=== **STRUCTURES OF ORGANIC COMPOUNDS** ===

X-ray Mapping in Heterocyclic Design: III. Diffractometric Study of the Crystal Structure of 1-Methyl-2-Oxo-2,3-Dihydroimidazo[1,2-*a*]pyridinium Bromide

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Abstract—The crystal structure of 1-methyl-2-oxo-2,3-dihydroimidazo[1,2-*a*]pyridinium bromide $C_8H_9BrN_2O$ is determined by X-ray diffraction. The structure is solved by the direct method and refined by the least-squares procedure to $R = 0.0599$. The geometry of the pyridinium fragment observed in the molecule corresponds to the limited number of centers at which the positive charge can be delocalized. Apparently, this delocalization predominantly occurs in the NCN fragment of the imidazole ring and only slightly affects the pyridine moiety of the molecule. © *2000 MAIK "Nauka/Interperiodica".*

Earlier [1, 2], we performed structural studies characterizing the transformation of pyridine **I** into imidazopyridine **II**. This work continues our investigations into the structure of the compounds obtained by consecutive transformations of compounds **I** and **II**. Formally, compound **II** is the hydrochloride of instable free base **III**. Compound **III**, which readily enters into the reactions with electrophilic chemical agents, can be prepared by a reaction between sodium methylate and salt **II** [3]. The object of the present work was compound **IV** (a homolog of salt **II**), which was obtained by the reaction between salt **II** and the base followed by the methylation (without isolation of intermediate compound **III**):
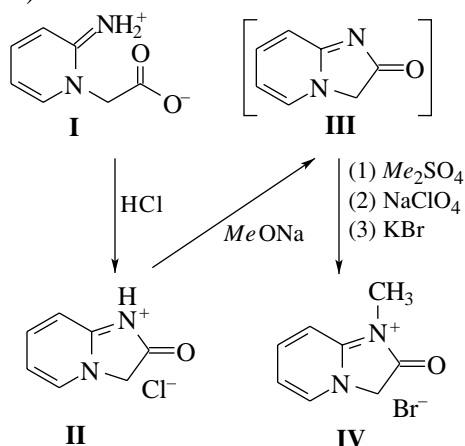
We determined the crystal structure of salt **IV** by X-ray diffraction analysis. Up to now, according to the data of the Cambridge Structural Database [4], the X-ray structure analysis of this compound has not been performed.

EXPERIMENTAL

Salt **IV** was initially isolated as the perchlorate according to the procedure described in [3]; however, we failed to prepare the satisfactory crystals of the isolated perchlorate and transformed the compound into the bromide salt. For this purpose, an aqueous solution of the perchlorate was treated by a saturated KBr solution. The precipitate of potassium perchlorate was filtered off, and the aqueous solution of bromide **IV** was evaporated to dryness. The dry residue was recrystallized from a 1 : 1 isopropanol–water solution and used for the X-ray diffraction analysis. Transparent colorless crystals of bromide **IV** have a platelike habit.

Crystals of bromide **IV**, $C_8H_9BrN_2O$, are monoclinic. The unit cell parameters were determined and refined on a CAD4 automated diffractometer using 25 reflections in the θ range 11°–13° [5] (λMoK_α, graphite monochromator). The crystal data are $a = 7.806(1)$ Å, $b = 6.404(1)$ Å, $c = 8.812(1)$ Å, $\beta = 97.44(2)°$, $V = 436.8(1)$ Å^3, $d_{calcd} = 1.742$ g/cm^3, $\mu(\lambda Mo) = 4.656$ mm^{-1}, $Z = 2$, and space group $P2_1/m$. A set of 934 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 [6]. The structure was solved by the direct method and refined in the anisotropic approximation by the least-squares procedure using the SHELX97 program package [7]. All the hydrogen atoms were located from the difference synthesis of electron density and included in the refinement in the isotropic approximation. The final discrepancy factors are $R1 = 0.0599$ and $wR2 = 0.1374$. The atomic coordinates and thermal parameters are listed in the table. The residual electron density lies between $\Delta\rho_{max} = 1.304$ and $\Delta\rho_{min}$

