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X-ray Mapping in Heterocyclic Design: II. Diffractometric Study of Crystalline 2-Oxo-2,3-Dihydroimidazo[1,2-*a*]pyridine Hydrochloride

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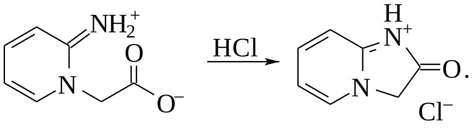
Abstract—The crystal structure of 2-oxo-2,3-dihydroimidazo[1,2-*a*]pyridine hydrochloride, $C_7H_7ClN_2O$, is determined by X-ray diffraction. The structure is solved by the direct method and refined by the least-squares procedure to $R = 0.0408$. The alternation of bond lengths in the molecule is inconsiderable, but does not disappear completely, since no aromatization occurs upon formation of the bicycle from the molecule. This structural change is apparently due to the increased conjugation of the NH group with the pyridine residue of the bicycle. One of the specific structural features of the salt is the formation of the $N^+–H\cdot\cdot Cl^-$ hydrogen bond (N–H, 0.792 Å; H···Cl, 2.260 Å; and N–H···Cl, 171.2). *© 2000 MAIK “Nauka/Interperiodica”.*

This work continues a series of investigations of heterocyclic compounds that enter into reactions of cyclization and ring transformation [1–5]. The structure of 1,2-dihydro-2-imino-1-carboxymethylpyridine (**I**) was studied in the preceding paper [5]. In the present work, we determined the structure of a product of its cyclization, 2-oxo-2,3-dihydroimidazo[1,2-*a*]pyridine hydrochloride (**II**).

The **I** ⟶ **II** cyclization was first carried out by Reindel in 1924 [6]. However, the compound obtained was by mistake assigned the structure of pyrrolo[2,3-*b*]pyridine. Tschitschibabin showed [7] that, in the course of cyclization, the imidazolone fragment is formed. No data on the crystal structure of **II** is present in the Cambridge Structural Database [8]. The synthesis of **II** was performed according to the procedure described in [6]

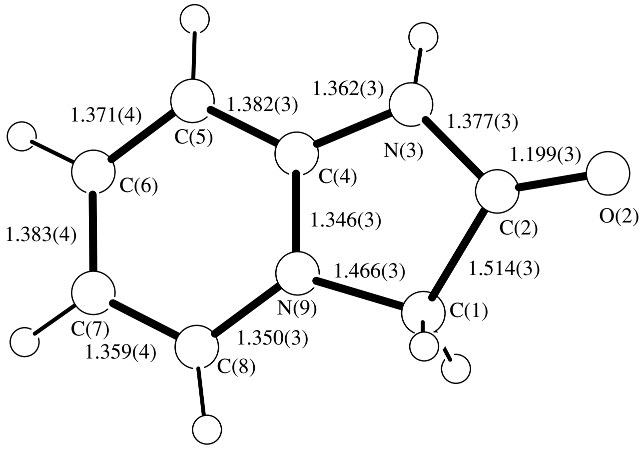


I **II**

Recrystallization from a 1 : 1 isopropanol–water solution yields transparent colorless crystals with a plate-like habit.

EXPERIMENTAL

Crystals **II**, $C_7H_7ClN_2O$, are triclinic. The unit-cell parameters were determined and refined on a CAD4 automated diffractometer using 25 reflections in the θ range 11°–14° [9] (λMoK_α, graphite monochromator). The crystal data are $a = 7.121(2)$ Å, $b = 7.621(2)$ Å, $c = 8.312(2)$ Å, $\alpha = 65.69(2)°$, $\beta = 67.45(2)°$, $\gamma = 70.24(2)°$, $V = 370.9(2)$ Å^3, $d_{calcd} = 1.528$ g/cm^3, $\mu(\lambda\text{Mo}) = 0.450$ mm^{-1}, $Z = 2$, and space group $P\bar{1}$. A set of 2187 unique reflections with $I \geq 2\sigma(I)$ was collected in the range $\theta \leq 26°$ on the same diffractometer by the ω-scan technique. The processing of the diffraction data measured was performed with the WinGX96 program package [10]. The coordinates of the non-hydrogen atoms were found by the direct method, and the structure was refined in the anisotropic approximation by the least-squares procedure using the SHELX97 program package [11]. All the hydrogen atoms were located from the difference synthesis of electron density and



The structure of the molecule studied and atomic numbering.

