

## STRUCTURES OF ORGANIC COMPOUNDS

# X-ray Mapping in Heterocyclic Design: VII. Diffraction Study of the Structure of *N*-Pyridoneacetic Acid and the Product of Its Intramolecular Dehydration

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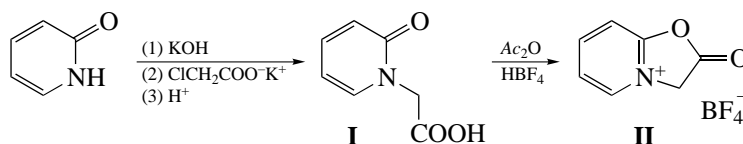
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**Abstract**—The structure of pyridoneacetic acid  $C_7H_7N_1O_3$  (**I**) is determined by the single-crystal X-ray diffraction technique. The crystals of **I** are monoclinic,  $a = 7.4502(15)$  Å,  $b = 10.006(6)$  Å,  $c = 9.960(3)$  Å,  $\beta = 109.96(2)^\circ$ ,  $Z = 4$ , and space group  $P2_1/c$ . The structure of pyridoneacetic acid is solved by the direct method and refined by the least-squares procedure in the anisotropic approximation to  $R = 0.0387$ . The structure of the product of its intramolecular dehydration,  $C_7H_6N_1O_2B_1F_4$  (**II**), is determined by the grid search procedure and refined by the Reitveld method ( $R_p = 0.045$ ,  $R_{wp} = 0.58$ ,  $R_e = 0.026$ , and  $\chi^2 = 4.69$ ). The crystals of **II** are monoclinic,  $a = 10.4979(3)$  Å,  $b = 11.4467(3)$  Å,  $c = 7.6027(1)$  Å,  $\beta = 100.83(2)^\circ$ ,  $Z = 4$ , and space group  $P2_1/n$ . The system of two conjugated heterocycles is planar. © 2002 MAIK "Nauka/Interperiodica".

### INTRODUCTION

This study continues our structural investigations of heterocyclic compounds that are able to enter readily into reactions of ring transformation [1–12]. In this paper, we concentrate on the structural study of pyridoneacetic acid,  $C_7H_7N_1O_3$  (**I**), and the product of its intramolecular dehydration (cyclization), namely, 2-oxo-2,3-dihydrooxazolo[1,2-*a*]pyridinium tetrafluoroborate,  $C_7H_6N_1O_2B_1F_4$  (**II**).

There are no data on the structures of **I** and **II** in the Cambridge Structural Database [13]. Pyridoneacetic acid **I** was synthesized by alkylation of pyridone with chloroacetic acid in the presence of an alkali. The cyclization of pyridone **I** into the oxazolopyridinium salt **II** was achieved by its treatment with acetic anhydride and the following careful addition of tetrafluoroboric acid



### EXPERIMENTAL

The unit cell parameters of **I** ( $C_7H_7NO_3$ ) were determined and refined using 25 reflections in the range  $14^\circ \leq \theta \leq 16^\circ$  on an Enraf–Nonius CAD4 automated diffractometer [14] ( $\lambda$ MoK $\alpha$ , graphite monochromator). Crystals **I** are monoclinic,  $a = 7.4502(15)$  Å,  $b = 10.006(6)$  Å,  $c = 9.960(3)$  Å,  $\beta = 109.96(2)^\circ$ ,  $V = 697.9(5)$  Å<sup>3</sup>,  $d_{\text{calcd}} = 1.457$  g/cm<sup>3</sup>,  $\mu(\lambda$ Mo) = 0.116 mm<sup>-1</sup>,  $Z = 4$ , and space group  $P2_1/c$ . A set of 1745 reflections with  $I \geq 2\sigma(I)$  was collected from a crystal no larger than  $0.48 \times 0.48 \times 0.06$  mm in size in the range  $2.98^\circ \leq \theta \leq 28.97^\circ$  on the same diffractometer ( $\omega$  scan mode) at room temperature. The primary processing of the set of diffraction data was performed with the WinGX98 pro-

