2)	0.2078 (2)	0.0235 (6)
C6	1.1500 (2)	0.1698 (2)	0.1439 (2)	0.0251 (6)
H6	1.1667	0.1666	0.0729	0.03*
C7	1.1204 (2)	0.2618 (2)	0.1855 (2)	0.0239 (6)
C8	1.0939 (2)	0.2643 (2)	0.2912 (2)	0.0264 (6)
H8	1.0766	0.3263	0.3208	0.032*
C9	1.1167 (2)	0.3573 (2)	0.1168 (2)	0.0293 (6)
H9A	1.1916	0.3719	0.1039	0.035*
H9B	1.0939	0.4135	0.1591	0.035*
C10	0.8876 (2)	0.3704 (2)	0.0228 (2)	0.0319 (6)
H10A	0.8899	0.4312	0.0679	0.038*
H10B	0.8335	0.382	−0.0438	0.038*
C11	0.8478 (2)	0.2830 (2)	0.0851 (2)	0.0262 (6)
C12	0.8177 (2)	0.1917 (2)	0.0317 (2)	0.0258 (6)
H12	0.819	0.1855	−0.0435	0.031*
C13	0.7856 (2)	0.1099 (2)	0.0899 (2)	0.0245 (6)
C14	0.7863 (2)	0.1176 (2)	0.2029 (2)	0.0259 (6)
H14	0.7663	0.0619	0.2419	0.031*
C15	0.8169 (2)	0.2080 (2)	0.2573 (2)	0.0262 (6)
C16	0.8450 (2)	0.2915 (2)	0.1975 (2)	0.0285 (6)
H16	0.862	0.3535	0.233	0.034*
C17	0.9315 (2)	0.8870 (2)	0.2122 (3)	0.0384 (7)
H17A	0.9419	0.9452	0.2602	0.058*
H17B	0.8602	0.8568	0.2148	0.058*
H17C	0.9347	0.908	0.1379	0.058*
C18	1.0211 (2)	0.8112 (2)	0.2489 (2)	0.0253 (6)
C19	1.0648 (2)	0.6477 (2)	0.3228 (2)	0.0288 (6)
H19A	1.1163	0.6716	0.3868	0.035*
H19B	1.1069	0.6315	0.2647	0.035*
C20	1.0040 (2)	0.5557 (2)	0.3521 (3)	0.0409 (7)
H20A	0.9601	0.5734	0.4073	0.061*
H20B	1.0568	0.5039	0.3805	0.061*
H20C	0.956	0.5308	0.2873	0.061*
O1	0.75162 (15)	0.01893 (14)	0.04032 (14)	0.0315 (5)
H1O	0.7668	0.0177	−0.0222	0.047*
O2	1.19101 (16)	−0.00557 (14)	0.16493 (15)	0.0322 (5)
H2O	1.1684	−0.0549	0.1956	0.048*
O3	1.11964 (14)	0.82409 (13)	0.24655 (14)	0.0285 (4)
O4	0.98224 (14)	0.72552 (13)	0.28542 (14)	0.0260 (4)
S1	0.91552 (6)	0.12469 (6)	0.46261 (5)	0.03039 (19)
S2	1.02408 (6)	0.35251 (5)	−0.01616 (5)	0.02919 (18)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0282 (15)	0.0450 (18)	0.0238 (14)	0.0036 (13)	0.0087 (11)	−0.0031 (12)
C2	0.0305 (15)	0.0429 (17)	0.0212 (14)	−0.0031 (13)	0.0037 (11)	−0.0043 (12)
