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## A New Cyclophane

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### Abstract

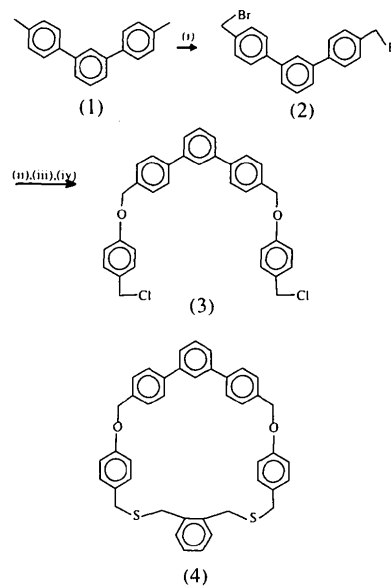
The X-ray diffraction studies of 9,25-dioxa-3,31-dithiaheptacyclo[31.4.0.2<sup>5,8</sup>.2<sup>11,14</sup>.1<sup>15,19</sup>.2<sup>20,23</sup>.2<sup>26,29</sup>]hexatetraconta-1(33),5,7,11,13,15,17,20,22,26,28,34,36,38,40,42(19),43,45-octadecaene, C<sub>42</sub>H<sub>36</sub>O<sub>2</sub>S<sub>2</sub>·3H<sub>2</sub>O, shows a distorted cyclic conformation with a hydrophobic cavity of size 8.56 × 8.55 Å<sup>2</sup> in the solid state. The compound exists as a trihydrate and the water molecules form a triangular cage caught inside the cavity. The molecules are held together by van der Waals interactions.

### Comment

Cyclophanes have received considerable attention in recent years as macrocyclic hosts for a variety of guest molecules (Odashima, Itai, Iitaka & Koga 1980; Diederich, 1991; Philip & Stoddart, 1991; Vogtle, 1992). The molecule possesses a non-collapsible rigid cavity, which gives the molecule a precise cavity size. The X-ray analysis of a cyclophane that has face-to-face arene rings is reported by Chiu, Hart & Ward (1993) and another cyclophane containing a 1,5,2,4,6,8-dithia-tetrazocine ring system is reported by Ho & Pascal (1994). The present paper reports the X-ray structure of a new cyclophane.

The scheme is based on a *m*-terphenyl framework (1), which can be obtained by the tandem aryne sequence (Hart & Ghosh, 1988). The dibromide (2)

was prepared from (1). Dichloride (3) was prepared from the dibromide (2) using *p*-hydroxymethylbenzoate. Coupling of dichloride (3) with *o*-xylene- $\alpha,\alpha'$ -dithiol under high dilution techniques in the presence of KOH in benzene–ethanol gave the title compound (4) (m.p. 473 K, 70%).



- (i) NBS (2 eq.), CCl<sub>4</sub>, Bz<sub>2</sub>O<sub>2</sub>,  $\Delta$   
 (ii) *p*-Hydroxymethylbenzoate (2.1 eq.), K<sub>2</sub>CO<sub>3</sub>/DMF  
 (iii) LAH/tmf,  $\Delta$   
 (iv) SOCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, Py  
 (v) Benzene-Ethanol/KOH

(1)

Even though the crystals were obtained from chloroform, three water molecules were revealed during structure solution. These molecules would have been trapped during synthesis of the compound and exhibit high temperature factors.

Bond lengths and angles around the cyclophane molecule are normal. The bond lengths of S—C<sub>sp<sup>3</sup></sub> vary from 1.78 (1) to 1.81 (1) Å and C—S—C angles are 100.9 (5) and 101 (4)°. These values agree with the average values obtained for different structures (Allen *et al.*, 1987). The S3···S31 distance is 4.398 (3) Å.

The conformation of the molecule starting from the bond C1—C2 is *g<sup>-</sup>g<sup>-</sup>ag<sup>-</sup>asasgaasaaaagasag<sup>-</sup>ggasaa-gag<sup>-</sup>s*. The torsion angles on the two halves of the molecule C1—C33—C32—S31, C33—C1—C2—S3 [−80.9 (10) and −78.9 (10)°] and C8—O9—C10—C11, C26—O25—C24—C23 [69.8 (10) and 71.1 (10)°] indicate an approximate mirror symmetry but the torsion angles C2—S3—C4—C5 and C32—S31—C30—C29 [−171.4 (10) and 84.2 (10)°] negate this. The bond C2—S3 is in a *gauche* orientation and C32—S31 in the opposite arm is in a *trans* orientation.

The phenyl rings on the opposite arms A [C5—C6—C7—C8—C45—C46] and B' [C20—C21—C22—C23—C40—C41] are inclined at an angle 38.3 (3)° to

each other and those on *B* [C11—C12—C13—C14—C43—C44] and *A'* [C26—C27—C28—C29—C38—C39] form an angle of 37.9(3)°. The molecule as a whole assumes a sofa conformation as seen by joining the centres of the adjacent phenyl rings.

The molecule has a cavity of approximately 8.56 × 8.55 Å<sup>2</sup> measured between the opposite sides of the molecule between the atoms C13—C39 and C41—C45, respectively.

