

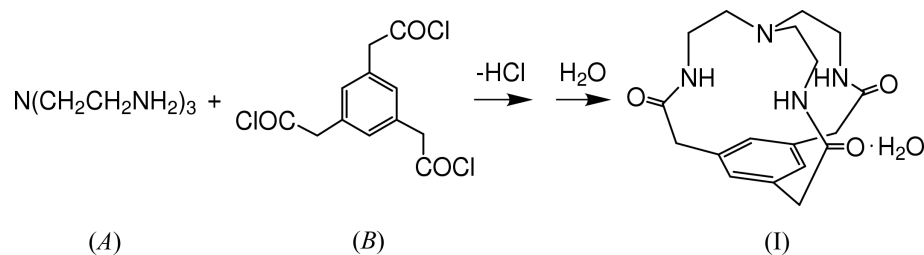
Tae Ho Kim, Sun Young Yang,
Shim Sung Lee, Jae Sang Kim and
Jineun Kim*Department of Chemistry and Research Institute
of Natural Sciences, Gyeongsang National
University, Chinju 660-701, South KoreaCorrespondence e-mail:
jekim@nongae.gsnu.ac.kr

Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
Disorder in main residue
 R factor = 0.043
 wR factor = 0.116
Data-to-parameter ratio = 14.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2,9,18-Trioxo-3,5,8,19-tetraaza-[5^{5,13}][11]meta-
cyclophane monohydrateIn the title compound, $\text{C}_{18}\text{H}_{26}\text{N}_4\text{O}_4$, the bridgehead N atom is located toward the inside of the cage and the displacement from the aromatic ring is 4.2110 (13) Å. The three C atoms adjacent to the bridgehead N atom are disordered with roughly equal occupancy between two sets of positions.Received 15 October 2001
Accepted 12 November 2001
Online 17 November 2001

Comment

The study of cyclophanes has been a subject of functional group interactions resulting from enforced mutual proximity (Pascal *et al.*, 1987, 1989; L'Esperance *et al.*, 1991). The unusual features of the cyclophanes are exotic IR and NMR signals, which are the direct result of steric compression and ring current effects, respectively. The synthesis and the crystal structure of the title compound, (I), is reported here; this has a slightly bigger cage size than the cyclophanes reported in previous papers (Pascal *et al.*, 1987, 1989; L'Esperance *et al.*, 1991). The title compound, (I), was synthesized by the ring-closure reaction of tris(2-aminoethyl)amine (A) with triacid chloride (B), *i.e.* (3,5-bis(chloroformyl)methylphenyl)acetyl chloride, according to the flow method (Dye *et al.*, 1973).



The basal aromatic ring is essentially planar with a mean deviation of 0.0105 Å (Fig. 1). Most of the distortion from ideal geometry is found in the three linking $\text{C}\alpha$ atoms. The $\text{C}\alpha$ atoms are located above the mean aromatic ring plane, as indicated by the angles $\text{C}10-\text{C}13\cdots\text{C}16$, $\text{C}11-\text{C}15\cdots\text{C}18$ and $\text{C}12-\text{C}17\cdots\text{C}14$ (Table 1). The $\text{C}_{\text{ring}}-\text{C}\alpha-\text{C}(=\text{O})$ angles range from 107.57 (12) to 114.72 (12)°. The bridgehead N atom is located toward the inside of the cage, its displacement from the aromatic ring being 4.2110 (13) Å. The three C atoms adjacent to the bridgehead N atom are disordered (Fig. 1).

