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Acta Cryst. (1985). **C41**, 1322–1324

The Structure of 13,14-Dimethoxy-3,10-diazabicyclo[10.2.2]hexadeca-12,14,15-triene-2,11-dione Monohydrate, C₁₆H₂₂N₂O₄·H₂O

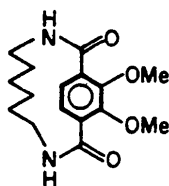
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(Received 20 August 1984; accepted 9 April 1985)

Abstract. $M_r = 324.37$, orthorhombic, $P2_12_12_1$, $a = 10.6103$ (11), $b = 12.6144$ (10), $c = 12.7713$ (13) Å, $V = 1709.3$ (5) Å³, $Z = 4$, $D_m = 1.258$ (4), $D_x = 1.261$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.877$ cm⁻¹, $F(000) = 696$, $T = 298$ K, $R = 0.0291$ for 2102 independent reflections with $F^2 > 3\sigma(F^2)$. The crystal structure shows the asymmetric orientation of the hexamethylene bridge. This bridge is tilted toward the methoxy groups. The benzene ring is slightly distorted, and the water molecule forms an intermolecular bridge between amide and carbonyl groups of adjacent molecules *via* hydrogen bonding.

Introduction. Macrocyclic ligands containing pyrocatechol moieties (1,2-benzenediol) are of interest as metal chelating agents, owing to their potentially enhanced strength and selectivity of bonding. The title compound (1) was prepared in an intermediate step of a program to synthesize such macrocyclic ligands. It was isolated along with higher-order cyclic oligomers (dimers, trimers *etc.*) from the high-dilution reaction of 2,3-dimethoxyterephthaloyl dichloride and 1,6-hexanediamine. Unlike the smaller-chain diamines, 1,6-hexanediamine was of sufficient length to bridge across one terephthalate moiety, yielding this monomeric compound whose physical properties were substantially different from the other cyclic oligomers. In particular, ¹H NMR shows a considerable upfield shift of the bridging methylene hydrogens, indicating that these protons are constrained to lie atop the benzene ring.



0108-2701/85/091322-03\$01.50

Experimental. Colorless hexagonal prisms, crystallized from water, provided by SJR, Dr Chui Ng and Dr K. N. Raymond; D_m by flotation in salt (K₂CO₃) water; crystal 0.45 × 0.34 × 0.40 mm; precession photographs, orthorhombic symmetry and systematic absences $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd; Enraf–Nonius CAD-4 diffractometer, unit cell: least squares on 24 high-angle reflections; graphite-monochromatized Mo $K\alpha$, θ – 2θ scans; 2507 intensities in quadrant $+h +k \pm l$ ($h = 0$ –11, $k = 0$ –13, $l = 0$ –13), $3 < 2\theta < 45^\circ$; no decrease in intensity in 3 standards nor did crystal orientation need to be redetermined during data collection; data corrected for background, scan speed, Lorentz and polarization factors (Frenz, 1982); empirical absorption correction, $T_{\min} = 97.81$, $T_{\max} = 99.87$, $\sin\theta/\lambda_{\max} = 0.5233$ Å⁻¹; systematically absent reflections and redundant data rejected yielding 2230 data, 2102 of which had $F^2 > 3\sigma(F^2)$. Structure solved by direct methods; first run of *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) unambiguously yielded positions of nitrogen atoms, four of five oxygen atoms and fourteen of sixteen carbon atoms; subsequent least-squares refinement and Fourier syntheses yielded positions of remaining carbon and oxygen atoms; majority of hydrogen atoms located following full anisotropic refinement of non-hydrogen atoms. All hydrogen atoms, except water hydrogens, assigned idealized coordinates, with bond lengths 0.95 Å; hydrogen atoms assigned thermal factors $B = 4.3$ to 10.8 Å², based on magnitude of thermal parameters of parent atoms; water hydrogens assigned coordinates of their associated peaks in difference Fourier map. Extinction coefficient refined to 8.033×10^{-7} (Darwin, 1922). $w = \{4F_o^2/\sigma^2(F_o^2)\}$, $\sigma^2(F_o^2) = \{\sigma_o^2(F_o^2) + (pF_o^2)^2\}$, $p = 0.02$, $\sum w(\Delta F)^2$ minimized; final least-squares cycle $R = 2.91$, $wR = 4.21\%$, enantiomeric structure refined to same R values; max. $\Delta/\sigma = 0.00$; final difference Fourier $\Delta\rho$

