

X-ray Mapping in Heterocyclic Design: IV. Crystal Structure Determination of 3-(*p*-Nitrobenzoyl)-2-Oxooxazolo[3,2-*a*]pyridine from Powder Diffraction Data

V. B. Rybakov*, S. G. Zhukov*, E. V. Babaev*, and E. J. Sonneveld**

* Faculty of Chemistry, Moscow State University, Vorob'evy gory, Moscow, 119899 Russia

e-mail: rybakov@biocryst.phys.msu.su

** Laboratory of Crystallography, Faculty of Chemistry, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands

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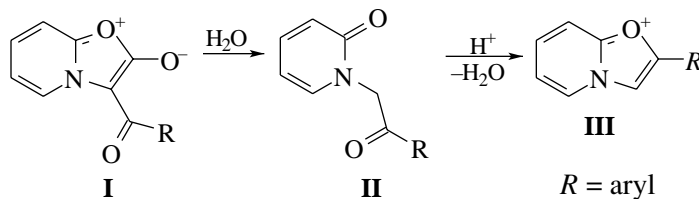
Abstract—The structure of 3-(*p*-nitrobenzoyl)-2-oxooxazolo[3,2-*a*]pyridine is determined by the powder diffraction technique. The crystals are monoclinic, $a = 13.642(2)$ Å, $b = 22.278(3)$ Å, $c = 3.917(1)$ Å, $\beta = 90.63(2)^\circ$, $Z = 4$, and space group $P2_1/n$. The structure is solved by a modified Monte Carlo method and refined by the Reitveld method. The six-membered heterocycle is characterized by the alternation of partially single and partially double bonds. The system of two conjugated heterocycles is planar and forms a dihedral angle of $46.1(1)^\circ$ with the plane of the phenyl ring. The nitro group is virtually coplanar with the phenyl fragment. An extensive system of intramolecular and intermolecular contacts involving hydrogen, oxygen, and nitrogen atoms is observed in the crystal. © 2001 MAIK "Nauka/Interperiodica".

INTRODUCTION

This paper continues a series of structural investigations of the heterocyclic compounds that are able to enter readily into reactions of ring transformations and various chemical rearrangements. Our previous studies in this field were reported in [1–7]. The crystal structure of the mesoionic compound 3-benzoyl-2-oxooxazolo[3,2-*a*]pyridine was determined by X-ray diffraction in [8]. In the present work, we concentrated on the structural study of its analogue, namely, 3-(*p*-nitroben-

zoyl)-2-oxooxazolo[3,2-*a*]pyridine. There are no data on its structure in the Cambridge Structural Database [9]. The compound was prepared according to the procedure described earlier in [10].

Our interest in the structure and properties of this subclass of mesoionic heterocycles is due to, first, the unusual (ilide) structural type of these heterocycles [8] and, second, the possibility of readily opening the oxazolone ring and its transforming into the oxazolium ring [11] according to the following scheme:



Earlier [2, 3], we performed the X-ray structure analysis of compounds **II** and **III** ($R = \text{C}_6\text{H}_5$), that is, both products of hydrolysis of the mesoionic system **I** [2]. Thus, the crystal structure determination of compound **I** with $R = p\text{-NO}_2\text{-C}_6\text{H}_4$ (**Ia**) as a precursor of compounds **II** and **III** provides one more example of the principle of the X-ray mapping of reactions [5–7].

EXPERIMENTAL

The diffraction experiment was performed using an evacuated Enraf–Nonius Guinier–Johansson FR552 camera ($\lambda\text{CuK}_{\alpha 1}$, quartz monochromator). The intensities of the X-ray spectrum were measured with an LS18 densitometer in 0.01° steps in the 2θ range $4^\circ\text{--}86^\circ$ and the hkl range $0 \leq h \leq 12$; $0 \leq k \leq 19$, $-3 \leq l \leq 3$. The unit

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters U_{iso} ($\text{\AA}^2 \times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
C(1)	4146(10)	3112(6)	5472(15)	49(6)
C(2)	4264(10)	3699(6)	4050(15)	49(6)
C(3)	5684(10)	4169(6)	999(17)	49(6)
C(4)	6651(10)	4060(6)	-29(15)	51(7)
C(5)	7074(10)	3476(6)	731(15)	51(7)
C(6)	6639(10)	3018(6)	2317(15)	49(7)
C(7)	5644(10)	3155(6)	3446(15)	49(7)
C(8)	3666(10)	4217(6)	3267(15)	49(7)
C(9)	2604(10)	4109(6)	4369(15)	49(7)
C(10)	2131(10)	4565(6)	6060(15)	49(7)
C(11)	1106(10)	4525(6)	6786(15)	49(7)
C(12)	648(10)	4004(6)	5890(15)	49(7)
C(13)	1065(10)	3515(6)	4150(15)	49(7)
N(1)	5251(8)	3692(6)	2745(12)	49(7)
O(1)	5084(10)	2759(6)	5105(15)	49(7)
O(2)	3575(10)	2802(6)	6992(15)	49(7)
C(14)	2093(10)	3577(6)	3478(15)	49(7)
N(12)	-476(10)	3949(6)	6708(15)	49(7)
O(3)	3904(6)	4705(6)	2475(11)	49(7)
O(12A)	-767(6)	4373(6)	8055(11)	109(11)
O(12B)	-782(6)	3474(5)	5695(15)	67(11)
H(3)	5338	4585	525	51*
H(4)	7048	4405	-1328	51*
H(5)	7855	3421	-169	51*
H(6)	6908	2571	2980	51*
H(10)	2526	4971	6841	51*
H(11)	740	4897	8106	51*
H(13)	685	3107	3517	51*
H(14)	2457	3210	2242	51*