gram package [15]. The structure was solved by the direct method and refined by the least-squares procedure in the anisotropic approximation using the SHELX97 program package [16]. All the hydrogen atoms of the molecule were located from the electron-density difference synthesis and refined in the isotropic approximation. The final discrepancy factors are  $R_1 = 0.0387$  and  $wR_2 = 0.0793$ . The residual electron density lies between  $\Delta\rho_{\text{max}} = 0.124$  and  $\Delta\rho_{\text{min}} = -0.132$  e/Å<sup>3</sup>. The atomic coordinates and thermal parameters are listed in Table 1.

The diffraction experiment for  $C_7H_6N_1O_2B_1F_4$  (**II**) was performed on an XRD7 automated powder diffractometer (Seifert-FPM, Freiburg) ( $\lambda$ CuK $\alpha$ , Ni filter) in

**Table 1.** Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for molecule **I**

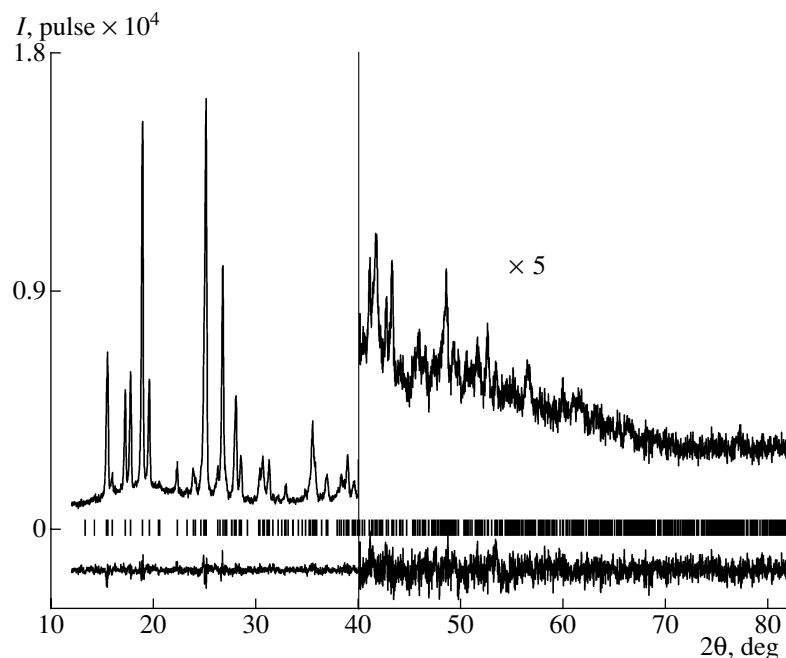
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
N(1)	6745(2)	1982(1)	502(1)	34(1)
C(2)	6691(2)	955(1)	1403(1)	34(1)
O(2)	5112(1)	701(1)	1553(1)	42(1)
C(3)	8427(2)	281(2)	2085(2)	46(1)
C(4)	10050(3)	636(2)	1854(2)	57(1)
C(5)	10030(3)	1702(2)	937(2)	61(1)
C(6)	8396(3)	2349(2)	288(2)	49(1)
C(7)	4980(2)	2696(2)	-217(2)	38(1)
C(8)	4411(2)	3690(1)	706(1)	33(1)
O(81)	2943(2)	4305(1)	226(1)	55(1)
O(82)	5628(2)	3828(1)	2001(1)	41(1)
H(3)	8440(20)	-421(19)	2727(19)	56(5)
H(4)	11190(30)	100(20)	2324(19)	63(5)
H(5)	11170(30)	1910(20)	760(20)	78(6)
H(6)	8190(30)	3100(20)	-370(20)	73(6)
H(7A)	3960(20)	2079(16)	-588(15)	38(4)
H(7B)	5130(20)	3178(18)	-1010(20)	60(5)
H(82)	5090(30)	4480(20)	2460(20)	80(6)

