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Structure of 4,10–Dinitro–2,6,8,12–tetraoxa–4,10–diazatetracyclo[5,5,0,0^{5,9}0^{3,11}]dodecane

by

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Structure of 4,10-Dinitro-2,6-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}0^{3,11}]dodecane

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Abstract. $C_6H_6N_4O_8$, M_r = 262.14, triclinic,, $P_{\bar{1}}$, a = 6.814(1), b = 7.622(1), c = 8.733(1)Å, α = 82.23(1), β = 75.02(1), γ = 79.45(1)°, V = 428.9(1)Å^3, Z = 2, D_m (298K) = 1.99(1) g cm^{-3}, D_x (100K) = 2.03 g cm^{-3}, λ (MoKα) = 0.71073 Å, μ = 1.796 cm^{-1}, F (000) = 268, T = 100(5) K, R = 0.033, wR = 0.055 for 2240 unique observed reflections. The title compound contains an *isowurtzitane* type cage which results in an unusually high density. There are no unusual intermolecular contacts.

Experimental. The title compound was prepared by condensation of glyoxal and 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine in the presence of sulfuric and nitric acids (Ramakrishnan, Vedachalam, & Boyer, 1990). Cooling the reaction mixture with ice yielded colorless crystals suitable for data collection. The density was measured at room temperature by flotation in a mixture of tribromomethane and bromochloromethane. A rectangular plate with approximate dimensions 0.6x0.2x0.6 mm was mounted on an Enraf-Nonius CAD4 diffractometer with graphite crystal monochromator and cooled to 100(5)K with a stream of cold N_2 gas. Lattice parameters were determined from least-squares refinement of 25 reflections measured with $43 < 2\theta < 59°$ using MoKα radiation. Integrated.intensities were measured using $\omega{:}2\theta$ scans in the range $2 \leq 2\theta \leq 60°$, $0 \leq h \leq 9$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$. The intensities of three standard reflections measured at 2h intervals decreased by 2.1% during data collection. A linear least-squares fit to the intensities of the standards was used to correct the data. Variation in the intensities of two reflections as a function of Ψ was measured at 10° intervals and used to apply an empirical absorption correction (maximum relative transmission 99.9%, minimum relative transmission 95.3%). Lorentz and polarization corrections were applied yielding a total of 2502 structure factors of which 2240 were considered observed $[|F| > 3\sigma(F)]$.

The structure was solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq, & Woolfson, 1980; modified by Frenz, 1982). Peaks corresponding to all 18 non-hydrogen atoms were located in the E map, and the positions of the six hydrogen atoms in a subsequent Fourier synthesis. Refinement was by full-matrix least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$ and $\sigma^2(F^2) = \sigma_{cs}^2 + (0.04F^2)^2$. Positions and anisotropic thermal parameters were refined for non-H atoms, positions and isotropic thermal parameters for H atoms. Examination of the largest structure factors revealed the presence of some extinction, and an extinction correction parameter was included in the refinement (maximum correction 7%). Final $R = 0.033$, $wR = 0.055$, $S = 2.20$, and $(\Delta/\sigma)_{max} = 0.01$ for 188 variables.* Maximum and minimum peaks in final difference Fourier synthesis were 0.42 and -0.31 eÅ^{-3}, respectively. Atomic scattering factors and anomalous dispersion corrections taken from the *International Tables for X-ray*

Crystallography (1974), and all computer programs from the *SDP* system (Frenz, 1982). Final atomic coordinates are listed in Table 1. Bond lengths and angles are given in Table 2. The molecular structure is depicted in Fig. 1 along with the atomic numbering scheme.

Related Literature. The title compound is the first example of a dioxaazepane and the densest dinitramine composed of C, H, N and O atoms that is known (Ramakrishnan, et al., 1990). It is closely related to the structures of two hexaazaisowurtzitane derivatives determined by Gilardi (1990), but with four nitrogen atoms replaced by oxygen atoms.