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Table 1. *Positional parameters and their e.s.d.'s*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)*
O(1)	0.5673 (1)	1.1756 (1)	0.0692 (1)	4.10 (3)
O(2)	-0.0090 (1)	0.9493 (1)	-0.1455 (1)	4.38 (3)
O(3)	0.4923 (1)	0.8821 (1)	0.0271 (1)	4.02 (3)
O(4)	0.2672 (1)	0.8027 (1)	-0.0460 (1)	4.61 (3)
O(5)	0.4016 (1)	0.3510 (1)	0.0934 (1)	4.97 (3)
N(1)	0.6485 (1)	1.0835 (1)	-0.0654 (1)	3.77 (3)
N(2)	0.1342 (2)	0.8764 (1)	-0.2533 (1)	3.68 (3)
C(1)	0.2086 (2)	0.9735 (1)	-0.1027 (1)	2.89 (4)
C(2)	0.2275 (2)	1.0826 (1)	-0.1058 (1)	3.04 (4)
C(3)	0.3369 (2)	1.1250 (1)	-0.0653 (1)	3.00 (4)
C(4)	0.4290 (2)	1.0598 (1)	-0.0230 (1)	2.91 (4)
C(5)	0.4050 (2)	0.9520 (1)	-0.0106 (1)	2.92 (3)
C(6)	0.2925 (2)	0.9096 (1)	-0.0495 (1)	3.14 (4)
C(7)	0.5548 (2)	1.1090 (1)	-0.0018 (2)	3.14 (4)
C(8)	0.1018 (2)	0.9293 (1)	-0.1680 (2)	3.19 (4)
C(9)	0.6433 (2)	1.0106 (2)	-0.1551 (2)	3.96 (4)
C(10)	0.5976 (2)	1.0613 (2)	-0.2557 (2)	4.30 (5)
C(11)	0.5825 (2)	0.9827 (2)	-0.3458 (2)	5.24 (5)
C(12)	0.4843 (2)	0.8954 (2)	-0.3283 (2)	4.65 (5)
C(13)	0.3495 (2)	0.9348 (2)	-0.3163 (2)	3.90 (4)
C(14)	0.2610 (2)	0.8456 (2)	-0.2849 (2)	3.93 (4)
C(15)	0.5414 (3)	0.8979 (2)	0.1279 (2)	6.38 (6)
C(16)	0.2616 (3)	0.7528 (3)	0.0514 (2)	10.21 (9)

* Anisotropically refined atoms are given the form of the isotropic equivalent thermal parameter defined as: $\frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23})$.

from 0.195 to 0.101 e Å⁻³, GOF with 209 variables 2.730, atomic scattering factors of C,N,O,H atoms and *f'* and *f''* values from *International Tables for X-ray Crystallography* (1974).*

Discussion. The final atomic parameters are listed in Table 1. Bond distances and angles are listed in Table 2. The molecular structure of the title compound is shown in Fig. 1 along with the crystallographic numbering scheme. The hexamethylene bridge is situated above the benzene ring causing a slight ring distortion, C(1) and C(4) are both displaced about 0.05 Å above the least-squares plane of the benzene ring. The bridge is bent toward the methoxy groups resulting in a dihedral angle of about 70° between the least-squares planes of the benzene ring and the amides (see Fig. 2). All other bond lengths and angles are consistent with literature values. The carbonyl oxygen is hydrogen bonded to one of the water hydrogens, with an OH distance of 1.763 (1) Å. The oxygen of the water molecule is hydrogen bonded to the amide hydrogen of an adjacent molecule, with an OH distance of 1.950 (1) Å.

