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### *cis*-1,5-Diamino-2,4,6,8-tetraazabicyclo-[3.3.0]octane-3,7-dione

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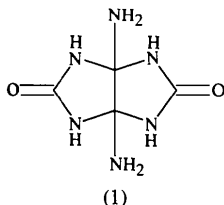
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#### Abstract

The title compound, C<sub>4</sub>H<sub>8</sub>N<sub>6</sub>O<sub>2</sub>, represents a virtually unknown vicinal orthoamide array, formally derivable from oxalic acid. The *cis*-fused imidazolidinone rings adopt a flattened envelope conformation. H atoms of the nearly eclipsed vicinal diamine groups [N1—C1—C5—N5 −9.5(3)°] are oriented inwards [H1a··H5a = 2.44(4) and H1b··H5b = 2.49(4) Å].

#### Comment

As part of our investigation of uricolytic pathways, we were interested in biomimetic oxidations of urate. A range of covalent adducts have been isolated from reaction with ferricyanide in an ammonia solution. The structure of the title compound, (1), was determined to corroborate the assignment of an unusual vicinal orthoamide array to the adduct. Details of the synthetic work and structural assignment based on chemical and spectroscopic data have been published previously (Popović, Sokolić, Modrić, Palković & Poje, 1991). This paper reports the structure of (1) as determined by X-ray crystallography.



An ORTEP92 (Vicković, 1994) drawing of the molecule is shown in Fig. 1. The *cis*-fused imidazolidinone rings are in a shallow half-chair (envelope) conformation. The angle between the least-squares planes through the rings is 61.63(6)°. The angular amino substituents, adopting a nearly synperiplanar conformation [N1—

C1—C5—N5 = −9.5(3)°], have their H atoms oriented inwards with intramolecular H1a··H5a and H1b··H5b distances of 2.44(4) and 2.49(4) Å, respectively; the amino groups thus adopt a conformation in which the N-atom lone pair is nearly antiperiplanar to the central C1—C5 bond. The compact structure involves a complex hydrogen-bonding network involving all H atoms of the molecule; this certainly accounts for the small cell volume, relatively high density of the crystals and the high melting point.

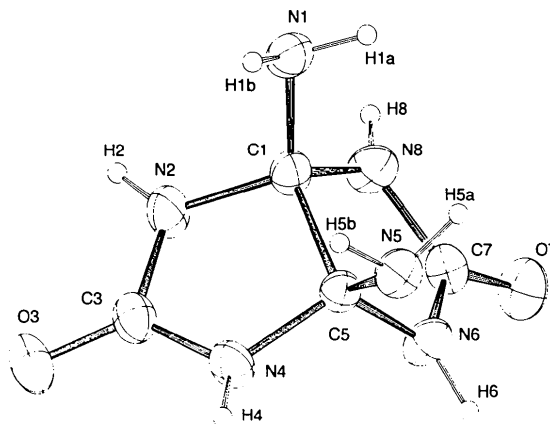


Fig. 1. View of the molecule (1) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

#### Experimental

Crystals of (1) (m.p. >600 K) were obtained through ferricyanide oxidation of uric acid in a concentrated ammonia solution (Popović, Sokolić, Modrić, Palković & Poje, 1991). *D<sub>m</sub>* was measured by flotation in bromoform–dichloromethane.

#### Crystal data

C<sub>4</sub>H<sub>8</sub>N<sub>6</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 172.15  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 10.640(3) Å  
*b* = 10.618(4) Å  
*c* = 5.976(2) Å  
 $\beta$  = 102.86(2)°  
*V* = 658.2(4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.7372 Mg m<sup>−3</sup>  
*D<sub>m</sub>* = 1.73 Mg m<sup>−3</sup>

Cu K $\alpha$  radiation  
 $\lambda$  = 1.54178 Å  
 Cell parameters from 16 reflections  
 $\theta$  = 13–20°  
 $\mu$  = 1.170 mm<sup>−1</sup>  
*T* = 293(2) K  
 Prism  
 0.36 × 0.27 × 0.09 mm  
 Colourless

#### Data collection

Philips PW1100/20 diffractometer  
 $\theta$  scans  
 Absorption correction: none  
 1142 measured reflections  
 1142 independent reflections  
 1138 observed reflections  
 [*I* > 2 $\sigma$ (*I*)]

$\theta_{\max}$  = 69.96°  
*h* = −12 → 12  
*k* = 0 → 12  
*l* = 0 → 7  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: none

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0420$   
 $wR(F^2) = 0.1207$   
 $S = 1.289$   
 1142 reflections  
 142 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.4406P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.004$

$\Delta\rho_{\max} = 0.302 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.318 \text{ e } \text{Å}^{-3}$   
 Extinction correction:  
*SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient:  
 0.1127 (65)  
 Atomic scattering factors  
 from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

(Sheldrick, 1993). Molecular graphics: *ORTEP92* (Vicković, 1994). Software used to prepare material for publication: *CSU* (Vicković, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ( $\text{Å}^2$ )