*Lists of structure factors, anisotropic temperature factors, H-atom positions, and bond distances and angles have been deposited with the British Library Document Supply Center as Supplementary Publication No. SUP XXXXX (XX pp.) Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Legends to Figures

Figure 1.   ORTEP plot (Johnson 1976) of the cation showing the atomic numbering scheme. Thermal ellipsoids are plotted at the 50% probability level.

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Table 1. Positional and Equivalent Isotropic Thermal Parameters
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Atom	x	y	z	$\cdot\ B(\overset{o}{A}{}^{2})$
O1	0.5389(1)	0.33149(9)	0.30929(8)	0.98(1)
O2	0.7165(1)	0.06685(9)	0.37613(8)	1.02(1)
O3	0.9335(1)	0.23289(9)	0.50261(8)	1.05(1)
O4	0.7553(1)	0.49657(9)	0.43645(8)	1.05(1)
C5	0.6700(1)	0.6053(1)	-0.01471(9)	1.63(1)
O6	0.7882(1)	0.7495(1)	0.1310(1)	1.91(1)
O7	1.1734(1)	-0.1140(1)	0.14412(9)	1.50(1)
O8	1.3467(1)	0.0142(1)	0.26128(9)	1.61(1)
N1	0.8400(1)	0.4481(1)	0.16036(9)	0.87(1)
N2	1.0380(1)	0.1531(1)	0.23495(9)	0.94(1)
N3	0.7566(1)	0.6135(1)	0.0893(1)	1.12(1)
N4	1.1958(1)	0.0072(1)	0.21423(9)	1.05(1)
C1	0.5996(1)	0.2246(1)	0.4409(1)	0.97(1)
C2	0.7297(1)	0.3246(1)	0.5167(1)	1.00(1)
C3	0.7130(1)	0.3078(1)	0.1792(1)	0.89(1)
C4	0.8366(1)	0.1247(1)	0.2259(1)	0.90(1)
C5	1.0409(1)	0.2797(1)	0.3439(1)	0.92(1)
C6	0.9165(1)	0.4640(1)	0.2980(1)	0.94(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

Table 2. Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
======	======	========	======	======	========
O1	C1	1.423(1)	O2	C1	1.414(1)
O4	C2	1.418(1)	O3	C2	1.418(1)
O1	C3	1.418(1)	O2	C4	1.417(1)
O4	C6	1.423(1)	O3	C5	1.422(1)
N1	C3	1.461(1)	N2	C4	1.451(1)
N1	C6	1.456(1)	N2	C5	1.449(1)
N1	N3	1.416(1)	N2	N4	1.394(1)
O5	N3	1.218(1)	O7	N4	1.226(1)
O6	N3	1.216(1)	O8	N4	1.214(1)
C3	C4	1.555(1)	C5	C6	1.562(1)
C1	C2	1.579(1)			

Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
========	========	========	=======	========	========	========	=======
C1	O1	C3	105.25(5)	O6	N3	N1	117.22(6)
C1	O2	C4	105.57(5)	O7	N4	O8	125.64(7)
C2	O3	C5	105.49(5)	O7	N4	N2	116.99(6)
C2	O4	C6	105.08(5)	O8	N4	N2	117.30(6)
N3	N1	C3	113.19(5)	O1	C1	O2	104.41(5)
N3	N1	C6	114.28(5)	O1	C1	C2	111.19(5)
C3	N1	C6	115.66(6)	O2	C1	C2	111.77(5)
N4	N2	C4	117.19(5)	O3	C2	O4	104.07(6)
N4	N2	C5	117.78(5)	O3	C2	C1	111.78(5)
C4	N2	C5	116.26(5)	O4	C2	C1	112.05(6)
O5	N3	O6	126.15(7)	O1	C3	N1	111.50(5)
O5	N3	N1	116.49(6)	O1	C3	C4	104.16(5)
N1	C3	C4	109.06(5)	O3	C5	C6	103.39(5)
O2	C4	N2	112.16(5)	N2	C5	C6	108.85(5)
O2	C4	C3	103.91(5)	O4	C6	N1	112.48(5)
N2	C4	C3	108.82(6)	O4	C6	C5	104.07(5)
O3	C5	N2	112.60(5)	N1	C6	C5	108.82(5)

