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Structure of a Pyridyl-Containing Macrobicyclic Molecule, Potential Transition-Metal Complexing Agent and NADH Model Precursor

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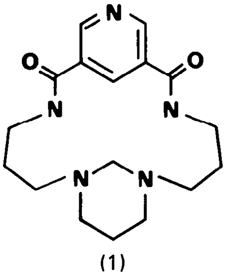
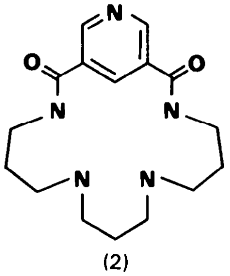
Abstract. $C_{17}H_{25}N_5O_2$, 1,5,9,13,17-pentaazatricyclo-[15.3.1.1^{7,11}]docosa-7,9,11-triene-6,12-dione, M_r = 331·42, orthorhombic, $Pbn2_1$, a = 10·734 (9), b = 20·806 (10), c = 7·625 (6) Å, V = 1703 (4) Å^3, Z = 4, D_x = 1·293 Mg m^{-3}, Mo $K\bar{\alpha}$, λ = 0·7107 Å, μ = 0·095 mm^{-1}, $F(000)$ = 712, T = 294 K, final R = 0·055 for 2702 reflections. The molecule defines a macrocyclic cavity with convergent amine N-atom lone pairs and amide H atoms. The hexahydropyrimidine ring is in a chair conformation and is roughly perpendicular to the main plane defined by the tetraazamacrocycle. The pyridine ring makes an angle of 21·7° to the macrocyclic plane. The molecule provides a well organized cavity for potential metal-ion recognition.

Introduction. Within the past decade, the chemistry of macrocyclic ring systems has developed rapidly, particularly related to host–guest chemistry which mimics biological complexation (Melson, 1979; Lehn, 1988). As part of our efforts to design and synthesize NADH models, we have focused our work on pyridyl-containing polyazamacrocycles (Dutasta, Gellon, Leuchter & Pierre, 1988). Some have a polycyclic structure as depicted below. (1) is the prototype of a new series of polyazamacrocyclic structures for which the conformation and the molecular shape are of great interest; the macrocyclic cavity must be defined in order to estimate its complexing properties toward metal ions. In this paper we describe the X-ray crystal structure of the pyridyl-containing tetraazamacrobicyclic molecule (1). The hexahydropyrimidine ring introduces rigidity compared to the parent compound (2), and imposes a well defined conformation. In solution at room temperature, the ^{1}H and ^{13}C NMR spectra are in agreement with the existence of one preferred rigid conformer.


(1)


(2)

Experimental. The synthesis and the characterization of the macrocyclic molecule (1) is described elsewhere (Dutasta *et al.*, 1988). Crystal size: 0·25 × 0·32 × 0·20 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 25 reflections (10·0 < θ < 16·3°) for refining unit-cell dimensions. ω scan, scan width: 1·20°, scan speed variable between 0·02 and 0·04° s^{-1}, total background measuring time: between 28 and 57 s. 3390 reflections collected; 3 < θ < 30°; h, k, l; h max. = 17, k max. = 33, l max. = 12. Existence conditions: $h0l$ ($h + l = 2n$), $0kl$ ($k = 2n$). Two orientation ($\bar{2}$,16,0 and 2,16,0) and two intensity ($\bar{5}31$ and $\bar{2}$,$\overline{16}$,0) control reflections with no significant variation. Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located by difference-Fourier synthesis. Anisotropic full-matrix least-squares refinements (on F),

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Table 1. *Final atomic coordinates and B_{eq} values for non-*H *atoms*

E.s.d.'s are given in parentheses.

