

STRUCTURE
OF ORGANIC COMPOUNDS

**X-ray Mapping in Heterocyclic Design:
V. Diffractometric Study of the Crystal Structure
of 2-Hydroxy-3-Trifluoroacetylimidazo[1,2-*a*]pyridine
Hydrochloride at 180 K**

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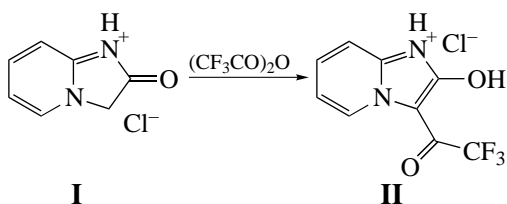
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Abstract—The crystal structure of 2-hydroxy-3-trifluoroacetylimidazo[1,2-*a*]pyridine hydrochloride $C_9H_6F_3ClN_2O_2$ is determined by X-ray diffraction at 180 K. The structure is solved by the direct method and refined by the least-squares procedure to $R = 0.0296$. The alternation of bond lengths in the six-membered fragment of the molecule is observed. One of the specific features of the crystal structure is the formation of a system of the $N-H\cdots Cl^-$ ($N\cdots Cl$, 3.09 Å; $N-H$, 0.83 Å; $H\cdots Cl$, 2.33 Å; and $N-H\cdots Cl$, 153°) and $O-H\cdots Cl^-$ ($O\cdots Cl$, 2.87 Å; $O-H$, 0.95 Å; $H\cdots Cl$, 1.92 Å; and $O-H\cdots Cl$, 178°) hydrogen bonds in which the chlorine atoms are related to the reference atom by different symmetry transformations. © 2001 MAIK "Nauka/Interperiodica".

INTRODUCTION

This work continues the series of our investigations of heterocyclic compounds that are able to enter into the reactions of cyclization and ring transformation [1–8]. Earlier [6], we described the structure of 2-oxo-2,3-dihydroimidazo[1,2-*a*]pyridine hydrochloride $C_7H_7ClN_2O$ (**I**). This salt was used as a starting substance for preparation of 2-hydroxy-3-trifluoroacetylimidazo[1,2-*a*]pyridine hydrochloride $C_9H_6F_3ClN_2O_2$ (**II**). Compound **II** was prepared by the reaction between **I** and trifluoroacetic anhydride



Colorless crystals of the prismatic habit precipitated in the reaction vessel. The crystals removed from the mother liquor cracked within 30 s. Because of the high volatility of trifluoroacetic anhydride, the X-ray-quality crystals were chosen under the flow of cooled nitrogen with a binocular microscope in polarized light.

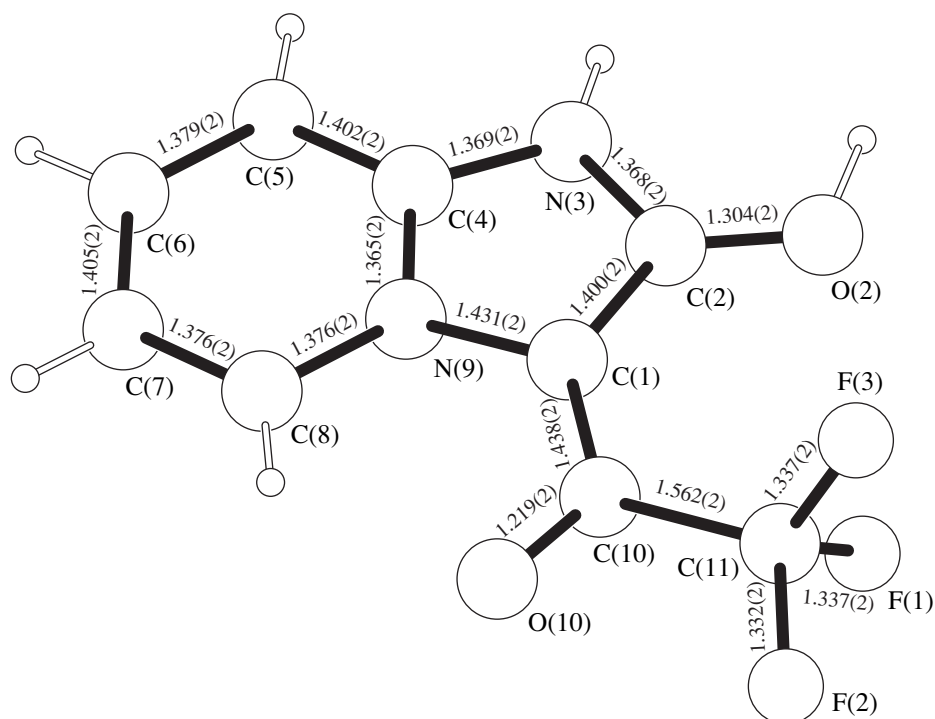
According to the data of the Cambridge Structural Database [9], the X-ray structure analysis of **II** has not been performed.