All bond lengths and angles for three amide bonds are within normal ranges. All amide O atoms and only atom N3 participate in intermolecular hydrogen bonds (Fig. 2). Two

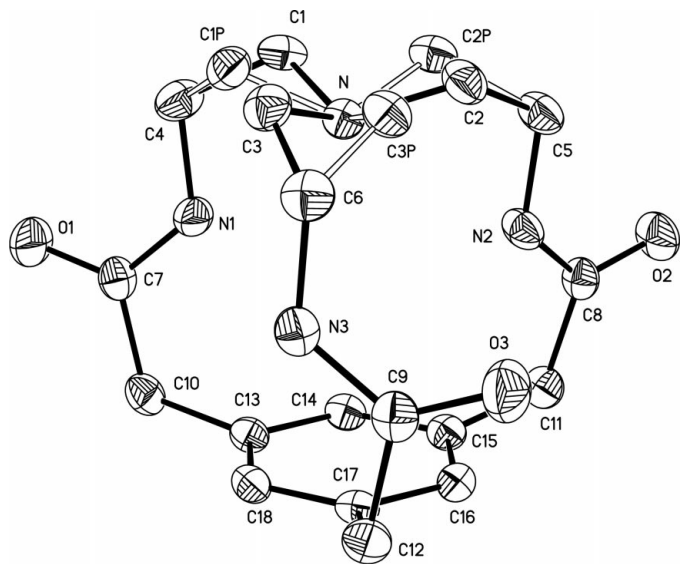


Figure 1

The structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms and a water molecule have been omitted for clarity. The molecule is partially disordered with C1, C2, C3 [solid lines, occupancy = 0.527 (3)] and C1P, C2P, C3P [open lines, occupancy = 0.473 (3)] atoms occupying two positions.

amide O atoms (O2 and O3) and two H atoms (H2N and H3N) from three amide bonds point towards the outside and the inside of the cage, respectively; the latter interact with the bridgehead N atoms, as shown in Table 2. This may play an important role in forming the inward conformation of the bridgehead N atom. The remaining amide bond is bent in order that N3 and O3 atoms may participate in the hydrogen bond with atom O2 and the water molecule, respectively. This eliminates the threefold axis of the molecule in the crystal; while this might exist in a conformation with C_3 symmetry in solution, as indicated by one ^{13}C NMR peak for three carbonyl C atoms. A water molecule (O1W) fills empty space and forms weak hydrogen bonds with the carbonyl O atoms of neighboring molecules. In addition, there are one intramolecular and three weak intermolecular C—H...O interactions. Molecules form a two-dimensional network structure as a result of these intermolecular hydrogen bonds.

Experimental

Tris(2-aminoethyl)amine (A) and 1,3,5-triacetylbenzene were purchased from Aldrich Chemical Co. and Lancaster Synthesis Ltd, respectively. The triacid chloride (B), *i.e.* (3,5-bis(chloroformylmethylphenyl)acetyl chloride, was prepared by a known method (Cochrane *et al.*, 1968) via 1,3,5-tricarboxymethylbenzene from 1,3,5-triacetylbenzene (Newman & Lowrie, 1954). The cyclophane, $\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_3$, was synthesized from equimolar amounts of (A) and (B) in anhydrous THF in the presence of triethylamine by the flow method (Dye *et al.*, 1973). The resulting mixture was filtered and removal of the solvent followed by chromatography (silica gel; methanol–ethyl

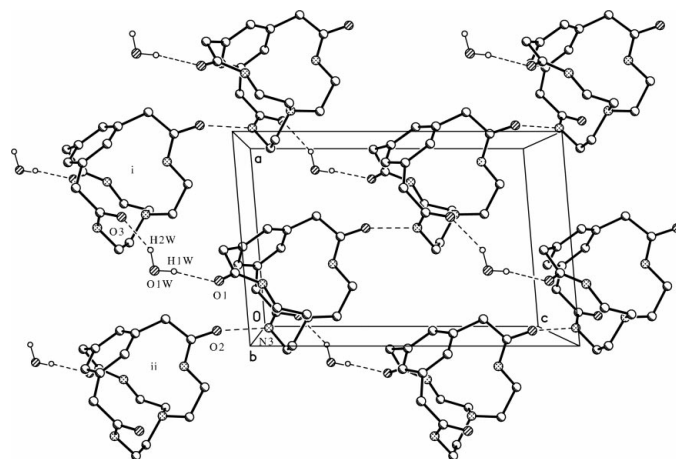


Figure 2

View along the *b* axis showing the intermolecular hydrogen bonds and N—H...O and O—H...O interactions, indicated by dashed lines. The disorder has been omitted for clarity. A set of molecules in a layer have also been omitted for clarity. [Symmetry codes: (i) $x+1/2, 3/2-y, z-1/2$; (ii) $x-1/2, 3/2-y, z-1/2$.]