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$(Å^2)
N(1)	0·1247 (2)	0·17783 (8)	0·000	3·46 (3)
N(2)	0·3276 (2)	0·13852 (9)	0·0798 (3)	3·61 (3)
N(3)	−0·0777 (2)	0·08930 (8)	0·0079 (3)	4·09 (4)
N(4)	0·0325 (2)	−0·13275 (9)	−0·0313 (4)	5·28 (5)
N(5)	0·3671 (2)	0·00561 (9)	0·1408 (3)	4·16 (4)
C(1)	0·2285 (2)	0·18389 (9)	0·1227 (3)	3·49 (4)
C(2)	0·3764 (2)	0·1538 (1)	−0·0950 (4)	4·77 (5)
C(3)	0·1674 (3)	0·1939 (1)	−0·1773 (4)	4·63 (5)
C(4)	0·2734 (3)	0·1498 (1)	−0·2269 (4)	4·93 (6)
C(5)	0·0213 (2)	0·2201 (1)	0·0563 (4)	4·28 (5)
C(6)	−0·1000 (2)	0·2047 (1)	−0·0363 (4)	4·64 (5)
C(7)	−0·1630 (2)	0·1435 (1)	0·0240 (4)	4·47 (5)
C(8)	−0·1150 (2)	0·0287 (1)	0·0170 (4)	4·02 (4)
C(9)	−0·0141 (2)	−0·02107 (9)	0·0136 (3)	3·41 (4)
C(10)	0·1080 (2)	−0·00971 (9)	0·0602 (3)	3·38 (4)
C(11)	0·1921 (2)	−0·0598 (1)	0·0643 (3)	3·50 (4)
C(12)	0·1488 (3)	−0·1199 (1)	0·0175 (4)	4·53 (5)
C(13)	−0·0462 (2)	−0·0836 (1)	−0·0300 (4)	4·45 (5)
C(14)	0·3225 (2)	−0·0537 (1)	0·1313 (4)	4·18 (5)
C(15)	0·4792 (2)	0·0221 (2)	−0·7607 (4)	5·21 (6)
C(16)	0·5231 (2)	0·0888 (1)	0·1955 (4)	5·07 (6)
C(17)	0·4263 (2)	0·1414 (1)	−0·7857 (4)	4·78 (5)
O(1)	−0·2239 (2)	0·01274 (9)	0·0266 (4)	6·27 (5)
O(2)	0·3813 (2)	−0·10176 (9)	0·1747 (3)	6·04 (5)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $C_{17}H_{25}N_5O_2$ (1)

E.s.d.'s are given in parentheses.

N(1)—C(1)	1·461 (3)	C(1)—N(1)—C(3)	109·4 (2)
N(1)—C(3)	1·466 (3)	C(1)—N(1)—C(5)	109·6 (2)
N(1)—C(5)	1·480 (3)	C(3)—N(1)—C(5)	111·5 (2)
N(2)—C(1)	1·459 (3)	C(1)—N(2)—C(17)	109·9 (2)
N(2)—C(2)	1·467 (4)	C(1)—N(2)—C(2)	108·9 (2)
N(2)—C(17)	1·475 (3)	C(2)—N(2)—C(17)	111·5 (2)
C(2)—C(4)	1·497 (4)	N(2)—C(2)—C(4)	109·5 (2)
C(4)—C(3)	1·509 (4)	C(2)—C(4)—C(3)	110·8 (2)
		N(1)—C(3)—C(4)	109·2 (2)
C(17)—C(16)	1·515 (4)	N(2)—C(17)—C(16)	113·4 (2)
C(16)—C(15)	1·504 (4)	C(17)—C(16)—C(15)	115·5 (2)
C(15)—N(5)	1·460 (3)	C(16)—C(15)—N(5)	111·1 (2)
N(5)—C(14)	1·325 (3)	C(15)—N(5)—C(14)	122·9 (2)
C(14)—O(2)	1·228 (3)	N(5)—C(14)—O(2)	123·9 (2)
C(14)—C(11)	1·495 (3)	O(2)—C(14)—C(11)	120·3 (2)
C(11)—C(12)	1·382 (3)	C(14)—C(11)—C(12)	118·7 (2)
C(12)—N(4)	1·330 (4)	C(11)—C(12)—N(4)	124·7 (2)
N(4)—C(13)	1·326 (3)	C(12)—N(4)—C(13)	116·2 (2)
C(13)—C(9)	1·386 (3)	N(4)—C(13)—C(9)	124·6 (2)
C(9)—C(10)	1·378 (3)	C(13)—C(9)—C(10)	117·3 (2)
C(10)—C(11)	1·379 (3)	C(9)—C(10)—C(11)	119·9 (2)
		C(10)—C(11)—C(12)	117·2 (2)
		C(14)—C(11)—C(10)	123·8 (2)
C(9)—C(8)	1·499 (3)	C(13)—C(9)—C(8)	118·3 (2)
		C(10)—C(9)—C(8)	124·3 (2)
C(8)—O(1)	1·218 (3)	C(9)—C(8)—O(1)	120·4 (2)
C(8)—N(3)	1·324 (3)	C(9)—C(8)—N(3)	116·0 (2)
		O(1)—C(8)—N(3)	123·6 (2)
N(3)—C(7)	1·459 (3)	C(8)—N(3)—C(7)	122·8 (2)
C(7)—C(6)	1·512 (3)	N(3)—C(7)—C(6)	110·1 (2)
C(6)—C(5)	1·515 (4)	C(7)—C(6)—C(5)	114·9 (2)
		N(1)—C(5)—C(6)	112·5 (2)