* The thermal parameter was fixed and not refined.

cell parameters were determined by the ITO indexing program [13], and the space group was determined from the systematic absences of reflections. Crystals **Ia** ($\text{C}_{14}\text{H}_8\text{N}_2\text{O}_5$) are monoclinic, $a = 13.642(2)$ \AA , $b = 22.278(3)$ \AA , $c = 3.917(1)$ \AA , $\beta = 90.63(2)^\circ$, $V = 1190.4(4)$ \AA^3 , $d_{\text{calcd}} = 1.653$ g/cm^3 , $\mu(\text{Cu}) = 10.8$ cm^{-1} , $Z = 4$, and space group $P2_1/n$.

The structure was solved by the modified Monte Carlo method [14, 15] with the use of the known molecular fragments. The full-profile refinement of the structure was performed by the Rietveld method with the MRIA program [16]. The reflection profiles were described by the function proposed in [17], and the background was approximated by the Chebyshev polynomials of the fifth order. The texture parameters were refined within the March–Dollase model [18] in the [001] direction. The procedure of the structural investigation of **Ia** is described in more detail in [19]. The final R factors of the full-matrix refinement were $R_p = 0.053$, $R_b = 0.155$, and $R_e = 0.024$, where $R_p = \sum |I_{\text{obs}} - I_{\text{calcd}}| / \sum I_0$, $R_b = \sum |I_{\text{obs}} - I_{\text{calcd}}| / \sum |I_{\text{obs}} - Bckgr|$, $R_e = \sum \sigma I_{\text{obs}} / \sum I_{\text{obs}}$, I_{obs} is the observed intensity, and I_{calcd} is the calculated intensity; the χ^2 criterion was equal to 6.9.

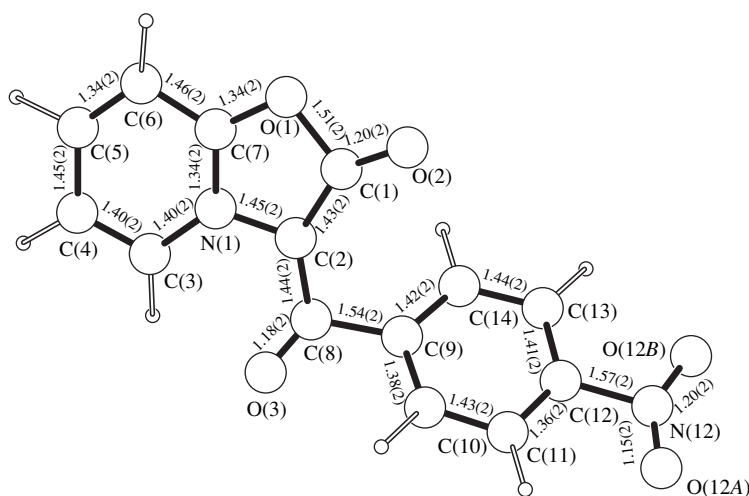
The atomic coordinates are listed in Table 1 (the positions of the H atoms were calculated from geometric considerations; in the course of the refinement, the H atoms were rigidly bound to the corresponding carbon atoms). The schematic drawing of the molecule (see figure) was obtained with the PLUTON96 program [20]. The atomic numbering in **Ia** is the same as that in [8] for convenient comparison of the geometric parameters of the molecules.

RESULTS AND DISCUSSION

The binuclear fragment of molecule **Ia** is planar, and its structure is essentially the same as that of its analogue **Ib** ($R = \text{C}_6\text{H}_5$) [8]; specifically, the bond lengths in the C(3)–C(4)–C(5)–C(6) fragment of the six-membered heterocycle alternate, the lengths of the C(1)–O(1) endocyclic bonds in the two structures completely coincide, and the O(1)–C(7) bond in **Ia** is only 0.05 \AA longer than that in **Ib**. This structure suggests that the six-membered fragment of the mesoionic bicyclic molecule can be represented by the pyridine-like (butadiene) structure to a greater extent than by the delocalized pyridine ring. From structural considerations, it follows that the positive charge is distributed over the N(1)–C(7)–O(1) bonds and the pyridine fragment of the molecule is not involved in delocalization.