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2$ ) for molecule **II**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}$
N(1)	9(7)	2021(8)	8178(11)	1.56(7)
C(2)	1313(10)	1858(9)	8553(16)	1.56
C(3)	1830(8)	715(9)	8354(14)	1.56
C(4)	942(11)	-153(8)	7795(13)	1.56
C(5)	-401(10)	83(8)	7412(13)	1.56
C(6)	-883(10)	1182(10)	7607(14)	1.56
C(7)	-282(10)	3240(10)	8468(12)	1.56
C(8)	1095(12)	3721(7)	9063(14)	1.56
O(2)	2001(6)	2839(6)	9089(8)	1.56
O(8)	1417(6)	4710(5)	9476(8)	1.56
B	961(17)	3254(15)	3844(24)	3.7(5)
F(1)	1134(8)	4387(5)	3513(10)	2.78(8)
F(2)	966(9)	2664(5)	2345(7)	2.78
F(3)	1927(6)	2763(5)	4970(8)	2.78
F(4)	-101(6)	3003(6)	4395(9)	2.78
H(3)	2697(71)	596(66)	8610(82)	4.0
H(4)	1254(75)	-915(56)	7655(96)	4.0
H(5)	-991(77)	-543(60)	7033(85)	4.0
H(6)	-1779(70)	1333(71)	7369(96)	4.0
H(7A)	-786(69)	3358(66)	9425(90)	4.0
H(7B)	-729(71)	3638(60)	7401(78)	4.0

0.02° steps. Compound **II** is very unstable and tends to undergo self-condensation. Because of the high hygroscopicity and instability of compound **II**, the powder to be studied was placed in a cell inside a dry box filled

with argon and then was isolated from the atmospheric moisture with a thin polyester film. The unit cell parameters were determined with the ITO indexing program [17] in the range of angles  $12^\circ \leq 2\theta \leq 150^\circ$  and indices

**Fig. 1.** Experimental and difference (Reitveld refinement) spectra for **II**.

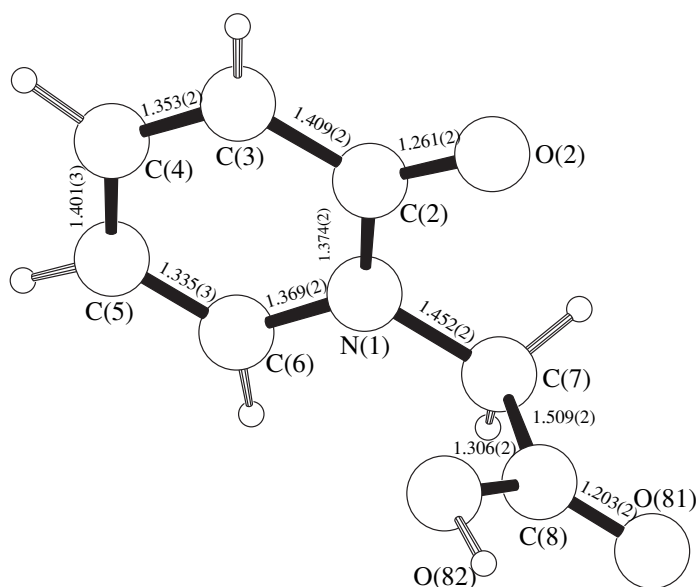


Fig. 2. Molecular structure, atomic numbering, and interatomic distances in **I**.