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

Atom	x	y	z	U_{eq}/U_{iso}
Br	4404(1)	7500	7737(1)	42(1)
C(1)	2386(4)	2500	8644(4)	35(1)
C(2)	741(4)	2500	9354(3)	36(1)
O(2)	578(3)	2500	10698(3)	53(1)
N(3)	−612(3)	2500	8179(3)	31(1)
C(3)	−2432(4)	2500	8381(4)	45(1)
C(4)	−12(4)	2500	6777(3)	23(1)
C(5)	−913(4)	2500	5322(4)	31(1)
C(6)	52(5)	2500	4116(4)	33(1)
C(7)	1835(5)	2500	4360(4)	35(1)
C(8)	2690(4)	2500	5811(4)	31(1)
N(9)	1725(3)	2500	7007(3)	26(1)
H(11)	3050(24)	1310(36)	8835(22)	20(5)
H(31)	−2694(46)	2500	9425(46)	53(12)
H(32)	−2983(35)	1197(49)	7881(34)	69(9)
H(5)	−2147(41)	2500	5161(38)	33(9)
H(6)	−667(47)	2500	3032(49)	69(15)
H(7)	2640(51)	2500	3670(50)	65(13)
H(8)	3737(36)	2500	6017(34)	17(8)

$= -1.265$ e/Å^3. Cation **IV** shown in the figure was drawn with the PLUTON96 program [8].

RESULTS AND DISCUSSION

The bromide anion serves as a counterion in salt **IV**. The heterocyclic cation occupies a special position in
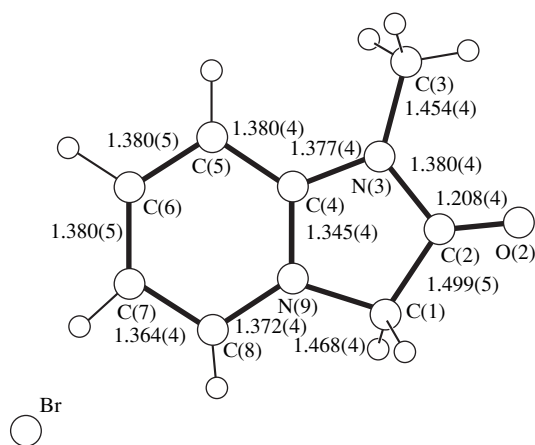

Structure of the heterocyclic cation **IV**.

the mirror plane. In the crystals of compound **IV** (in distinction to **II**), hydrogen bonds are absent.

A comparison of the geometries of the NH derivative **II** and the homologous NCH$_3$ derivative **IV** reveals that introduction of the methyl group results only in a slight lengthening of the C(4)–N(3) bond in compound **IV** as compared to **II**. The lengths of all the other skeleton bonds in **II** and **IV** are virtually identical. This result supports our conclusion [2] that compound **II** actually exists in the NH tautomeric form, since its structure and geometry coincide with those of the NCH$_3$ derivative **IV**.

Cations **II** and **IV** can be represented by three resonance structures—*A*, *B*, and *C* (R = H or CH$_3$)
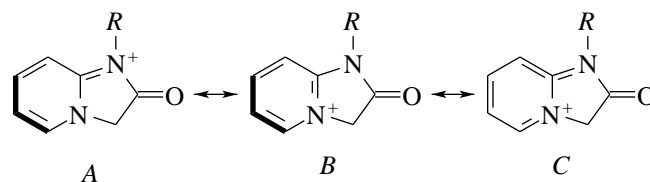
Consider the C(6)C(7)C(8) fragment (distinguished by heavy lines in structures *A* and *B*). In **II** and **IV**, the mean C(6)–C(7) bond length is 1.381(4) Å, whereas the length of the adjacent C(7)–C(8) bond is 1.362(4) Å. These bond lengths in the C(6)C(7)C(8) fragment are consistent with resonance structures *A* and *B*, but contradict structure *C*, which implies the reverse ratio of the bond lengths: the C(6)–C(7) bond should be shorter than the C(7)–C(8) bond. Of the two structures *A* and *B*, the latter structure is preferential for **IV**, since, bearing the positive charge, the nitrogen atom of the pyridine fragment should attract the bromide anion; that is, the N(9)···Br distance should be shorter than the N(3)···Br distance, which is the case in crystal structure **IV** [3.833(1) and 5.112(2) Å, respectively]. In structure **II** [2], the chloride anion approaches the N(3) atom rather than the N(9) atom [the shortest distances, other than hydrogen bonds, are N(3)···Cl = 3.045(2) Å and N(9)···Cl = 5.025(2) Å], indicating that structure *A* is preferential for **II**. A partial fixation of the geometry of the pyridine fragment results in a limited number of centers at which the positive charge can be delocalized. Apparently, this delocalization predominantly occurs in the N(9)C(4)N(3) fragment of the imidazole ring and only slightly affects the pyridine ring.

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