C3	0.0176 (13)	0.0401 (16)	0.0165 (12)	−0.0027 (11)	−0.0004 (10)	−0.0038 (11)
C4	0.0219 (13)	0.0339 (15)	0.0188 (13)	−0.0039 (11)	0.0012 (10)	0.0039 (11)
C5	0.0198 (13)	0.0307 (15)	0.0199 (13)	−0.0011 (11)	0.0028 (10)	−0.0039 (11)
C6	0.0204 (13)	0.0370 (16)	0.0181 (13)	−0.0025 (11)	0.0036 (10)	0.0007 (11)
C7	0.0172 (13)	0.0322 (15)	0.0213 (13)	−0.0027 (11)	0.0003 (10)	0.0000 (11)
C8	0.0208 (13)	0.0337 (16)	0.0240 (14)	−0.0013 (11)	0.0012 (11)	−0.0060 (12)
C9	0.0261 (14)	0.0338 (16)	0.0270 (14)	−0.0055 (12)	0.0017 (11)	0.0007 (12)
C10	0.0282 (15)	0.0358 (16)	0.0304 (15)	0.0029 (12)	0.0012 (12)	0.0031 (13)
C11	0.0185 (13)	0.0353 (16)	0.0243 (14)	0.0041 (11)	0.0020 (10)	0.0031 (12)
C12	0.0204 (13)	0.0380 (16)	0.0186 (13)	0.0038 (12)	0.0023 (10)	0.0032 (12)
C13	0.0180 (13)	0.0333 (15)	0.0214 (13)	0.0012 (11)	0.0014 (10)	−0.0029 (11)
C14	0.0182 (13)	0.0372 (16)	0.0232 (13)	0.0009 (11)	0.0061 (10)	0.0039 (12)
C15	0.0189 (13)	0.0377 (16)	0.0224 (13)	0.0048 (11)	0.0050 (10)	0.0007 (12)
C16	0.0222 (14)	0.0347 (16)	0.0275 (14)	0.0020 (12)	0.0016 (11)	−0.0053 (12)
C17	0.0296 (16)	0.0331 (16)	0.0498 (18)	0.0004 (13)	−0.0007 (14)	0.0057 (14)
C18	0.0267 (15)	0.0304 (15)	0.0184 (13)	0.0008 (12)	0.0029 (11)	−0.0015 (11)
C19	0.0260 (14)	0.0341 (16)	0.0259 (14)	0.0055 (12)	0.0033 (11)	0.0042 (12)
C20	0.0348 (17)	0.0374 (18)	0.0510 (19)	0.0059 (14)	0.0090 (14)	0.0095 (15)
O1	0.0362 (11)	0.0373 (11)	0.0218 (10)	−0.0073 (9)	0.0074 (8)	−0.0031 (8)
O2	0.0430 (12)	0.0287 (11)	0.0286 (10)	0.0006 (9)	0.0169 (9)	0.0018 (8)
O3	0.0258 (10)	0.0334 (11)	0.0269 (10)	−0.0006 (8)	0.0060 (8)	0.0009 (8)
O4	0.0248 (10)	0.0282 (10)	0.0251 (10)	0.0013 (8)	0.0043 (8)	0.0022 (8)
S1	0.0306 (4)	0.0433 (4)	0.0182 (3)	−0.0024 (3)	0.0068 (3)	0.0020 (3)
S2	0.0317 (4)	0.0357 (4)	0.0204 (3)	−0.0016 (3)	0.0052 (3)	0.0034 (3)

