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TECHNICAL REPORT # 43

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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Published in

ACTA CRYST., SECT. C, accepted

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July 15, 1991

Handwritten checkmark and stamp area with text: A-1

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91-06095



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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE Unclassified			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report # 43 Contract N00014-85-K-0896			7a. NAME OF MONITORING ORGANIZATION		
6a. NAME OF PERFORMING ORGANIZATION University of New Orleans Department of Chemistry	6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code)			
6c. ADDRESS (City, State, and ZIP Code) University of New Orleans New Orleans, LA 70148		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-85-K-0896			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS			
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Structure of 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo [5,5,0,0 ^{5,9} 0 ^{3,11}] dodecane					
12. PERSONAL AUTHOR(S) D. T. Miranda, E. D. Stevens, V. T. Ramakrishnan, M. Vedachalam, and J. H. Boyer					
13a. TYPE OF REPORT Technical Report	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) July 1, 1991		15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
See Attached Report					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Joseph H. Boyer			22b. TELEPHONE (Include Area Code) (504) 286-7225		22c. OFFICE SYMBOL

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

BY

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Abstract. $C_6H_6N_4O_8$, $M_r = 262.14$, triclinic, $P\bar{1}$, $a = 6.814(1)$, $b = 7.622(1)$, $c = 8.733(1)\text{\AA}$, $\alpha = 82.23(1)$, $\beta = 75.02(1)$, $\gamma = 79.45(1)^\circ$, $V = 428.9(1)\text{\AA}^3$, $Z = 2$, $D_m(298K) = 1.99(1)\text{ g cm}^{-3}$, $D_x(100K) = 2.03\text{ g cm}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71073\text{ \AA}$, $\mu = 1.796\text{ cm}^{-1}$, $F(000) = 268$, $T = 100(5)\text{ K}$, $R = 0.033$, $wR = 0.055$ 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-tetrahydropiperazine 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 N₂ gas. Lattice parameters were determined from least-squares refinement of 25 reflections measured with $43 < 2\theta < 59^\circ$ using MoK α radiation. Integrated intensities were measured using $\omega:2\theta$ scans in the range $2 \leq 2\theta \leq 60^\circ$, $0 \leq h \leq 9$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$. 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 $\sum w(|F_o| - |F_c|)^2$, 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 dioxazepane 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 XXXXXX (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.

Table 1. Positional and Equivalent Isotropic Thermal Parameters

Atom	x	y	z	$B(A^2)$
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)
O5	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.

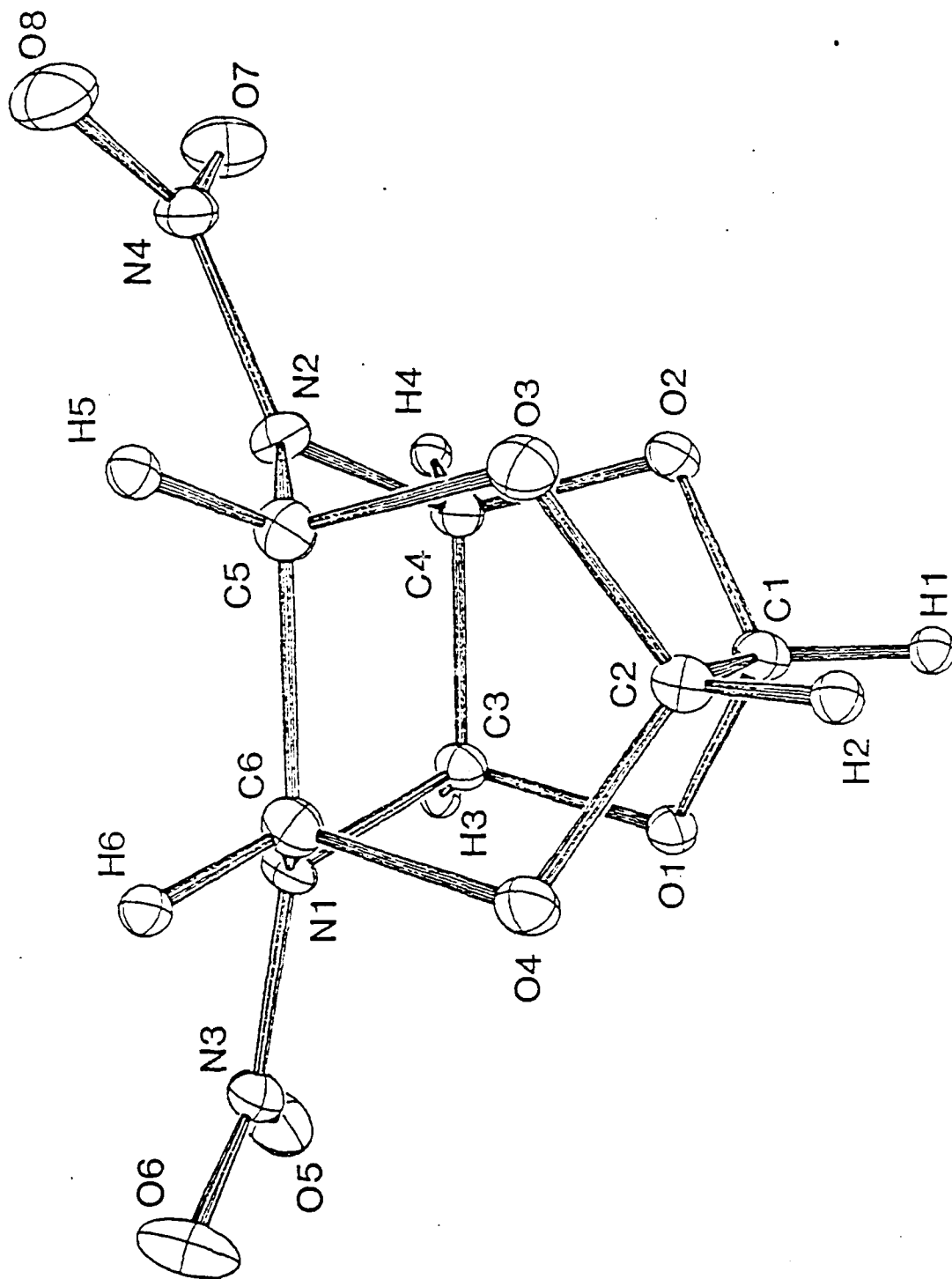


Figure 1