According to the above scheme, the C(1)–C(2) bond should be of the double type, but it is actually substantially longer [1.43(2) \AA]. On the other hand, the length of the C(1)–O(2) exocyclic bond [1.20(2) \AA] corresponds to the double bond. Therefore, the geometry of the O(2)–C(1)–C(2)–C(8)–O(3) fragment corresponds to a combination of two carbonyl groups connected through the C(2) atom without significant delocalization. Possibly, this indicates that the negative charge is localized at the C(2) atom.

The molecular structures under comparison considerably differ in the arrangement of the phenyl rings with respect to the heterocyclic nucleus. The angles



Structure of the molecule studied and the atomic numbering.

between the planes of the phenyl ring and the oxazolo[3,2-*a*]pyridine bicyclic fragment are $66.8(2)^\circ$ and $46.1(2)^\circ$ in molecules **Ib** [8] and **Ia**, respectively. The pronounced decrease in the angle of ring rotation in the molecule studied is most likely due to the packing effects caused by the nitro group in the *para* position of the phenyl fragment. The nitro group itself is

virtually coplanar with the phenyl ring: the rotation angle is $1(1)^\circ$.

A system of intramolecular and intermolecular C–H \cdots O and C–H \cdots N contacts is formed in the crystal (Table 2). These contacts were calculated with the PARST95 program [21].

Table 2. Parameters of the interatomic contacts* [19]

<i>D</i> –H	<i>d</i> (<i>D</i> –H)	<i>d</i> (<i>D</i> \cdots <i>A</i>)	<i>d</i> (H \cdots <i>A</i>)	ω DHA	<i>A</i> (symmetry operation)
C(3)–H(3)	1.06(9)	2.77(2)	2.13(8)	117(6)	O(3) (<i>x</i> ; <i>y</i> ; <i>z</i>)
C(13)–H(13)	1.07(9)	2.60(2)	2.33(8)	92(5)	O(12B) (<i>x</i> ; <i>y</i> ; <i>z</i>)
C(11)–H(11)	1.10(8)	2.63(2)	2.36(8)	91(5)	O(12A) (<i>x</i> ; <i>y</i> ; <i>z</i>)
C(10)–H(10)	1.10(9)	2.83(1)	2.62(7)	89(4)	O(3) (<i>x</i> ; <i>y</i> ; <i>z</i>)
C(14)–H(14)	1.08(8)	2.98(2)	2.56(7)	103(5)	O(2) (<i>x</i> ; <i>y</i> ; <i>z</i>)
C(3)–H(3)	1.06(9)	2.91(2)	2.23(8)	120(5)	O(3) (1 – <i>x</i> ; 1 – <i>y</i> ; – <i>z</i>)
C(4)–H(4)	1.07(8)	3.01(2)	2.41(9)	114(5)	O(3) (1 – <i>x</i> ; 1 – <i>y</i> ; – <i>z</i>)
C(11)–H(11)	1.10(8)	3.13(2)	2.91(7)	91(4)	O(12A) (– <i>x</i> ; 1 – <i>y</i> ; 1 – <i>z</i>)
C(11)–H(11)	1.10(8)	3.22(2)	2.22(7)	150(5)	O(12A) (– <i>x</i> ; 1 – <i>y</i> ; 2 – <i>z</i>)
C(10)–H(10)	1.10(9)	3.48(1)	2.94(7)	111(4)	O(3) (<i>x</i> ; <i>y</i> ; 1 + <i>z</i>)
C(14)–H(14)	1.08(8)	3.69(2)	2.73(7)	149(4)	O(2) (<i>x</i> ; <i>y</i> ; <i>z</i> – 1)
C(4)–H(4)	1.07(8)	3.68(2)	2.99(8)	122(5)	O(12A) (1 + <i>x</i> ; <i>y</i> ; <i>z</i> – 1)
C(5)–H(5)	1.13(8)	3.86(2)	2.85(8)	148(5)	N(12) (1 + <i>x</i> ; <i>y</i> ; <i>z</i> – 1)
C(5)–H(5)	1.13(8)	3.72(2)	2.92(9)	127(5)	O(12A) (1 + <i>x</i> ; <i>y</i> ; <i>z</i> – 1)
C(5)–H(5)	1.13(8)	3.55(1)	2.48(7)	156(5)	O(12B) (1 + <i>x</i> ; <i>y</i> ; <i>z</i> – 1)
C(5)–H(5)	1.13(8)	3.49(1)	2.94(6)	110(4)	O(12B) (1 + <i>x</i> ; <i>y</i> ; <i>z</i>)

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

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