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

	x	y	z	$U_{\text{eq}}$
C1	0.7850 (2)	-0.1307 (2)	0.3971 (3)	0.0234 (5)
C3	0.6462 (2)	-0.3011 (2)	0.4055 (4)	0.0270 (5)
C5	0.6552 (2)	-0.1159 (2)	0.2010 (3)	0.0217 (5)
C7	0.6769 (2)	0.0531 (2)	0.4589 (3)	0.0253 (5)
N1	0.9048 (2)	-0.1452 (2)	0.3269 (3)	0.0284 (5)
N2	0.7559 (2)	-0.2422 (2)	0.5135 (3)	0.0319 (5)
N4	0.5880 (2)	-0.2314 (2)	0.2215 (3)	0.0279 (5)
N5	0.6647 (2)	-0.0982 (2)	-0.0328 (3)	0.0274 (5)
N6	0.5991 (2)	-0.0047 (2)	0.2794 (3)	0.0278 (5)
N8	0.7865 (2)	-0.0155 (2)	0.5254 (3)	0.0292 (5)
O3	0.6071 (2)	-0.40240 (15)	0.4647 (3)	0.0380 (5)
O7	0.6531 (2)	0.1537 (2)	0.5435 (3)	0.0350 (5)

Table 2. *Selected bond lengths* ( $\text{Å}$ ) *and angles* ( $^\circ$ )

C1—N1	1.436 (3)	C5—N5	1.435 (3)
C1—N2	1.442 (3)	C5—N4	1.439 (3)
C1—N8	1.442 (3)	C5—N6	1.448 (3)
C1—C5	1.608 (3)	C7—O7	1.232 (3)
C3—O3	1.233 (3)	C7—N6	1.348 (3)
C3—N2	1.354 (3)	C7—N8	1.357 (3)
C3—N4	1.356 (3)		
N1—C1—N2	110.7 (2)	N4—C5—N6	114.8 (2)
N1—C1—N8	110.0 (2)	N5—C5—C1	119.2 (2)
N2—C1—N8	114.7 (2)	N4—C5—C1	102.6 (2)
N1—C1—C5	118.2 (2)	N6—C5—C1	101.16 (15)
N2—C1—C5	100.9 (2)	O7—C7—N6	125.1 (2)
N8—C1—C5	102.1 (2)	O7—C7—N8	126.0 (2)
O3—C3—N2	125.2 (2)	N6—C7—N8	108.9 (2)
O3—C3—N4	125.9 (2)	C3—N2—C1	113.8 (2)
N2—C3—N4	108.9 (2)	C3—N4—C5	112.8 (2)
N5—C5—N4	109.8 (2)	C7—N6—C5	113.8 (2)
N5—C5—N6	109.4 (2)	C7—N8—C1	113.1 (2)

Table 3. *Hydrogen-bonding geometry* ( $\text{Å}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1a...O3 <sup>i</sup>	0.90 (3)	2.22 (3)	3.098 (3)	164 (3)
N1—H1b...O7 <sup>ii</sup>	0.89 (3)	2.15 (3)	3.039 (3)	170 (3)
N2—H2...O7 <sup>iii</sup>	0.86 (3)	2.01 (3)	2.833 (3)	159 (3)
N4—H4...N1 <sup>iv</sup>	0.92 (3)	2.09 (3)	3.005 (3)	177 (3)
N5—H5a...O3 <sup>i</sup>	0.93 (3)	2.25 (3)	3.153 (3)	165 (3)
N5—H5b...O7 <sup>ii</sup>	0.94 (3)	2.40 (3)	3.280 (3)	155 (3)
N6—H6...N5 <sup>v</sup>	0.88 (3)	2.19 (3)	3.066 (3)	177 (3)
N8—H8...O3 <sup>ii</sup>	0.85 (3)	2.49 (4)	3.236 (3)	146 (3)

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

Data collection: Philips PW1100/20 software. Cell refinement: Philips PW1100/20 software. Data reduction: locally written software. Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELXL93*

**References**

- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.  
 Popović, T., Sokolić, L., Modrić, N., Palković, A. & Poje, M. (1991). *Tetrahedron*, **47**, 317–322.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.  
 Vicković, I. (1988). *J. Appl. Cryst.* **21**, 987–990.  
 Vicković, I. (1994). *J. Appl. Cryst.* **27**, 437.

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## A Precursor to Highly Unsaturated Cyclophanes: 7,19,28-Trithiatetrapoly[11.11.7.1<sup>3,23</sup>.1<sup>11,15</sup>]tritriacontacyclo[1,3(32),11(33),12,14,23-hexaene-4,9,16,22,25,30-hexayne

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**Abstract**

The title compound,  $\text{C}_{30}\text{H}_{18}\text{S}_3\cdot\text{CH}_2\text{Cl}_2$ , has an almost eclipsed conformation with the aromatic rings showing normal van der Waals contacts. The alkyne units in the bridges show some deviation from linearity as a result. The crystal contains solvent dichloromethane which was partially lost in data collection, resulting in a final effective occupancy of 0.55.

**Comment**

Multiply bonded cyclophanes have been known for some time (Mitchell & Boekelheide, 1970; Boekelheide & Hollins, 1970; Boekelheide, 1973; Vögtle & Neumann, 1969; Vögtle, 1969). Recently there has been a resurgence of interest in these compounds because of the potential for their conversion to  $\text{C}_{60}$  derivatives (Vollhardt, Boese, Green, Mittendorf & Mohler, 1992). In