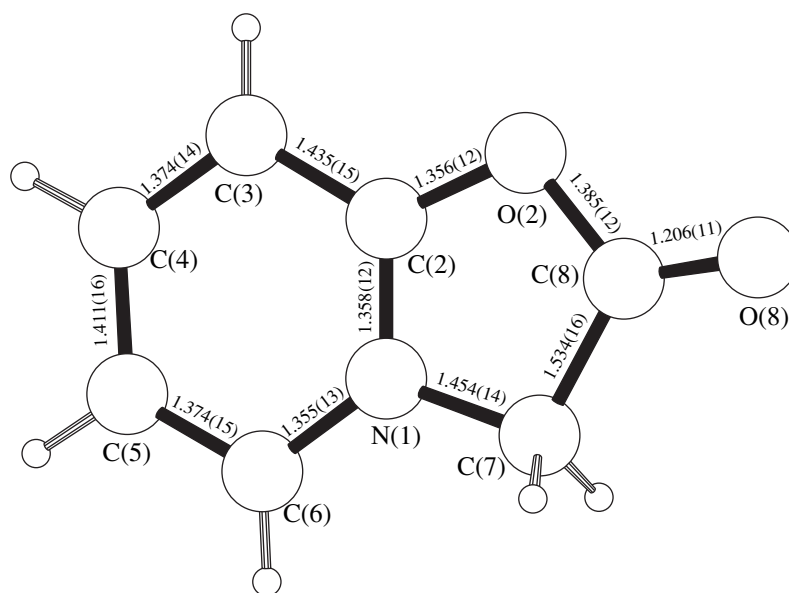


Fig. 3. Molecular structure, atomic numbering, and interatomic distances in **II**.

$0 \leq h \leq 6$ ;  $0 \leq k \leq 7$ ; and  $-5 \leq l \leq 5$ . The space group was determined from the systematic absences of reflections. Crystals **II** are monoclinic,  $a = 10.4979(3)$  Å,  $b = 11.4467(3)$  Å,  $c = 7.6027(1)$  Å,  $\beta = 100.83(3)^\circ$ ,  $V = 897.3(1)$  Å<sup>3</sup>,  $d_{\text{calcd}} = 1.6502$  g/cm<sup>3</sup>,  $\mu(\lambda\text{Cu}) = 15.369$  cm<sup>-1</sup>,  $Z = 4$ , and space group  $P2_1/n$ .

The data of the NMR spectroscopic study of **II** were used as preliminary structural data. The initial geometrical model of the molecule was constructed using semiempirical and empirical methods with the MOPAC 6.0 [18] and PCMODEL [19] programs. The structure was solved according to the grid search procedure [20]

based on the given molecular fragments. The full-profile refinement of the structure was performed by the Reitveld method with the MRJA program [21]. The pseudo-Voigt function was used as a profile function, and the background was approximated by the Chebyshev polynomials of the fifth order. The texture parameters were refined within the March–Dollase model [22] in the [010] direction. In the refinement, the thermal parameters of the non-hydrogen atoms of the cation were averaged. The thermal parameters of the fluorine atoms of the anion were also averaged. The final parameters of the refinement had the following values:

**Table 3.** Parameters of interatomic contacts [24] in **I**

<i>D</i> – <i>H</i>	<i>d</i> ( <i>D</i> – <i>H</i> )	<i>d</i> ( <i>D</i> ⋯ <i>A</i> )	<i>d</i> ( <i>H</i> ⋯ <i>A</i> )	ω <i>DHA</i>	<i>A</i>	Symmetry code
C(7)–H(7A)	0.95(2)	2.643(2)	2.44(2)	92(1)	O(2)	( <i>x</i> , <i>y</i> , <i>z</i> )
C(3)–H(3)	0.95(2)	3.322(2)	2.60(2)	134(1)	O(81)	(1 – <i>x</i> , <i>y</i> – 1/2, 1/2 – <i>z</i> )
C(4)–H(4)	0.98(2)	3.315(2)	2.80(2)	114(1)	O(81)	( <i>x</i> + 1, 1/2 – <i>y</i> , <i>z</i> + 1/2)
C(4)–H(4)	0.98(2)	3.526(2)	2.57(2)	166(2)	O(82)	(2 – <i>x</i> , <i>y</i> – 1/2, 1/2 – <i>z</i> )
C(5)–H(5)	0.95(2)	3.612(3)	2.87(2)	136(2)	O(81)	( <i>x</i> + 1, <i>y</i> , <i>z</i> )
C(6)–H(6)	0.97(2)	3.481(3)	2.75(2)	132(2)	O(81)	(1 – <i>x</i> , 1 – <i>y</i> , – <i>z</i> )
C(7)–H(7B)	0.96(2)	3.377(3)	2.87(2)	114(1)	O(81)	(1 – <i>x</i> , 1 – <i>y</i> , – <i>z</i> )
C(7)–H(7B)	0.96(2)	3.626(2)	2.67(2)	172(2)	O(2)	( <i>x</i> , 1/2 – <i>y</i> , <i>z</i> – 1/2)
C(7)–H(7B)	0.96(2)	3.339(2)	2.93(2)	107(1)	O(82)	( <i>x</i> , 1/2 – <i>y</i> , <i>z</i> – 1/2)
O(82)–H(82)	0.96(2)	2.535(2)	1.61(2)	162(2)	O(2)	(1 – <i>x</i> , <i>y</i> + 1/2, 1/2 – <i>z</i> )

