(Martìnez-Ripoll & Cano, 1975) and *PARST* (Nardelli, 1983). All H atoms were located in a difference Fourier synthesis. One nitro group of the picrate anion was refined at two sites with 0.77 (1) and 0.23 (1) occupancy factors. The *R* factor probably could not be lowered because of the crystal shape (thin plate), absorption and the disorder of one nitro group.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data, along with details of the weighting scheme, have been deposited with the IUCr (Reference: AB1234). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unexpected Intermediate in the Synthesis of Substituted Pyridones

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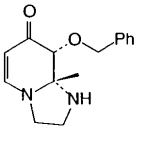
Abstract

The title compound, 8-benzyloxy-8a-methyl-1,2,3,7,8,-8a-hexahydroimidazo[1,2-*a*]pyridin-7-one, (I), is a novel cyclic intermediate in the synthesis of 1-(2-aminoethyl)-3-hydroxy-2-methyl-4(1*H*)-pyridone, (II), a well known Fe^{III} chelator, following a standard route for the synthesis of substituted pyridones. Compound (I) is the major solid intermediate in this reaction and its structural identity has been established conclusively by single-crystal X-ray crystallography. It is a monohydrate in the solid state, $C_{15}H_{18}N_2O_2.H_2O$, and it is obtained upon trituration of the colored oil obtained from the reaction of ethylenediamine with 3-benzyloxy-2-methyl-4-pyrone. Each water molecule bridges two molecules of (I), hydrogen bonding with the carbonyl O atom of one molecule [O···*OW* 2.796 (4) Å] and with the N atom of the other [N···*OW* 2.903 (4) Å]. The methyl group at the bridgehead is axially located in a *trans* position with respect to the bulky benzyloxy group. The pyridone ring assumes a slightly distorted half-chair conformation.

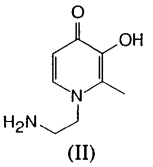
Comment

The use of N-substituted 3-hydroxy-2-methyl-4(1*H*)-pyridones as orally active Fe^{III} chelators for possible application in the treatment of iron overload has received considerable attention in recent years (Van der Does, Feng & Bantjes, 1993). Our interest was drawn to the 2-aminoethyl analog, (II), for use as a starting material in the synthesis of substituted pyridones. Compound (II), structurally related to the natural product mimosine, has been reported in numerous papers (Van der Does, Feng & Bantjes, 1992, 1993; Orvig, Nelson, Karpishin & Rettig, 1988; Brady *et al.*, 1989; Kontoghiorghes, 1986). Its synthesis is always performed by adaptations of the maltol route (Orvig, Nelson, Karpishin & Rettig, 1988), wherein maltol is protected as the 3-benzyloxy ether, treated with ethylenediamine to give an uncharacterized intermediate and then deprotected with HCl to yield the desired final product as the dichloride salt. A recent publication (Van der Does, Feng & Bantjes, 1993), applying this chemistry,

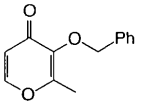
described the presumed intermediate as (IV) (without specific experimental conditions or characterization). In our study, this chemistry proceeded as expected to provide compound (II). However, the spectra and physical properties of the solid intermediate were not what would be expected for compound (IV). Based on the NMR data, the solid was tentatively assigned the structure of the previously unknown 8-benzyloxy-8a-methyl-1,2,3,7,8,8a-hexahydroimidazo[1,2-*a*]pyridin-7-one, (I). From the mother liquors of the trituration, however, a yellow oil with a lower R_f was recovered in low yield. The spectral properties of this oil were consistent with compound (IV). The X-ray structure confirms the identity and relative stereochemistry of (I). Although compounds (I) and (IV) may undergo similar reactions in certain instances, as exemplified by their mutual conversion to compound (II), they may not always be equivalent in other applications, *e.g.* in iron binding or *in vitro* assays (Van der Does, Feng & Bantjes, 1993).