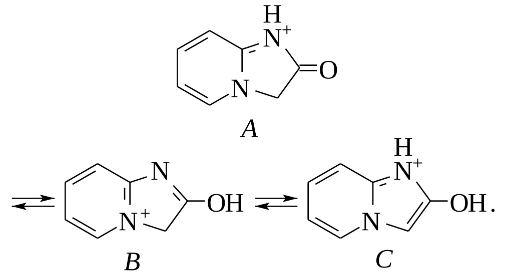
Atomic coordinates ($\times 10^4$) and equivalent (isotropic) thermal parameters U_{eq}/U_{iso} (Å$^2 \times 10^3$) for molecule **II**

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Cl	3283(1)	1424(1)	8058(1)	44(1)
C(1)	1527(5)	8296(3)	2928(3)	40(1)
C(2)	1959(4)	7252(3)	4782(3)	40(1)
O(2)	1793(3)	7963(3)	5889(3)	58(1)
N(3)	2584(3)	5279(3)	4961(3)	40(1)
C(4)	2623(3)	4945(3)	3459(3)	34(1)
C(5)	3171(4)	3200(3)	3088(3)	42(1)
C(6)	3022(4)	3304(4)	1453(4)	44(1)
C(7)	2365(4)	5090(4)	219(4)	43(1)
C(8)	1866(4)	6783(4)	613(3)	38(1)
N(9)	2016(3)	6668(2)	2226(2)	31(1)
H(11)	2420(39)	9159(37)	2174(35)	41(7)
H(12)	108(49)	8941(42)	3078(39)	55(8)
H(3)	2762(43)	4332(42)	5847(40)	51(8)
H(5)	3563(40)	2025(38)	3951(36)	40(6)
H(6)	3492(40)	2152(39)	1119(35)	47(7)
H(7)	2256(44)	5137(42)	–911(42)	62(8)
H(8)	1490(39)	8035(38)	–119(35)	41(7)

included in the refinement in the isotropic approximation. The final discrepancy factors are $R1 = 0.0408$ and $wR2 = 0.0930$. The atomic coordinates and thermal parameters are listed in the table. The residual electron density lies between $\Delta\rho_{max} = 0.253$ and $\Delta\rho_{min} = -0.255$ e/Å^3. The organic cation shown in the figure was drawn with the PLUTON96 program [12].

RESULTS AND DISCUSSION

The chloride anion serves as a counterion in compound **II**. The heterocyclic cation is planar. The largest atomic deviation from the plane of the bicycle is 0.011(2) Å. In theory, three tautomeric forms of **II** are possible: *A*, *B*, and *C*

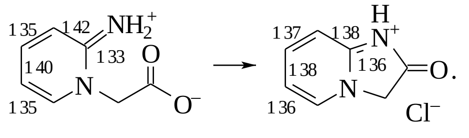


A

B *C*

However, the C(1)–C(2) bond (figure) is a single C–C bond (1.51 Å), which eliminates the *C* tautomer. The C(2)–O(2) bond is the normal double bond C=O (1.20 Å), which eliminates the *B* tautomer. Therefore, the structure of cation **II** is unambiguously described by the *A* tautomer.

It is interesting to reveal the structural changes upon the **I** ⟶ **II** cyclization. As we already noted in [5], the bond lengths in the ring of **I** distinctly alternate: actually, molecule **I** contains a quazi-diene fragment. In the course of cyclization, the bonds in the six-membered fragment tend to become equal, and the alternation of bond lengths in **II** becomes inconsiderable.



I **II**

This structural feature is remarkable, since no aromatization occurs upon formation of the bicycle from the monocycle. The above structural change is apparently due to the increased conjugation of the NH group with the pyridine residue of the bicycle.

Another structural feature of salt **II** is the formation of the $N(3)^+$–H(3)···Cl^- hydrogen bond [N(3)–H(3), 0.79 Å; H(3)···Cl, 2.26 Å; and N(3)–H(3)···Cl, 171°].

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