Geometric parameters (Å, º)

C1—C15	1.509 (3)	C11—C12	1.384 (4)
C1—S1	1.821 (3)	C11—C16	1.390 (3)
C1—H1A	0.97	C12—C13	1.383 (4)
C1—H1B	0.97	C12—H12	0.93
C2—C3	1.507 (3)	C13—O1	1.371 (3)
C2—S1	1.826 (3)	C13—C14	1.389 (3)
C2—H2A	0.97	C14—C15	1.381 (4)
C2—H2B	0.97	C14—H14	0.93
C3—C4	1.386 (4)	C15—C16	1.394 (4)
C3—C8	1.384 (4)	C16—H16	0.93
C4—C5	1.390 (3)	C17—C18	1.488 (4)
C4—H4	0.93	C17—H17A	0.96
C5—C6	1.385 (4)	C17—H17B	0.96
C5—O2	1.372 (3)	C17—H17C	0.96
C6—C7	1.382 (4)	C18—O3	1.216 (3)
C6—H6	0.93	C18—O4	1.328 (3)

C7—C8	1.390 (3)	C19—O4	1.451 (3)
C7—C9	1.508 (4)	C19—C20	1.491 (4)
C8—H8	0.93	C19—H19A	0.97
C9—S2	1.820 (3)	C19—H19B	0.97
C9—H9A	0.97	C20—H20A	0.96
C9—H9B	0.97	C20—H20B	0.96
C10—C11	1.504 (4)	C20—H20C	0.96
C10—S2	1.820 (3)	O1—H1O	0.82
C10—H10A	0.97	O2—H2O	0.82
C10—H10B	0.97		

C15—C1—S1	115.46 (18)	C12—C11—C10	120.1 (2)
C15—C1—H1A	108.4	C16—C11—C10	120.5 (2)
S1—C1—H1A	108.4	C11—C12—C13	120.2 (2)
C15—C1—H1B	108.4	C11—C12—H12	119.9
S1—C1—H1B	108.4	C13—C12—H12	119.9
H1A—C1—H1B	107.5	O1—C13—C14	117.2 (2)
C3—C2—S1	114.70 (18)	O1—C13—C12	122.5 (2)
C3—C2—H2A	108.6	C14—C13—C12	120.2 (2)
S1—C2—H2A	108.6	C15—C14—C13	120.1 (2)
C3—C2—H2B	108.6	C15—C14—H14	119.9
S1—C2—H2B	108.6	C13—C14—H14	119.9
H2A—C2—H2B	107.6	C14—C15—C16	119.3 (2)
C4—C3—C8	119.4 (2)	C14—C15—C1	120.1 (2)
C4—C3—C2	120.1 (2)	C16—C15—C1	120.6 (2)
C8—C3—C2	120.5 (2)	C11—C16—C15	120.6 (3)
C3—C4—C5	119.4 (2)	C11—C16—H16	119.7
C3—C4—H4	120.3	C15—C16—H16	119.7
C5—C4—H4	120.3	C18—C17—H17A	109.5
C6—C5—O2	117.7 (2)	C18—C17—H17B	109.5
C6—C5—C4	120.6 (2)	H17A—C17—H17B	109.5
O2—C5—C4	121.7 (2)	C18—C17—H17C	109.5
C5—C6—C7	120.2 (2)	H17A—C17—H17C	109.5
C5—C6—H6	119.9	H17B—C17—H17C	109.5
C7—C6—H6	119.9	O3—C18—O4	122.4 (2)
C6—C7—C8	118.8 (2)	O3—C18—C17	125.1 (2)
C6—C7—C9	120.3 (2)	O4—C18—C17	112.6 (2)
C8—C7—C9	120.9 (2)	O4—C19—C20	107.5 (2)
C3—C8—C7	121.4 (2)	O4—C19—H19A	110.2
C3—C8—H8	119.3	C20—C19—H19A	110.2
C7—C8—H8	119.3	O4—C19—H19B	110.2
C7—C9—S2	115.30 (18)	C20—C19—H19B	110.2
C7—C9—H9A	108.4	H19A—C19—H19B	108.5
S2—C9—H9A	108.4	C19—C20—H20A	109.5
C7—C9—H9B	108.4	C19—C20—H20B	109.5
S2—C9—H9B	108.4	H20A—C20—H20B	109.5
H9A—C9—H9B	107.5	C19—C20—H20C	109.5
C11—C10—S2	115.02 (19)	H20A—C20—H20C	109.5

C11—C10—H10A	108.5	H20B—C20—H20C	109.5
S2—C10—H10A	108.5	C13—O1—H1O	109.5
C11—C10—H10B	108.5	C5—O2—H2O	109.5
S2—C10—H10B	108.5	C18—O4—C19	115.8 (2)
H10A—C10—H10B	107.5	C1—S1—C2	103.45 (13)
C12—C11—C16	119.3 (2)	C9—S2—C10	102.34 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O2^{i}	0.82	1.91	2.732 (3)	176
O2—H2*O*···O3^{ii}	0.82	1.84	2.656 (3)	172

Symmetry codes: (i) −*x*+2, −*y*, −*z*; (ii) *x*, *y*−1, *z*.