This structure determination was undertaken as part of a course in X-ray crystallography taught by the Chemistry Department at the University of California,

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and hydrogen-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42160 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths (Å) and angles (°) with their e.s.d.'s in parentheses*

C(1)—C(2)	1.392 (2)	C(1)—C(6)	1.379 (2)
C(2)—C(3)	1.378 (2)	C(6)—C(5)	1.400 (2)
C(3)—C(4)	1.386 (2)	C(5)—C(4)	1.393 (2)
C(5)—O(3)	1.366 (1)	C(6)—O(4)	1.376 (1)
O(3)—C(15)	1.403 (2)	O(4)—C(16)	1.395 (2)
C(1)—C(8)	1.513 (2)	C(4)—C(7)	1.497 (2)
C(8)—O(2)	1.237 (1)	C(7)—O(1)	1.243 (2)
C(8)—N(2)	1.323 (2)	C(7)—N(1)	1.324 (2)
N(2)—C(14)	1.458 (2)	N(1)—C(9)	1.470 (2)
C(14)—C(13)	1.519 (2)	C(9)—C(10)	1.515 (2)
C(13)—C(12)	1.522 (2)	C(10)—C(11)	1.527 (2)
C(12)—C(11)	1.533 (2)	O(5)—H(O5)	1.045 (1)
O(5)—H'(O5)	0.905 (1)		
C(2)—C(3)—C(4)	120.67 (10)	C(3)—C(2)—C(1)	119.63 (11)
C(3)—C(4)—C(5)	119.65 (11)	C(2)—C(1)—C(6)	119.90 (11)
C(3)—C(4)—C(7)	116.97 (10)	C(2)—C(1)—C(8)	117.17 (11)
C(5)—C(4)—C(7)	123.14 (10)	C(6)—C(1)—C(8)	122.64 (10)
C(4)—C(5)—C(6)	119.22 (11)	C(1)—C(6)—C(5)	120.17 (11)
C(4)—C(5)—O(3)	123.16 (11)	C(1)—C(6)—O(4)	117.60 (11)
O(3)—C(5)—C(6)	117.19 (10)	O(4)—C(6)—C(5)	121.91 (11)
C(5)—O(3)—C(15)	118.93 (11)	C(6)—O(4)—C(16)	118.66 (13)
O(1)—C(7)—C(4)	120.46 (10)	O(2)—C(8)—C(1)	120.56 (11)
O(1)—C(7)—N(1)	122.15 (11)	O(2)—C(8)—N(2)	122.73 (11)
C(4)—C(7)—N(1)	117.26 (11)	C(1)—C(8)—N(2)	116.50 (11)
C(7)—N(1)—C(9)	127.01 (10)	C(8)—N(2)—C(14)	126.97 (10)
N(1)—C(9)—C(10)	114.10 (11)	N(2)—C(14)—C(13)	116.51 (11)
C(9)—C(10)—C(11)	113.48 (12)	C(14)—C(13)—C(12)	111.46 (11)
C(10)—C(11)—C(12)	115.30 (12)	C(13)—C(12)—C(11)	114.80 (12)

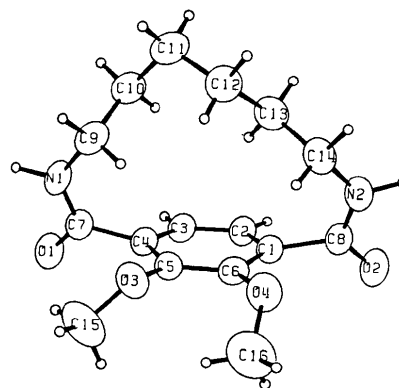


Fig. 1. View of the C₁₆H₂₂N₂O₄ molecule with the crystallographic numbering scheme.