acetate, 1:1) yielded the product (~20%). ^1H NMR (500 MHz, CDCl_3): δ (p.p.m.) 2.36 (*m*, 6H, $-\text{CH}_2\text{NH}-$), 3.27 (*m*, 6H, NCH_2-), 3.66 (*s*, 6H, $-\text{CH}_2\text{CO}-$), 4.96 (*s*, 3H, NH-), 7.16 (*s*, 3H, ArH); ^{13}C NMR (500 MHz, CDCl_3): δ (p.p.m.) 34.62, 43.58, 49.37, 130.55, 138.95, 170.33; MS, *m/z*: 342, 343, 344, 345, 346; calculated for $\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_3$ 344.41; UV (methanol) λ_{max} 270, 276 nm; IR (KBr disc) 3542, 3431, 3406, 3321, 2937, 2884, 2922, 1656, 1602, 1537, 1461, 1346, 1309, 1284, 1247, 1164, 1059, 955, 902, 886, 786, 734, 688 cm^{-1} . Crystals of (I) were obtained from a methanol solution upon slow evaporation.

Crystal data

$\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_3 \cdot \text{H}_2\text{O}$	$D_x = 1.345 \text{ Mg m}^{-3}$
$M_r = 362.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 11 459 reflections
$a = 9.3436$ (8) Å	$\theta = 2.1\text{--}28.3^\circ$
$b = 13.4554$ (12) Å	$\mu = 0.10 \text{ mm}^{-1}$
$c = 14.2888$ (12) Å	$T = 298$ (2) K
$\beta = 94.748$ (2)°	Plate, colorless
$V = 1790.3$ (3) Å ³	$0.50 \times 0.35 \times 0.25 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	$\theta_{\text{max}} = 28.3^\circ$
φ and ω scans	$h = -12 \rightarrow 8$
11 459 measured reflections	$k = -17 \rightarrow 17$
4316 independent reflections	$l = -18 \rightarrow 19$
2794 reflections with $I > 2\sigma(I)$	156 standard reflections
$R_{\text{int}} = 0.064$	frequency: 360 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.0871P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
4316 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
295 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

