

Crystal structure determination of 2-oxo-3-benzoyloxazolo[3,2-a]pyridine from X-ray powder data

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Abstract. The crystal structure of the mesoionic compound 2-oxo-3-benzoyloxazolo[3,2-a]pyridine (C₁₄H₉NO₃) has been determined from X-ray powder data using the grid search procedure.

The crystal symmetry is orthorhombic (space group *Pna*2₁, *a* = 7.940(1) Å, *b* = 24.562(3) Å, *c* = 5.402(1) Å). The results of Rietveld refinement (*R*_{wp} = 11.9%; *R*_{exp} = 3.7%) with gradually relaxed bond restraints show that the delocalization of positive charge does not involve the entire pyridine fragment and occurs along the triad N–C–O, whereas the negative charge is localized on the carbon atom.

Introduction

The well-known feature of mesoionic compounds, such as sydnones (Eade, Earl, 1946) and munchnones (Huisgen, 1967), is that they can not be successfully represented by classical covalent structures using localized σ - and π -bond without a dipolar structure (Newton, Ramsden, 1982). Munchnones are usually unstable, and the stablest class is represented by mesoionic oxazolones with fused pyridine ring. A member of this series – 2-oxo-3-benzoyloxazolo[3,2-a]pyridine – was first synthesized long ago (Boyd, Wright, 1970). Recently, this subfamily of mesoionic heterocycles has attracted special attention due to their capability to undergo ring transformation to cationic oxazolo[3,2-a]pyridinium salts (Babaev, 1997; Babaev, Orlova, 1997). Although 2-oxo-3-benzoyloxazolo[3,2-a]pyridine is more stable at normal conditions than the other known mesoionic oxazolones, it is difficult to grow single crystals for an X-ray experiment. The aim of this work was to determine the crystal structure of this mesoionic compound from X-ray powder data.

Experimental

2-oxo-3-benzoyloxazolo[3,2-a]pyridine, light-yellow powder, was synthesized following the Boyd-Wright method (Boyd, Wright, 1970).

The X-ray powder pattern was measured using an evacuated Guinier-Johanson camera (Enraf-Nonius FR552) with quartz monochromatized CuK α ₁ radiation during 3 hrs. Digitized intensities were collected with a LS18 microdensitometer from 4.0 to 83.0° degrees 2 θ in steps of 0.01°.

Initially we failed to determine the cell parameters using the peak positions, extracted from the powder pattern. Although TREOR (Werner, Eriksson, Westdahl, 1985) and ITO (Visser, 1969) programs gave the same results, several peaks remained unindexed. A careful scrutiny of the synthesized powder revealed the presence of a small amount of tiny transparent microcrystals about ~0,05 mm. Despite of its small size we succeeded to determine the cell parameters with a single-crystal CAD4 diffractometer. A search in Cambridge Structural Database (Allen, Kennard, 1993) showed that the second phase is triethylammonium chloride Et₃NHCl (*a* = 8.369, *c* = 7.058, Sp.gr. *P*6₃*mc*) with known structure (James, Cameron, Knop, Neuman, Falk, 1985). After excluding the peaks of the second phase the orthorhombic cell parameters were easily determined (*a* = 7.940(1), *b* = 24.562(3), *c* = 5.402(1) Å, *M*₂₀ = 61, *F*₂₀ = 124 (0.006; 26)). The space group extinctions were not clear due to overlapping of reflections, therefore we tried several orthorhombic space groups. Eventually it turned out that *Pna*2₁ (No. 33) is the right one.

Structure solution and discussion

The crystal structure of 2-oxo-3-benzoyloxazolo[3,2-a]pyridine was solved using the grid search method (Chernyshev, Schenk, 1998).

The starting geometry of the mesoionic molecule was calculated on the AM1 level with MOPAC 6.0 program (Stewart, 1990). Several models of the molecule were calculated with a different orientation of the phenyl fragment with respect to the plane containing the oxazolo[3,2-a]pyridine bicycle. It was found that the energy minimum (*E*_h ~ -5.03 kcal) corresponds to the model with the dihedral angle $\varphi_d \cong \pm 49^\circ$ (see Fig. 1). These models were chosen for the grid search procedure.

Full-pattern decomposition was made using the revised MRJA program (Zlokazov, Chernyshev, 1992). Atomic co-

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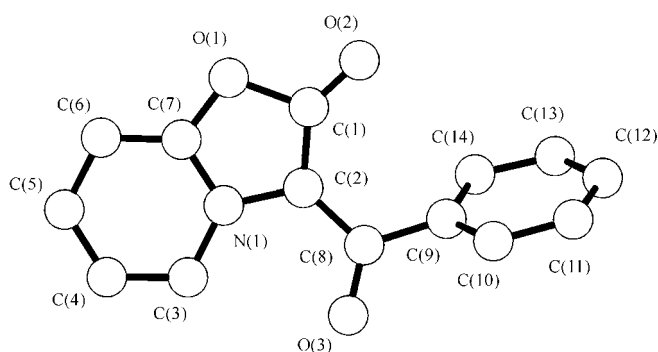
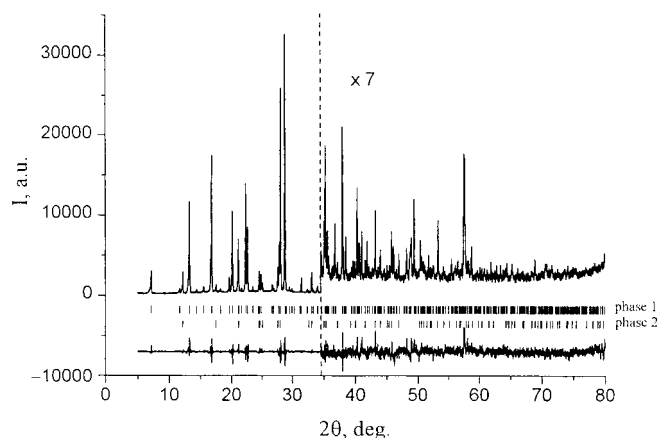
Table 1. Crystal data and results of Rietveld refinement.