Numbers in parentheses are estimated standard deviations
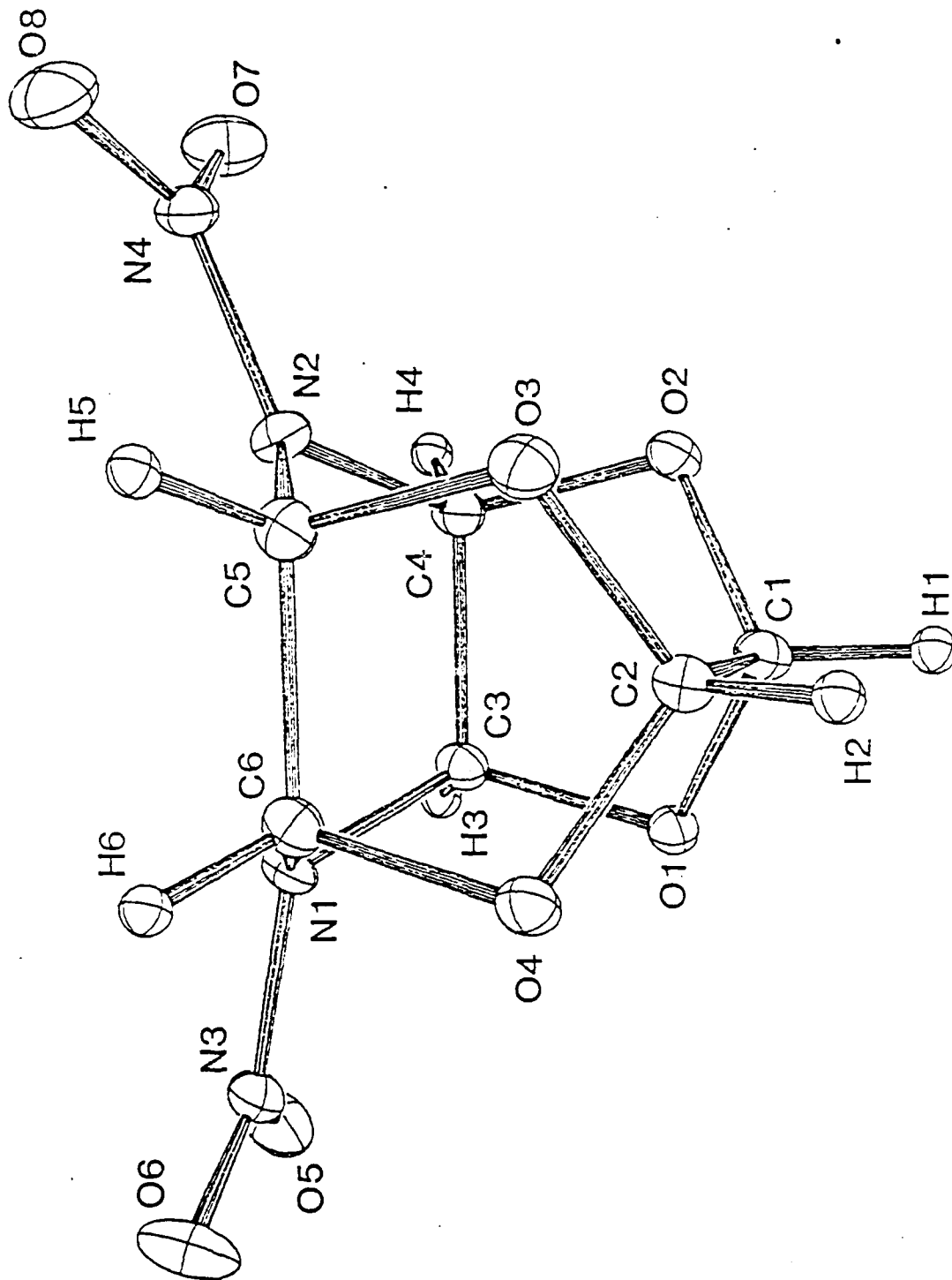in the least significant digits.

Figure 1