Russian Journal of Coordination Chemistry, Vol. 26, No. 9, 2000, pp. 670–676. Translated from Koordinatsionnaya Khimiya, Vol. 26, No. 9, 2000, pp. 714–720.

1,3-Di(2-oxopyridyl-1)acetone and Its Hydroperchlorate: Formation in the Hydrolysis of Annelated Munchnone and X-Ray Diffraction Study

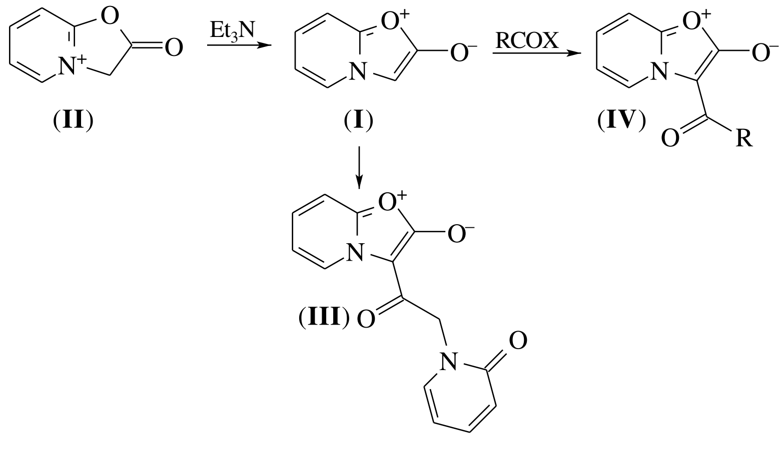
V. B. Rybakov, S. G. Zhukov, K. Yu. Pasichnichenko, and E. V. Babaev

Moscow State University, Vorob'evy gory, Moscow, 119899 Russia

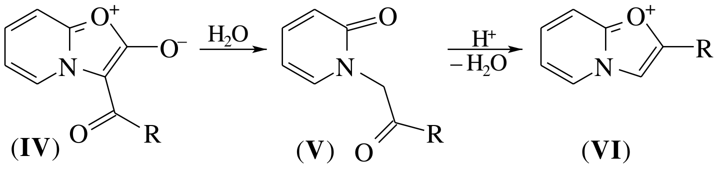
Received April 13, 2000

Abstract—1,3-Di(2-oxopyridyl-1)acetone is formed in the hydrolysis of mesoionic anhydro-3-[(1,2-dihydro-2-oxopyridyl-1)acetyl]-2-hydroxyoxazolo[3,2-a]pyridinium hydroxide; attempts to perform cyclization of the obtained compound by acting with sulfuric and perchloric acids only yield the protonated product. The structures of some compounds are established by X-ray diffraction analysis.

Heterocyclic system **I**, containing coupled pyridine and oxazole fragments, has a mesoionic nature and is classified as a condensed munchnone [1]. The first members of this family were synthesized as early as in 1959 [2], and their chemical properties were investigated in detail in [3]. Unsubstituted munchnone **I**, formed in the deprotonation of salts **II**, is unstable and readily dimerizes to give compound **III**. Introduction of the acyl group remarkably stabilizes the mesoionic system; therefore, the acyl derivatives with general formula **IV** (to which, in particular, dimer **III** should be referred) are quite stable.



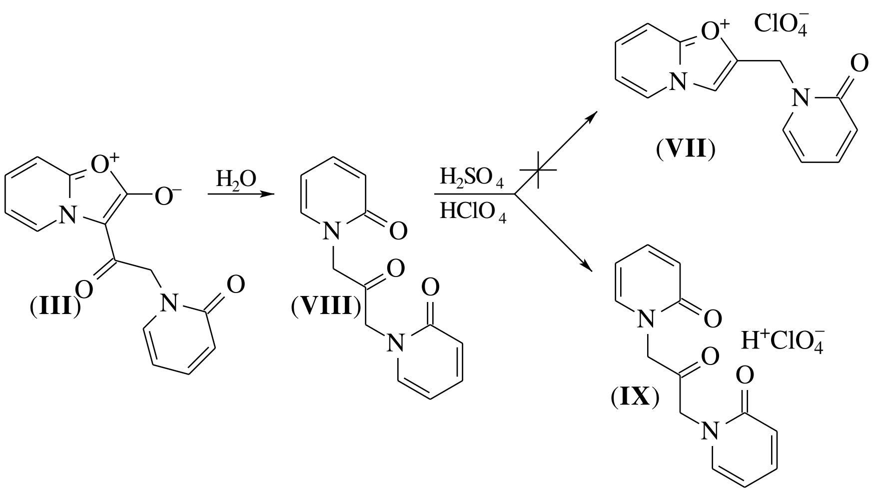
Our interest in the chemistry of this class of mesoionic heterocycles is due to their structural properties and the possibility of using them in heterocyclic synthesis. Earlier [4], on the basis of the X-ray powder diffraction data, we proved the unusual ilide structure of the molecule **IV** (R = Ph). In addition, we discovered a new type of recyclization of mesoionic compounds **IV** resulting in the formation of oxazolopyridinium salts **VI** [5]:



Such a recyclization proceeds via the stage of formation of pyridones **V**, which can be separated as intermediates; this transformation can be run without their separation (a *one-pot* process).