EXPERIMENTAL

Crystals of compound **II** are monoclinic. The unit cell parameters were determined and refined at

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

Atom	x	y	z	U_{eq}/U_{iso}
Cl	4755(1)	1286(1)	1458(1)	31(1)
C(1)	3540(1)	4336(3)	2447(1)	20(1)
C(2)	3885(1)	6417(3)	2227(1)	20(1)
O(2)	3887(1)	7359(2)	1538(1)	25(1)
N(3)	4231(1)	7391(2)	2873(1)	21(1)
C(4)	4123(1)	6006(3)	3505(1)	21(1)
C(5)	4354(1)	6330(3)	4286(1)	26(1)
C(6)	4148(1)	4654(3)	4803(1)	30(1)
C(7)	3721(1)	2694(3)	4548(1)	31(1)
C(8)	3501(1)	2434(3)	3778(1)	26(1)
N(9)	3704(1)	4117(2)	3262(1)	20(1)
C(10)	3099(1)	2626(3)	2024(1)	22(1)
O(10)	2867(1)	733(2)	2301(1)	31(1)
C(11)	2904(1)	3220(3)	1149(1)	26(1)
F(1)	2773(1)	5869(2)	1006(1)	34(1)
F(2)	2434(1)	1766(2)	885(1)	45(1)
F(3)	3305(1)	2518(2)	743(1)	35(1)
H(2)	4186(9)	8630(40)	1523(12)	49(5)
H(3)	4488(8)	8570(40)	2893(10)	37(5)
H(5)	4635(7)	7800(40)	4407(10)	31(4)
H(6)	4300(7)	4780(40)	5344(10)	36(4)
H(7)	3585(8)	1560(40)	4901(11)	37(4)
H(8)	3208(7)	1230(30)	3562(9)	29(4)

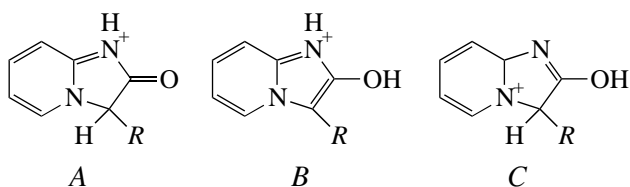
Structure of heterocyclic cation **II**.

180(2) K on an IPDS automated diffractometer using 1097 reflections in the θ range 5° – 25° (λ MoK α , graphite monochromator). The crystal data are $a = 23.761(5)$ Å, $b = 4.856(1)$ Å, $c = 17.713(4)$ Å, $\beta = 100.41(3)^\circ$, $V = 2010.1(7)$ Å³, $Z = 8$, space group $C2/c$, $d_{\text{calcd}} = 1.762$ g/cm³, and $\mu(\lambda\text{Mo}) = 0.415$ mm⁻¹. A set of 4505 reflections with $I \geq 2\sigma(I)$ was collected on the same diffractometer and at the same temperature by the ω -scan technique in the θ range 3.16° – 26.19° . The diffraction data measured were processed with the X-RED-107 program package. The non-hydrogen atoms were located by the direct method and refined in the anisotropic approximation by the least-squares procedure according to the SHELX97 program package [10]. All the hydrogen atoms were located from the difference Fourier syntheses of electron density. The structure was refined by the least-squares procedure in the anisotropic approximation (isotropic, for H atoms) to $R1 = 0.0296$ ($wR2 = 0.0642$). The atomic coordinates and isotropic thermal parameters that are equivalent to the corresponding anisotropic parameters are listed in the table. The residual (maximum and minimum) electron densities are $\Delta\rho_{\text{max}} = 0.240$ and $\Delta\rho_{\text{min}} = -0.184$ e/Å³. The drawing of the cation with the atomic numbering (see figure) was obtained with the PLUTON96 program [11].

RESULTS AND DISCUSSION

The chloride ion serves as a counterion in compound **II**. The heterocyclic cation is planar: the largest

atomic deviation from the plane of the bicyclic fragment is $0.015(1)$ Å. The cations of salts **I** and **II** can be represented by one of the three structures ($R = \text{H}$ or COCF_3):

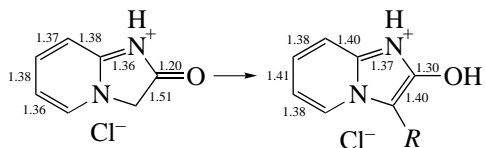


In our earlier work [6], we found that the structure of salt **I** is of the **A** type. The localization of the protons at the N(3) and O(2) atoms and the absence of a proton at the C(1) atom suggest that the structure of salt **II** (which is prepared by acylation of **I**) should be unambiguously assigned to the **B**-type structure rather than to the **C** type.

It is of interest to reveal the structural changes upon the **I** \rightarrow **II** acylation. A comparison of the bond lengths in the cations studied shows that the quasi-diene character of the C(5)C(6)C(7)C(8) moiety of the six-membered heterocycle in **II** is pronounced more than that in **I**. Protonation of the exocyclic O atom results in a redistribution of the bond lengths in the five-membered ring.

In particular, the C(2)–O(2) bond lengthens and the C(1)–C(2) bond shortens. This is consistent with the expected bond-length distribution in the ketonic compound **I** and the enolic compound **II**. We conclude that

the attachment of the COCF_3 group to the C(1) atom in the ketonic *A* form increases the acidity of the remaining proton and stabilizes the enolic *B* form. Since the C(1)–C(10) bond (heterocycle–acyl) is rather long (1.44 Å), the COCF_3 group in **II** is apparently weakly conjugated with the enolic fragment.

**I** (the *A* form)**II** (the *B* form; $R = \text{COCF}_3$)

Another specific structural feature of **II** is the formation of the hydrogen-bond system. The N(3)–H(3)···Cl[−] hydrogen bond, in which the chlorine atom is related to the reference atom by the $(1 - x, 1 + y, 1/2 - z)$ symmetry transformation, is characterized by the following parameters: N(3)···Cl[−], 3.09 Å; N(3)–H(3), 0.83 Å; H(3)···Cl[−], 2.33 Å; and N(3)–H(3)···Cl[−], 153°. In the O(2)–H(2)···Cl[−] hydrogen bond [O(2)···Cl[−], 2.87 Å; O(2)–H(2), 0.95 Å; H(2)···Cl[−], 1.92 Å; and O(2)–H(2)···Cl[−], 178°], the chlorine atom is related to the reference atom by the $(x, 1 + y, z)$ symmetry transformation.

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