Note: *D* is a donor atom, *A* is an acceptor atom, and *H* is a hydrogen atom (the *d* distances and ω angles are given in Å and degrees, respectively).

**Table 4.** Parameters of interatomic contacts [24] in **II**

<i>D</i> – <i>H</i>	<i>d</i> ( <i>D</i> – <i>H</i> )	<i>d</i> ( <i>D</i> ⋯ <i>A</i> )	<i>d</i> ( <i>H</i> ⋯ <i>A</i> )	ω <i>DHA</i>	<i>A</i>	Symmetry code
C(7)–H(7B)	0.97(6)	3.15(1)	2.60(7)	116(4)	F(4)	( <i>x</i> , <i>y</i> , <i>z</i> )
C(6)–H(6)	0.94(7)	3.49(1)	2.88(7)	124(6)	O(8)	( <i>x</i> – 1/2, 1/2 – <i>y</i> , <i>z</i> – 1/2)
C(6)–H(6)	0.94(7)	3.33(1)	2.75(7)	121(5)	O(2)	( <i>x</i> – 1/2, 1/2 – <i>y</i> , <i>z</i> – 1/2)
C(6)–H(6)	0.94(7)	3.53(1)	2.63(8)	162(6)	F(1)	( <i>x</i> – 1/2, 1/2 – <i>y</i> , <i>z</i> + 1/2)
C(6)–H(6)	0.94(7)	3.40(1)	2.80(8)	122(6)	F(3)	( <i>x</i> – 1/2, 1/2 – <i>y</i> , <i>z</i> + 1/2)
C(7)–H(7A)	0.99(8)	3.53(1)	2.82(8)	129(5)	F(3)	( <i>x</i> – 1/2, 1/2 – <i>y</i> , <i>z</i> + 1/2)
C(5)–H(5)	0.96(7)	3.21(1)	2.47(7)	134(5)	F(2)	(– <i>x</i> , – <i>y</i> , 1 – <i>z</i> )
C(4)–H(4)	0.95(7)	3.69(1)	2.98(7)	133(5)	F(4)	(– <i>x</i> , – <i>y</i> , 1 – <i>z</i> )
C(3)–H(3)	0.91(7)	3.29(1)	2.87(7)	110(5)	O(8)	(1/2 – <i>x</i> , <i>y</i> – 1/2, 3/2 + <i>z</i> )
C(3)–H(3)	0.91(7)	3.26(1)	2.68(7)	123(5)	F(1)	(1/2 – <i>x</i> , <i>y</i> – 1/2, 3/2 + <i>z</i> )
C(4)–H(4)	0.95(7)	3.49(1)	2.81(7)	129(5)	F(3)	(1/2 – <i>x</i> , <i>y</i> – 1/2, 3/2 + <i>z</i> )
C(4)–H(4)	0.95(7)	3.63(1)	2.84(8)	142(5)	O(2)	(1/2 – <i>x</i> , <i>y</i> – 1/2, 3/2 + <i>z</i> )
C(3)–H(3)	0.91(7)	3.49(1)	2.78(7)	136(6)	F(4)	( <i>x</i> + 1/2, 1/2 – <i>y</i> , <i>z</i> + 1/2)
C(7)–H(7A)	0.99(8)	3.17(1)	2.50(8)	126(5)	O(8)	(– <i>x</i> , 1 – <i>y</i> , 2 – <i>z</i> )
C(7)–H(7A)	0.99(8)	3.06(1)	2.72(6)	101(4)	F(2)	( <i>x</i> , <i>y</i> , 1 + <i>z</i> )
C(7)–H(7B)	0.97(6)	3.15(1)	2.38(7)	136(5)	F(1)	(– <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i> )