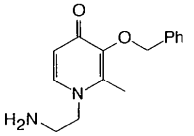
(I)



(II)



(III)



(IV)

The monohydrate of compound (I), as it exists in the solid state, is depicted in Fig. 1, together with the atomic numbering. Each water molecule bridges a pair of symmetry-related molecules of the compound, hydrogen bonding with the O atom of one molecule [O(2)···O(1*W*) 2.796 (4) Å] and interacting with the N atom of the other [N(2)···O(1*W*) 2.903 (4) Å] (Fig. 2). The H atom on N(2) is located in the axial position of the imidazole ring and appears to be in a position to form a weak intramolecular hydrogen bond with atom O(1) [N(2)···O(1) 2.742 (4) Å]. The H atom of the water molecule is directed towards N(2) at the equatorial position. The methyl group at ring-junction atom C(5) is axially situated in a *trans* position with respect to the H atom on N(2). It is also *trans* to the bulky benzyloxy group on the pyridone ring, for steric reasons. The pyridone ring assumes a slightly distorted half-chair conformation. The shorter N(1)—C(4) bond distance [1.319 (5) *versus* 1.416 (8) Å for a normal C_{sp^2}—N_{sp^3}] and the longer C(3)—C(4) bond distance [1.365 (5) *versus* 1.331 (8) Å for a normal C_{sp^2}=C_{sp^2}] suggest the possibility of conjugation of the nitrogen lone pair with the double bond, as was also probably the case in a comparable pyridone structure (Fregona, Sitran, Vigato & Casellato, 1986). The imidazole ring has a shallow-envelope conformation with atoms N(2) and C(5) lying about 0.2 Å from the mean plane of the ring. The phenyl ring of the benzyloxy group is planar and its mean plane is approximately perpendicular to the general plane of the imidazopyridone unit. The aromatic bond lengths range from 1.341 (7) to 1.394 (6) Å, with a mean value of 1.362 Å. The atoms in the aromatic ring have larger displacement parameters than the other ring atoms of the molecule, presumably because of the flexibility about the C(9)—O(1) linkage to the imidazopyridone group. No unusual intermolecular contacts were observed.

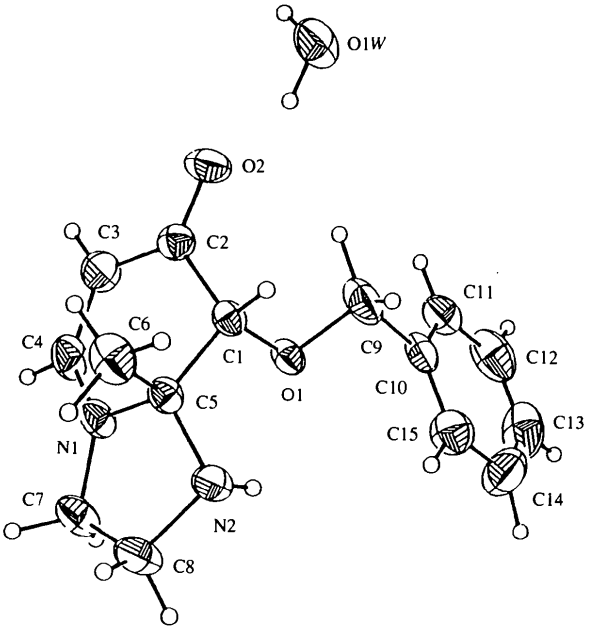


Fig. 1. The molecular structure of the monohydrate of compound (I) with the atomic numbering. Displacement ellipsoids are plotted at the 30% probability level.

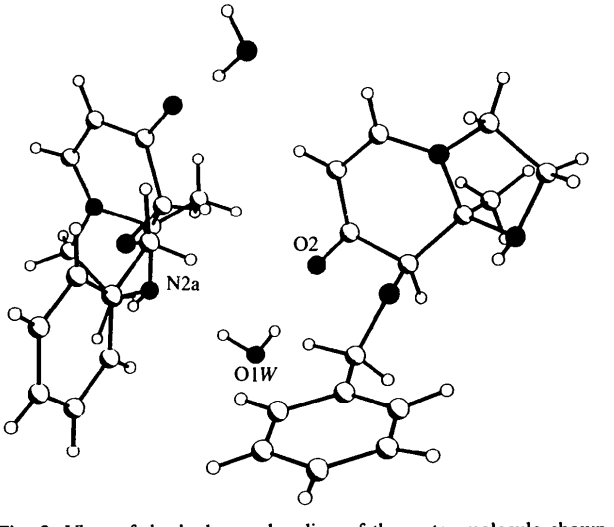


Fig. 2. View of the hydrogen bonding of the water molecule shown bridging two symmetry-related molecules.