O1—C7	1.227 (2)	N—C1P	1.423 (4)
O2—C8	1.2276 (17)	N1—C4	1.443 (2)
O3—C9	1.2252 (19)	N1—C7	1.324 (2)
N—C3	1.505 (3)	N2—C8	1.3340 (19)
N—C1	1.483 (3)	N2—C5	1.443 (2)
N—C2	1.417 (3)	N3—C6	1.446 (2)
N—C3P	1.481 (4)	N3—C9	1.332 (2)
N—C2P	1.515 (3)		
C1—N—C2	113.1 (2)	N2—C5—C2	109.97 (15)
C1—N—C3	107.24 (17)	N3—C6—C3	112.96 (16)
C1P—N—C2P	110.9 (2)	N3—C6—C3P	115.30 (15)
C1P—N—C3P	112.8 (2)	O1—C7—C10	120.77 (13)
C2—N—C3	112.20 (18)	N1—C7—C10	117.22 (14)
C2P—N—C3P	106.09 (18)	O1—C7—N1	121.98 (15)
C4—N1—C7	125.12 (14)	O2—C8—C11	120.56 (13)
C5—N2—C8	125.17 (13)	O2—C8—N2	122.18 (14)
C6—N3—C9	123.84 (13)	N2—C8—C11	117.27 (12)
N—C1—C4	116.4 (2)	N3—C9—C12	115.90 (13)
N—C1P—C4	114.5 (3)	O3—C9—C12	121.69 (14)
N—C2—C5	115.8 (2)	O3—C9—N3	122.34 (14)
N—C2P—C5	115.5 (3)	C7—C10—C13	114.72 (12)
N—C3—C6	115.32 (19)	C8—C11—C15	113.89 (12)
N—C3P—C6	115.5 (2)	C9—C12—C17	107.57 (12)
N1—C4—C1	110.84 (17)	C10—C13...C16	171.00 (10)
N1—C4—C1P	110.71 (19)	C11—C15...C18	168.92 (10)
N2—C5—C2P	112.47 (16)	C12—C17...C14	167.97 (10)
N1—C7—C10—C13	10.2 (2)	O2—C8—C11—C15	179.11 (14)
O1—C7—C10—C13	−171.80 (14)	N3—C9—C12—C17	70.72 (16)
N2—C8—C11—C15	−1.4 (2)	O3—C9—C12—C17	−106.26 (16)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...N	0.85 (2)	2.443 (18)	2.8240 (18)	108.2 (14)
O1W—H1W...O1	0.85 (3)	1.99 (3)	2.834 (2)	173 (3)
N2—H2N...N	0.870 (18)	2.451 (18)	2.8593 (17)	109.4 (14)
O1W—H2W...O3 ⁱ	0.93 (5)	2.09 (5)	2.940 (2)	151 (4)
N3—H3N...O2 ⁱⁱ	0.84 (2)	2.168 (19)	2.9540 (18)	156.3 (17)
C5—H5A...O3 ⁱⁱⁱ	0.97	2.52	3.465 (2)	165
C6—H6A...O3	0.97	2.40	2.799 (2)	104
C12—H12B...O1W ^{iv}	0.97	2.55	3.504 (2)	167
C14—H14...O1 ^v	0.975 (16)	2.525 (16)	3.438 (2)	155.9 (13)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$; (v) $1 - x, 2 - y, -z$.

The first 50 frames were retaken after complete data collection, showing no significant decay of the crystal. The H atoms of ethylene- and methylene-C atoms were added at their calculated positions ($U = 1.2$ times that of the corresponding C atom) and refined using a riding model. The other eight H atoms were located from difference Fourier maps and were included at the final cycle of the refinement. The C—H, N—H and O—H bond lengths are 0.95 (2)–0.98 (2), 0.84 (2)–0.87 (2) and 0.85 (3)–0.93 (5) Å, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SHELXTL* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *PLATON* (Spek, 2001).

Support from the Korea Research Foundation (project No. 99-005-D00004) is gratefully acknowledged. The authors wish to thank the Central Laboratory, Gyeongsang National University for provision of a Siemens SMART CCD diffractometer and Jae Sung Seo for his technical support.

References

- Cochrane, W. P., Pauson, P. L. & Stevens, T. S. (1968). *J. Chem. Soc. C*, pp. 630–632.
- Dye, J. L., Lok, M. T., Tehan, F. J., Ceraso, J. M. & Voorhees, K. J. (1973). *J. Org. Chem.* **38**, 1773–1775.
- L'Esperance, R. P., West, A. P. Jr, Engen, D. V. & Pascal, R. A. Jr (1991). *J. Am. Chem. Soc.* **113**, 2672–2676.
- Newman, M. S. & Lowrie, H. S. (1954). *J. Am. Chem. Soc.* **76**, 6196–6197.
- Pascal, R. A. Jr, Grossman, R. B. & Engen, D. V. (1987). *J. Am. Chem. Soc.* **109**, 6878–6880.
- Pascal, R. A. Jr, Winans, C. G. & Engen, D. V. (1989). *J. Am. Chem. Soc.* **111**, 3007–3010.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Siemens (1996). *SMART*, *SAINT* (Version 4.0) and *SHELXTL* (Version 5.03). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2001). *PLATON*. Version 31001. Utrecht University, The Netherlands.