Note: *D* is a donor atom, *A* is an acceptor atom, and *H* is a hydrogen atom (the *d* distances and ω angles are given in Å and degrees, respectively).

$R_p = 0.045$ ,  $R_{wp} = 0.58$ ,  $R_e = 0.026$ , and  $\chi^2 = 4.69$ , where  $R_p = \sum |I_o - I_c| / \sum I_o$ ,  $R_{wp} = \sum w |I_o - I_c| / \sum w I_o$ ,  $R_e = \sum \sigma I_o / \sum I_o$ ,  $I_o$  is the observed intensity, and  $I_c$  is the calculated intensity. The observed and difference X-ray diffraction patterns are shown in Fig. 1. The atomic coordinates and isotropic thermal parameters are listed in Table 2.

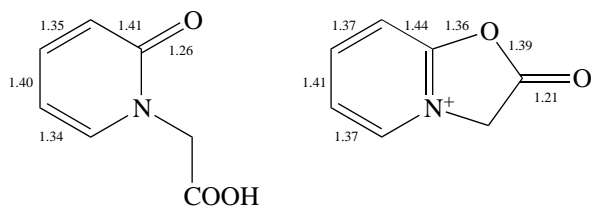
The molecular structures of **I** and **II** with the atomic numberings are shown in Figs. 2 and 3, respectively. The drawings were obtained with the PLUTON96 program [23].

## RESULTS AND DISCUSSION

Earlier, we studied the structures of the *N*-substituted pyridones-2 containing the phenacyl [3] and *para*-nitrophenacyl [8] groups at the nitrogen atom. The structure of the pyridine fragment in molecule **I** is similar to those in the pyridones studied earlier. The O(2) and C(7) atoms lie in the plane of the heterocycle. In the pyridine fragment (Fig. 2), formally single and double bonds alternate to form the quasi-diene structural fragment C(3)=C(4)–C(5)=C(6). The C(2)–N(1)–C(7)–C(8) tor-

sion angle is equal to  $77.2(2)^\circ$ , which rules out the formation of the  $O(2)\cdots H(82)-O(82)$  intramolecular hydrogen bond. A similar molecular structure is observed in 1,2-dihydro-2-imino-1-carboxymethylpyridine [5], in which the planes of the carboxyl group and the pyridine ring form a dihedral angle of  $80.81(5)^\circ$ . In crystal structure **I**, a network of intermolecular hydrogen bonds is observed. The parameters of the hydrogen bonds are listed in Table 3.

The heterocyclic cation **II** has a planar structure. The largest atomic deviation from the plane of the bicyclic fragment is 0.01 Å. The O(8) atom lies in this plane. It is interesting to reveal structural changes that accompany the **I**  $\rightarrow$  **II** cyclization. As was noted above, the bond lengths in the six-membered ring of molecule **I** alternate. Upon cyclization, the diene-like structure is retained but the bond alternation becomes less pronounced (due to the stronger bond delocalization in the cation). At the same time, upon cyclization, the carbonyl fragment of the amide group loses the double-bond character. Most likely, this indicates significant charge localization at the nitrogen atom of the cation.



The aforementioned specific structural feature of cation **II** suggests that no aromatization occurs in the bicyclic fragment formed from the monocycle. A system of intermolecular contacts involving the hydrogen, oxygen, and fluorine atoms is formed in crystal structure **II** (Table 4). These contacts were calculated using the PARST95 program [24]. The mean B–F bond length in the tetrahedral anion is 1.321(19) Å.

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