Compound (I) clearly arises from an intramolecular Michael reaction involving the primary amine and enone groups. This cyclization is obviously reversible, explaining the success of the subsequent deprotection to give compound (II) under the strong acid conditions employed. The identity of this cyclic intermediate may provide a new synthetic route to substituted 1,4-diazabicyclo[4.3.0]nonanes.

Experimental

The standard literature procedure of Harris (1976) was followed for the reaction of 3-benzyloxy-2-methyl-4-pyrone (III) with ethylenediamine to give a colored oil which upon trituration yielded the solid intermediate (I). The compound was recrystallized by slow evaporation from hot ethyl acetate/hexane solution to give clear plates which were used for the single-crystal X-ray experiment. The crystals melted slowly over the range 359–370 K. ^{1}H NMR (300 MHz, $CDCl_3$) 1.25 (*s*, 3H), 3.2–3.5 (*m*, 5H), 3.55 (*t*, 1H), 4.6 (*dd*, 2H), 4.95 (*d*, 1H), 7.2 (*d*, 1H), 7.3 (*s*, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) 18.0, 44.1, 49.0, 71.7, 78.9, 79.7, 94.0, 127.9, 128.3, 128.4, 137.4, 147.7, 189.7. If instead of triturating the colored oil, the entire reaction mixture was chromatographed on a silica-gel column using a 95:5:1 CH_2Cl_2:MeOH:NH_3OH solvent system, a viscous yellow compound with R_f = 0.5 (thin-layer chromatography) was obtained in low yield. This minor component has spectral properties consistent with compound (IV). ^{1}H NMR (300 MHz, $CDCl_3$) 2.0 (*s*, 3H), 2.85 (*t*, 2H), 3.7 (*t*, 2H), 5.1 (*s*, 2H), 6.3 (*d*, 1H), 7.2–7.4 p.p.m. (*m*, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) 12.6, 42.0, 56.1, 72.9, 116.9, 128.0, 128.2, 129.0, 137.5, 138.9, 140.9, 146.0, 173.3 p.p.m . Either compound (I) or (IV) can be treated with HCl to yield the well known Fe^{III} chelator, (II). The NMR spectra were measured on a Bruker AC-300 instrument using standard operating procedures. The chemical shifts are reported downfield with respect to external tetramethylsilane.

Crystal data

$C_{15}H_{18}N_2O_2.H_2O$
M_r = 276.3
Monoclinic
$P2_1/a$
a = 9.248 (2) Å
b = 16.521 (4) Å
c = 10.359 (2) Å
β = 109.31 (1)°
V = 1493.7 (6) Å^3
Z = 4
D_x = 1.2 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 15–22°
μ = 0.67 mm^{-1}
T = 294 K
Plate
0.4 × 0.4 × 0.03 mm
Colorless