isotropic for H atoms. Unit weights. Final refinement cycles with 2702 reflections ($I > 1\sigma_I$). Final $R = 0·055$ ($wR = 0·046$). $S = 0·447$, max. $\Delta/\sigma = 0·01$. Max. peak height in the final difference-Fourier synthesis 0·206 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX II.*

Discussion. Final atomic coordinates are given in Table 1 while bond length and angles appear in Table 2. The atom-numbering scheme for the structure is shown in Fig. 1 together with two *ORTEP* (Johnson, 1976) views of the molecule.

The 16-membered tetraazamacrocycle approaches coplanarity with the pyridine ring. Deviations of

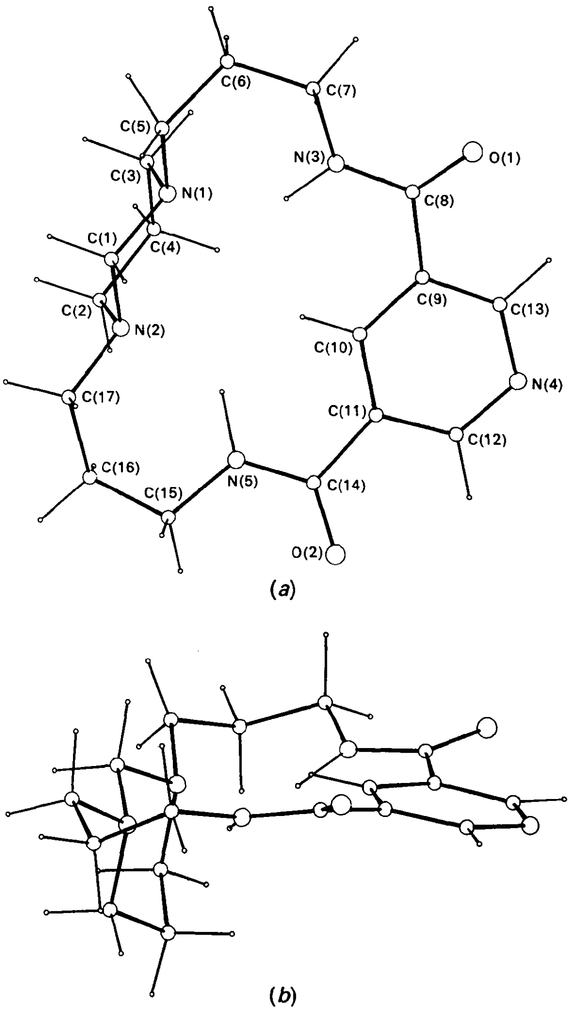

Fig. 1. *ORTEP* views of the macrocycle (1). (*a*) Top view, (*b*) side view.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52256 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0·057, −0·058, −0·026, 0·027 Å from the best least-squares tetraaza plane are observed for N(1), N(2), N(3) and N(5), with the pyridine ring making an angle of 21·7° to this plane. Both amide H atoms are directed inside the macrocycle and are hydrogen bonded to the adjacent amine N atoms. The hexahydropyrimidine ring is in a chair conformation with equatorial N(1)—C(5) and N(2)—C(17) bonds. It is roughly perpendicular to the monocyclic plane defined above, as shown by the angle of 79·9° between the N(1), N(2), N(3), N(5) and C(1), C(2), C(3), C(4), N(1), N(2) least-squares planes. The lone pairs of the N(1) and N(2) atoms point inside the cavity of the macroring. The whole structure adopts a pseudo-C_s symmetry with a pseudo-mirror plane passing through atoms N(4), C(10), C(1) and C(4). This configuration is rather rigid and is maintained in solution as evidenced by ^{1}H and ^{13}C NMR spectroscopy. We can conclude that the existence of a well defined cavity is largely due to the rigidification introduced by the C(1) bridge between N(1) and N(2) compared to the more flexible compound (2), and to hydrogen bonding between amide protons and amine N atoms. Compound (1) is well designed for complexation studies of metal ions inside the cavity.