Three water molecules forming a triangular moiety are connected by hydrogen bonds and they are caught inside the cavity. The hydrogen-bonding distances are O47···O48 = 2.76 (2), O48···O49 = 2.95 (2) and O47···O49 = 2.68 (2) Å.

The packing of the molecules reveals that the planes formed by the three water molecules are stacked one above the other. The cyclophane molecules are held in the lattice by van der Waal's interactions.

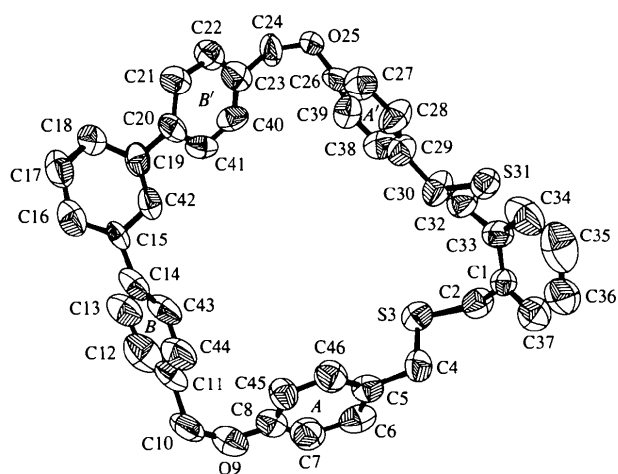


Fig. 1. An ORTEPII (Johnson, 1976) diagram of the cyclophane molecule with 50% probability ellipsoids.

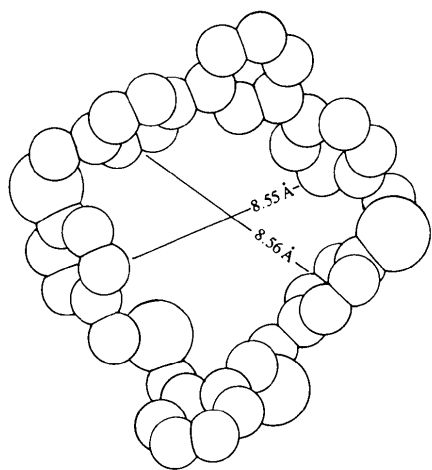


Fig. 2. Space-filling model of the cyclophane molecule showing the cavity size.

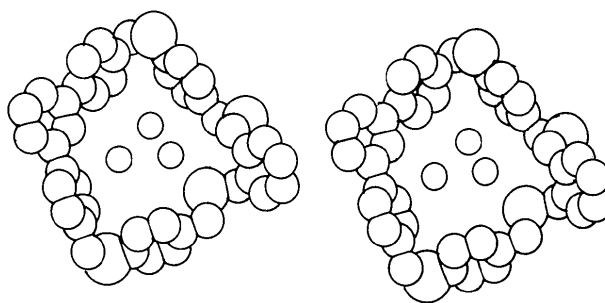


Fig. 3. Stereo packing of the cyclophane molecule.

## Experimental

### Crystal data

C<sub>42</sub>H<sub>36</sub>O<sub>2</sub>S<sub>2</sub>·3H<sub>2</sub>O

*M<sub>r</sub>* = 690.9

Orthorhombic

*Pna*2<sub>1</sub>

*a* = 11.721 (3) Å

*b* = 15.778 (2) Å

*c* = 20.879 (4) Å

*V* = 3861 (1) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.19 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Cu *K*α radiation

λ = 1.5418 Å

Cell parameters from 25

reflections

θ = 10–25°

μ = 1.58 mm<sup>-1</sup>

*T* = 293 K

Flaky

0.40 × 0.25 × 0.10 mm

Colorless

Crystal source: crystals from chloroform

### Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

none

3483 measured reflections

3483 independent reflections

2172 observed reflections

[*I* > 3σ(*I*)]

θ<sub>max</sub> = 60°

*h* = 0 → 13

*k* = 0 → 18

*l* = 0 → 24

3 standard reflections

monitored every 200

reflections

frequency: 60 min

intensity decay: 3%

### Refinement

Refinement on *F*

*R* = 0.070

*wR* = 0.077

*S* = 1.04

2172 reflections

208 parameters

All H-atom parameters

refined

*w* = 1/[σ<sup>2</sup>(*F*) + 0.006580*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.65

Δρ<sub>max</sub> = 0.63 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.32 e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
C46	0.2665 (8)	0.8298 (6)	0.2868 (1)	0.074 (5)
S3	0.1016 (2)	0.9786 (1)	0.3721 (1)	0.077 (1)
C36	0.3858 (9)	1.2067 (6)	0.3988 (5)	0.083 (6)
C1	0.2165 (7)	1.1213 (5)	0.4185 (4)	0.059 (4)
C37	0.2828 (8)	1.1714 (6)	0.3779 (5)	0.074 (5)
C2	0.1053 (9)	1.0875 (6)	0.3945 (4)	0.074 (5)