Data collection

Rigaku AFC-5*R* RU200 diffractometer
θ–2θ scans
Absorption correction: none
2476 measured reflections
2224 independent reflections
1529 observed reflections [$F \geq 4\sigma(F)$]
R_{int} = 0.02
θ_{max} = 60°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = -11 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.052
wR = 0.035
S = 2.43
1529 reflections
181 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
O(1)	0.1969 (2)	0.8675 (1)	0.0022 (2)	0.048 (1)
O(2)	−0.0063 (3)	0.7331 (1)	−0.1773 (2)	0.075 (1)
O(1*W*)	0.0607 (2)	0.5686 (1)	−0.1286 (3)	0.092 (1)
N(1)	−0.0059 (3)	0.9778 (2)	−0.2106 (3)	0.052 (1)
N(2)	0.2565 (3)	0.9894 (2)	−0.1526 (3)	0.054 (1)
C(1)	0.1458 (3)	0.8529 (2)	−0.1418 (3)	0.042 (1)
C(2)	−0.0078 (4)	0.8078 (2)	−0.1812 (3)	0.052 (1)
C(3)	−0.1383 (4)	0.8563 (2)	−0.2061 (3)	0.066 (2)
C(4)	−0.1303 (4)	0.9388 (2)	−0.2107 (3)	0.064 (2)
C(5)	0.1314 (3)	0.9339 (2)	−0.2149 (3)	0.044 (1)
C(6)	0.1160 (4)	0.9170 (2)	−0.3645 (3)	0.070 (2)
C(7)	0.0241 (4)	1.0646 (2)	−0.1961 (4)	0.067 (2)
C(8)	0.1893 (4)	1.0709 (2)	−0.1907 (4)	0.070 (2)
C(9)	0.2643 (5)	0.7974 (2)	0.0784 (3)	0.086 (2)
C(10)	0.3365 (4)	0.8200 (2)	0.2264 (4)	0.060 (2)
C(11)	0.2911 (4)	0.7787 (2)	0.3215 (4)	0.074 (2)
C(12)	0.3584 (6)	0.7977 (3)	0.4597 (5)	0.097 (3)
C(13)	0.4642 (6)	0.8565 (3)	0.4969 (5)	0.116 (3)
C(14)	0.5069 (5)	0.8975 (3)	0.4034 (6)	0.110 (3)
C(15)	0.4419 (5)	0.8788 (2)	0.2666 (5)	0.080 (2)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(1)	1.428 (4)	C(3)—C(4)	1.365 (5)
O(1)—C(9)	1.424 (4)	C(5)—C(6)	1.534 (5)
O(2)—C(2)	1.235 (4)	C(7)—C(8)	1.514 (5)
N(1)—C(4)	1.319 (5)	C(9)—C(10)	1.503 (5)
N(1)—C(5)	1.476 (4)	C(10)—C(11)	1.373 (6)
N(1)—C(7)	1.459 (4)	C(10)—C(15)	1.342 (5)
N(2)—C(5)	1.450 (4)	C(11)—C(12)	1.394 (6)
N(2)—C(8)	1.480 (4)	C(12)—C(13)	1.341 (7)
C(1)—C(2)	1.535 (4)	C(13)—C(14)	1.344 (9)
C(1)—C(5)	1.521 (4)	C(14)—C(15)	1.379 (7)
C(2)—C(3)	1.400 (5)		
C(1)—O(1)—C(9)	112.0 (2)	N(2)—C(5)—C(1)	114.2 (2)
C(4)—N(1)—C(5)	121.2 (3)	N(1)—C(5)—C(6)	109.0 (2)
C(4)—N(1)—C(7)	128.1 (3)	N(2)—C(5)—C(6)	111.0 (3)
C(5)—N(1)—C(7)	110.5 (3)	C(1)—C(5)—C(6)	107.8 (2)
C(5)—N(2)—C(8)	104.7 (2)	N(1)—C(7)—C(8)	103.1 (3)
O(1)—C(1)—C(2)	108.5 (3)	N(2)—C(8)—C(7)	106.1 (3)
O(1)—C(1)—C(5)	108.4 (2)	O(1)—C(9)—C(10)	109.2 (3)
C(2)—C(1)—C(5)	111.9 (2)	C(9)—C(10)—C(11)	118.1 (3)
O(2)—C(2)—C(1)	118.5 (3)	C(9)—C(10)—C(15)	121.9 (4)
O(2)—C(2)—C(3)	125.3 (3)	C(11)—C(10)—C(15)	120.0 (4)
C(1)—C(2)—C(3)	115.9 (3)	C(10)—C(11)—C(12)	119.1 (4)
C(2)—C(3)—C(4)	121.6 (3)	C(11)—C(12)—C(13)	119.5 (5)
N(1)—C(4)—C(3)	123.1 (3)	C(12)—C(13)—C(14)	121.2 (5)
N(1)—C(5)—N(2)	104.1 (2)	C(13)—C(14)—C(15)	119.7 (4)
N(1)—C(5)—C(1)	110.6 (3)	C(10)—C(15)—C(14)	120.4 (5)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	H···A	D···A	D—H···A
O(1*W*)—H···N(2^i)	2.01	2.903 (4)	176
O(1*W*)—H···O(2)	1.89	2.796 (4)	164
N(2)—H···O(1)	2.29	2.742 (4)	115

Symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z$.