Compound	2-oxo-3-benzoyloxazolo[3,2-a]pyridine	
Formula	C ₁₄ H ₉ NO ₃	
Sp.gr.	Pna2 ₁	
<i>a</i> , Å	7.940(1)	
<i>b</i> , Å	24.562(6)	
<i>c</i> , Å	5.402(1)	
<i>V</i> , Å ³	1054	
<i>Z</i>	4	
Absorption coef. μ (cm ⁻¹)	1.1	
Calculated density d_x (g cm ⁻³)	1.52	
<i>F</i> (000)	496	
	Full pattern decomposition	Rietveld refinement
R_{wp} , % ^a	10.0	11.9
R_{exp} , %	3.7	3.7
χ^2	7.3	9.9

a: R_{wp} , R_{exp} are defined in (Young, Wiles, 1982)

ordinates of Et₃NHCl were taken from (James *et al.*, 1985). The background was approximated by Chebyshev polynomials and the peak profile by the split-type pseudo-Voigt function (Toraya, 1986).

The grid search procedure was run with default parameters (see details in Chernyshev, Schenk, 1998) using the intensities of 100 reflections up to $2\theta = 50^\circ$. The minimum value of $R \cong 48\%$ was obtained for both molecule models. The comparison of the molecule positions showed, that these structural models are enantiomorphs and, therefore, indistinguishable in our case.

**Fig. 1.** Model of 2-oxo-3-benzoyloxazolo[3,2-a]pyridine molecule.**Fig. 2.** Rietveld plot for 2-oxo-3-benzoyloxazolo[3,2-a]pyridine crystal structure.

phase 1: 2-oxo-3-benzoyloxazolo[3,2-a]pyridine
phase 2: triethylammonium chloride

Subsequent Rietveld refinement was carried out using gradually relaxing bond restraints. An overall temperature factor was applied for the non-hydrogen atoms, the temperature factor of the H-atoms and all hydrogen bonds were fixed. The texture parameter was refined using the March-Dollase method (Dollase, 1986). The crystal data, Rietveld refinement results and atomic coordinates are given in Tables 1–2. The Rietveld plot is shown in Fig. 2.

The angle between the planes of the phenyl ring and the oxazolo[3,2-a]pyridine bicyclic system is $67.8(6)^\circ$. Molecules are stacked along [100] direction without any hydrogen bonding. Rietveld refinement leads to a rather intriguing conclusion with the respect to the structure of the mesoionic oxazolopyridine. A pronounced difference is displayed

Table 2. Atomic coordinates ($\times 10^3$) and thermal isotropic parameters U_{iso} ($\times 10^3$, Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
C(1)	398(1)	339(1)	-200	17(3)
C(2)	294(1)	329(1)	7(2)	17
C(3)	191(1)	241(1)	196(2)	17
C(4)	207(1)	186(1)	186(2)	17
C(5)	307(1)	162(1)	6(2)	17
C(6)	385(1)	192(1)	-172(2)	17
C(7)	369(1)	248(1)	-154(2)	17
C(8)	224(1)	367(1)	179(2)	17
C(9)	223(1)	420(1)	103(2)	17
C(10)	310(1)	450(1)	275(2)	17
C(11)	333(1)	506(1)	234(2)	17
C(12)	252(1)	531(1)	40(2)	17
C(13)	163(1)	501(1)	-132(2)	17
C(14)	157(1)	445(1)	-106(2)	17
N(1)	286(1)	272(1)	34(2)	17
O(1)	436(1)	285(1)	-302(2)	17
O(2)	462(1)	377(1)	-299(2)	17
O(3)	135(1)	351(1)	360(2)	17
H(1)	120(5)	258(3)	309(8)	51
H(2)	130(4)	164(3)	275(8)	51
H(3)	314(5)	124(2)	0(9)	51
H(4)	457(5)	176(2)	-288(9)	51
H(5)	343(5)	435(2)	423(8)	51
H(6)	383(4)	527(2)	356(8)	51
H(7)	282(5)	567(2)	2(9)	51
H(8)	123(5)	518(3)	-275(9)	51
H(9)	131(5)	423(3)	245(8)	-51
Texture parameter <i>r</i>				1.37(1)

in the length of two endocyclic C–O bonds: C₇–O₁ and C₁–O₁, where the first bond is significantly shorter than the another one (1.33 and 1.46 Å). This fact leads to the conclusion that the six-membered fragment of the mesoionic bicycle can better be represented as a pyridone-like structure (with butadiene pattern) than as a delocalized pyridinium ring. From the structural viewpoint, therefore, the delocalization of the positive charge occurs along the triad N₁–C₇–O₁ and does not involve the entire pyridine fragment. The length of the bond C₁–C₂, which was expected to be a double-like bond, is actually rather long (1.40 Å), whereas the exocyclic C₁–O₂ bond is rather short (1.20 Å). Therefore, the fragment C₂–C₁–O₂ resembles the exocyclic keto-group C₂–C₈=O₃. Hence, the geometry of the fragment O₂–C₁–C₂–C₈–O₃ corresponds to a combination of two regular carbonyl groups attached to the carbon atom C₂ without significant delocalization. This effect may be treated in terms of localization of the negative charge in the mesoionic molecule on the atom C₂.

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