We are indebted to Dr Anne Renault for helpful discussions and skillful assistance.

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Structure of a 1,2,3,5-Tetrazin-4-one

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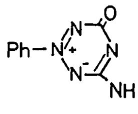
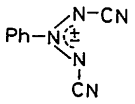
Abstract. 6-Amino-2-phenyl-1,2,3,5-tetrazin-4-one, $C_8H_7N_5O$, $M_r = 189·2$, monoclinic, $P2_1/n$, $a = 12·880\,(1)$, $b = 9·427\,(1)$, $c = 7·166\,(1)$ Å, $\beta = 100·95\,(1)°$, $V = 854·2\,(2)$ Å^3, $Z = 4$, $D_x = 1·471$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1·54050$ Å, $\mu = 0·899$ mm^{-1}, $F(000) = 392$, $T = 293$ K, final $R = 0·054$ for 1206 observed reflexions. The six-membered tetrazine ring is planar indicating extensive electron delocalization. There are two intermolecular hydrogen bonds: N(8)···N(5) 3·041 (4) and N(8)···O(7) 2·883 (4) Å.

Introduction. 1,2,3,5-Tetrazines, of which few derivatives have been reported (Baydar, Boyd, Lindley & Walton, 1985; Butler, Cunningham, McArdle & O'Halloran, 1988), are the rarest studied class of the three possible tetrazine ring systems (Neunhoeffer, 1984). Recently, we obtained a 1,2,3,5-tetrazine (6-amino-2-phenyl-1,2,3,5-tetrazin-4-one) (I) from photoreaction of (*E*,*Z*)-1,3-dicyano-2-phenyltriazene (II). The present paper describes details of the structure analysis of this novel heterocyclic compound having a 1,3-dipolar azimine moiety.


(I)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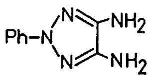
(III)

Experimental. Compound (II) was prepared by oxidation of 4,5-diamino-2-phenyl-1,2,3-triazole (III) (Thiele & Schleussner, 1897) using $Pb(OAc)_4$ in CH_2Cl_2. A solution of (II) in CH_3OH (hygroscopic) was irradiated by a medium-pressure mercury lamp for 7·5 min to give the compound (I). Recrystallization from C_2H_5OH gave colourless prisms having m.p. 530–532 K. The combustion analysis was consistent with the structure for this compound.

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