The structure was solved and refined using the *SHELXTL-Plus* (Sheldrick, 1990) software package on a MicroVAX 3500 computer. Refinement was by full-matrix least-squares methods, minimizing $\Sigma w|(|F_o|-|F_c|)|^2$. All non-H atoms were located on an *E* map and refined anisotropically. H atoms were assigned positions that were consistent with minor peaks on an intermediate difference Fourier map and were considered as riding atoms in the subsequent refinement cycle. Their isotropic displacement parameters were fixed at 0.08 Å^2.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: CR1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1407–1411

$(H_4\text{-Hexaaza-18-crown-6})^{4+}.4CF_3SO_3^-$ and its Hydrated Form

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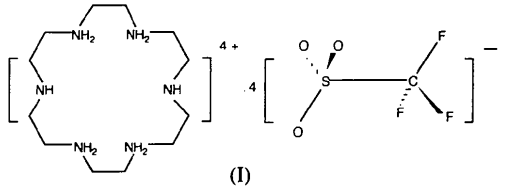
Abstract

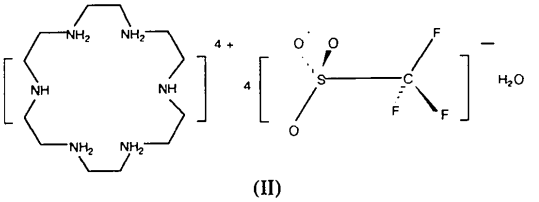
The structures of the two compounds reported here involve the tetraprotonated form of the macrocycle 1,4,7,10,13,16-hexaazacyclooctadecane (hexaaza-18-crown-6 = $C_{12}H_{30}N_6$): (H_4-hexaaza-18-crown-6).4(trifluoromethanesulfonate), $C_{12}H_{34}N_6^{4+}.4CF_3SO_3^-$, and the hydrated form (H_4-hexaaza-18-crown-6).4(trifluoromethanesulfonate).H_2O, $C_{12}H_{34}N_6^{4+}.4CF_3SO_3^-.H_2O$. In both compounds, the conformation of the macrocycle is $g^+g^-g^+g^-g^+g^-$. The counterions and the water molecule are hydrogen bonded to protonated N atoms.

Comment

In the course of our work on inclusion complexes between the uranyl ion and macrocycles, we have reported recently the structures of the inclusion complexes obtained with hexaaza-18-crown-6 (Nierlich, Sabattié, Keller, Lance & Vigner, 1994) and diaza-18-crown-6 (Thuéry, Keller, Lance, Sabattié, Vigner & Nierlich, 1995) with trifluoromethanesulfonate $CF_3SO_3^-$ as counterion. In the latter compound, one of the two amine functional groups is deprotonated, which is uncommon for this ligand. In the present paper, we report the structures of two compounds, (I) and (II), containing $(H_4\text{-hexaaza-18-crown-6})^{4+}$ and $CF_3SO_3^-$. The binding properties of protonated hexaaza-18-crown-6 with the anions Cl^-, NO_3^-, Br^-, ClO_4^-, $C_6H_5SO_3^-$, CF_3COO^- and IO_3^- have already been investigated by pH-potentiometry, conductometry and X-ray diffraction (Margulis & Zompa, 1981; Cullinane, Gelb, Margulis & Zompa, 1982; Gelb, Lee & Zompa, 1985), and with biologically important polyanions such as polycarboxylates and phosphates by polarography and NMR experiments (Kimura, Sakonaka, Yatsunami & Kodama, 1981; Kimura, Kodama & Yatsunami, 1982). In all cases, the ion-pair formation arises from electrostatic and/or ionic hydrogen bonding of the form $N^+—H\cdots X^-$, as evidenced in the structures of (H_6-hexaaza-18-crown-6)$(NO_3)_4Cl_2$ (Margulis & Zompa, 1981) and (H_4-hexaaza-18-crown-6)$(NO_3)_2Cl_2.2H_2O$ (Cullinane *et al.*, 1982).



(I)



(II)

In the present work, two crystalline species were isolated: $(H_4\text{-hexaaza-18-crown-6})^{4+}.4CF_3SO_3^-$, (I), and the hydrated form $(H_4\text{-hexaaza-18-crown-6})^{4+}.4CF_3SO_3^-.H_2O$, (II). In agreement with protonation experiments (Bencini *et al.*, 1992), the only species present is (H_4-hexaaza-18-crown-6)$^{4+}$; the occurrence of this tetraprotonated species in anion complexation both in solution and in the solid state has already been indicated (Cullinane *et al.*, 1982; Gelb *et al.*, 1985). The geometric parameters of the $CF_3SO_3^-$ moieties, which are normal, are not reported here. *ORTEP*II (Johnson, 1976) drawings of the molecules are given in Figs. 1 and 2.