C4	0.1961 (10)	0.9789 (5)	0.3036 (5)	0.079 (6)
C45	0.2581 (8)	0.7488 (6)	0.2609 (5)	0.077 (6)
C8	0.1655 (9)	0.7286 (7)	0.2198 (5)	0.076 (6)
C7	0.0907 (9)	0.7910 (7)	0.2045 (5)	0.085 (7)
C6	0.0992 (10)	0.8741 (8)	0.2298 (5)	0.090 (7)
C5	0.1886 (9)	0.8922 (6)	0.2717 (4)	0.069 (5)
O9	0.1461 (6)	0.6531 (5)	0.1929 (3)	0.089 (4)
C10	0.2167 (10)	0.5836 (7)	0.2099 (4)	0.087 (7)
C11	0.2020 (9)	0.5493 (6)	0.2785 (4)	0.074 (6)
C44	0.2909 (9)	0.5083 (7)	0.3082 (6)	0.083 (6)
C43	0.2768 (8)	0.4737 (6)	0.3666 (5)	0.079 (6)
C14	0.1761 (7)	0.4806 (5)	0.4008 (4)	0.061 (4)
C13	0.0899 (8)	0.5249 (6)	0.3707 (5)	0.075 (5)
C12	0.1047 (8)	0.5559 (6)	0.3121 (5)	0.075 (6)
C15	0.1630 (7)	0.4472 (5)	0.4667 (4)	0.057 (4)
C16	0.2099 (7)	0.3710 (6)	0.4867 (5)	0.072 (5)
C42	0.1092 (8)	0.4954 (5)	0.5127 (4)	0.060 (4)
C20	0.0396 (7)	0.5248 (5)	0.6225	0.056 (4)
S31	0.0652 (2)	1.0987 (1)	0.5611 (1)	0.077 (1)
O25	-0.0487 (6)	0.7740 (3)	0.7612 (3)	0.069 (3)
C41	-0.0551 (7)	0.5736 (5)	0.6063 (4)	0.062 (5)
C40	-0.1056 (8)	0.6289 (6)	0.6494 (4)	0.069 (5)
C26	-0.0520 (8)	0.8272 (5)	0.7095 (4)	0.059 (4)
C21	0.0835 (8)	0.5342 (5)	0.6855 (4)	0.067 (5)
C33	0.2547 (8)	1.1066 (5)	0.4818 (4)	0.068 (5)
C17	0.1990 (9)	0.3436 (6)	0.5504 (6)	0.088 (6)
C23	-0.0642 (7)	0.6367 (5)	0.7099 (4)	0.063 (5)
C19	0.0976 (7)	0.4700 (4)	0.5756 (4)	0.059 (4)
C38	-0.1372 (8)	0.9110 (7)	0.6256 (5)	0.081 (6)
C24	-0.1149 (8)	0.6987 (5)	0.7569 (4)	0.072 (5)
C22	0.0321 (8)	0.5902 (5)	0.7279 (4)	0.065 (5)
C39	-0.1461 (8)	0.8454 (7)	0.6738 (5)	0.078 (6)
C32	0.1863 (9)	1.0477 (6)	0.5254 (4)	0.083 (6)
C29	-0.0395 (8)	0.9495 (6)	0.6116 (5)	0.072 (5)
C34	0.3557 (10)	1.1443 (8)	0.5013 (6)	0.091 (7)
C30	-0.0380 (9)	1.0141 (7)	0.5591 (7)	0.098 (8)
C35	0.4183 (10)	1.1948 (8)	0.4603 (8)	0.109 (9)
C18	0.1451 (9)	0.3939 (6)	0.5940 (4)	0.074 (5)
C27	0.0474 (8)	0.8699 (7)	0.6957 (5)	0.078 (6)
C28	0.0528 (9)	0.9316 (7)	0.6498 (5)	0.086 (7)
O47	0.3337 (10)	0.8410 (7)	0.4587 (5)	0.148 (4)
O48	0.3079 (11)	0.6683 (8)	0.4418 (7)	0.168 (4)
O49	0.1701 (16)	0.7709 (12)	0.5312 (11)	0.255 (8)

Table 2. Selected geometric parameters (Å)

S3—C2	1.78 (1)	S31—C32	1.79 (1)
S3—C4	1.81 (1)	S31—C30	1.80 (1)
C8—O9	1.34 (1)	O25—C26	1.37 (1)
O9—C10	1.42 (1)	O25—C24	1.42 (1)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978); *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Ethyl Cyano(4-oxo-3-phenyl-1,3-thiazolidin-2-ylidene)acetate

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## Abstract

There are two crystallographically independent but chemically equivalent molecules present in the asymmetric unit of the title compound, C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S. There are no unusual intra- or intermolecular distances or angles. The crystal packing is dominated mainly by hydrogen bonds and all rings in the molecules are essentially planar.

## Comment

The X-ray structure analysis of the title compound, (I), was undertaken in order to confirm the structure proposed from spectroscopy studies (González, Enriquez, Castañedo & Kellin, 1990). This compound shows strong possible activity as an adrenergic  $\beta$ -blocker, hypotensor and cardiotoxic agent based on the results