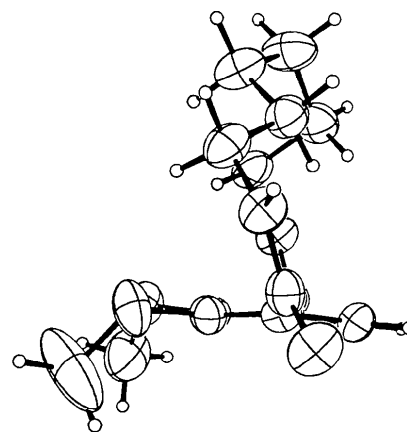


Fig. 2. View of the molecule along the plane of the benzene ring.

Berkeley. We wish to thank Dr F. J. Hollander for his assistance and the instructors of the course, Professor K. N. Raymond, Professor D. H. Templeton and Diane Fisher. The equipment used was funded in part by the National Science Foundation, grant CHE79-007027.

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Acta Cryst. (1985). **C41**, 1324–1327

N-Isopropyl-D-gluconamide (1), C₉H₁₉NO₆, and *N,N*-Diethyl-D-gluconamide (2), C₁₀H₂₁NO₆

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(Received 8 January 1985; accepted 1 May 1985)

Abstract. (1): $M_r = 237.2$, orthorhombic, $P2_12_12_1$, $a = 25.153$ (4), $b = 8.615$ (1), $c = 5.350$ (1) Å, $V = 1159.4$ (6) Å³, $Z = 4$, $D_m = 1.37$ (1), $D_x = 1.359$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 8.73$ cm⁻¹, $F(000) = 512$, $T = 293$ K, $R = 0.049$ for 585 independent observed reflections. (2): $M_r = 251.3$, orthorhombic, $P2_12_12_1$, $a = 6.870$ (1), $b = 7.655$ (1), $c = 24.029$ (4) Å, $V = 1263.7$ (6) Å³, $Z = 4$, $D_m = 1.33$ (1), $D_x = 1.321$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 8.26$ cm⁻¹, $F(000) = 544$, $T = 293$ K, $R = 0.059$ for 982 independent observed reflections. In both crystals, molecules are associated by hydrogen bonds. In the case of *N,N*-diethyl-D-gluconamide, one of the ethyl groups is found to be disordered. The analysis of this disorder gives two positions for this group, with occupancies 0.25 and 0.75 respectively. The carbonyl bond introduces dissymmetry in the bond lengths around the N atoms.

Introduction. The structural analyses of *N*-isopropyl-D-gluconamide and *N,N*-diethyl-D-gluconamide have been integrated into a general program of synthesis of

such compounds, to find the relation between conformational properties and the sweetening or souring power of these molecules.

Experimental. Compounds studied herein synthesized following the Ishikawa (1964) procedure. Single crystals obtained at room temperature, by evaporation of a methanol solution for compound (1) and an ethanol-ethoxide solution for compound (2), D_m by flotation in hexane/CCl₄. Colorless, transparent crystals [truncated sticks for (1), parallelograms for (2)]. For data collection the crystals were cut to a cubic shape [respectively 0.18 and 0.15 mm side for (1) and (2)]. Cell parameters refined using 25 reflections. Nonius CAD-4 diffractometer, graphite monochromator, θ - 2θ scan mode, aperture $(1.6 + 0.5 \text{tg}\theta)^\circ$, max. scan time 60 s, $(\sin\theta)_{\text{max}}/\lambda = 0.620$ Å⁻¹. Three standard reflections monitored every 75 reflections, 3% variation. Range of hkl : h 0→30, k 0→10, l 0→6 for (1) and h 0→8, k 0→9, l 0→29 for (2), 1328 and 1502 symmetry-independent reflections collected respectively for compound (1) and compound (2), 585 reflections in