Dimer **III** can be formally classified as the acyl derivative **IV**, and, therefore, one can expect that mesoionic system **III** will undergo recyclization to produce cationic heterocycle **VII**. In this paper, the data obtained in our attempt to carry out the hydrolytic cleavage and recyclization of mesoionic compound **III** are reported.

We found that the hydrolytsis of molecule **III** gives 1.3-di(2-oxopyridyl-1)acetone (**VIII**) with a high yield. Compound **VIII** was described and previously synthesized by another method [6]. The constants of the compound, which we obtained, agree with the literature data. The structure of the compound was confirmed by X-ray diffraction analysis.



A common procedure used for cyclization of pyridones **V** into cations **VI** consists in their subsequent treatment with sulfuric and perchloric acids. In attempts to convert pyridone **VIII** into salt **VII** through such a cyclocondensation under similar conditions, we obtained an ionic compound, whose structure, however, did not correspond to that of the expected perchlorate **VII** (the expected downfield singlet of oxazole fragment was lacking in the ^1H NMR spectrum of the obtained compound). The ^1H NMR spectrum of compound **VII** resembles that of starting compound **VIII**. According to X-ray diffraction data, the obtained compound has structure **IX**. A systematic search for the above-mentioned structures and their analogs in the Cambridge Crystallographic Database (version 5.18 1999) [7] was unsuccessful, which triggered their study by X-ray diffraction analysis.

EXPERIMENTAL

Synthesis and spectral data. Compound **III** ($C_{14}H_{10}N_2O_4$) was obtained from perchlorate **I** using the procedure reported in [3]. The yield was 65%.

^1H NMR spectrum (DMSO-d_6; δ, ppm): 7.74, d (OC–C–CH–C); 8.06, dd (N–C–C–CH–C–CO); 7.43, dd (N–C–CH–C); 6.21, d (N–CH–C); 5.15, s (CO–CH_2); 7.59, m (N–CH–C + N–CO–C–CH); 6.39, d (N–CO–CH–C); 6.21, dd (N–C–CH–C).

The ^1H NMR spectrum of compound **III** in trifluoroacetic acid was described in [3].

Synthesis of compound VIII. Compound **III** (1.58 g, 5.9 mmol) was boiled in 10 ml of H_2O for several hours until it completely dissolved. After the transparent solution was cooled, compound **VIII** precipitated and was filtered off, washed with 5 ml of ice-cooled water, and dried. The yield of compound **VIII** ($C_{13}H_{12}N_2O_3$) was 1.2 g (83%); T_m = 222°C (223°C [6]).

The ^1H NMR spectrum (DMSO-d_6; δ, ppm): 7.55, dd (N–CH–C); 6.24, m (NC–CH–C); 7.42, m (OC–C–CH); 6.40, d (OC–CH–C); 4.93, s (CO–CH_2–N) or 7.55, dd (6-CH + 15-CH); 6.24, m (5-CH + 14-CH); 7.42, m (4-CH + 13-CH); 6.40, d (3-CH + 12-CH); 4.93, s (7-CH + 9-CH).

IR spectrum (ν, cm^{-1}): 1665 ν(NC=O), 1747 ν(CC=O).

Synthesis of compound IX. Compound **VIII** (0.417 g, 1.7 mmol) was dissolved with stirring in concentrated H_2SO_4 (4.3 g) and allowed to stand overnight. The obtained solution was filtered off through a glass porous plate; the filtrate was diluted with 100 ml of cold water, and 1.5 ml of 70% $HClO_4$ were added to it. The precipitated white needle crystals of compound **IX** were filtered off, washed with ice-cold water (2 × 5 ml), and dried. The yield of compound **IX** ($C_{13}H_{13}N_2O_3^+ \cdot ClO_4^-$) was 0.416 g (51%); T_m = 278°C.

The ^1H NMR spectrum (DMSO-d_6, δ, ppm): 7.55, dd (N–CH–C); 6.24, m (NC–CH–C); 7.44, m (OC–C–CH); 6.40, d (OC–CH–C); 4.93, s (CO–CH_2–H) or 7.55, dd (6-CH + 15-CH); 6.24, m (5-CH + 14-CH); 7.44, m (4-CH + 13-CH); 6.40, d (3-CH + 12-CH); 4.93, s (7-CH + 9-CH).

Table 1. Crystallographic data and summary of data collection for compounds **VIII** and **IX**

Parameter	**VIII**	**IX**
Empirical formula	$C_{13}H_{12}N_2O_3$	$C_{13}H_{13}N_2O_3^+ \cdot ClO_4^-$
Crystal system	Monoclinic	Monoclinic
a, Å	9.167(4)	11.3328(19)
b, Å	12.924(3)	12.4738(12)
c, Å	10.372(3)	10.6234(18)
β, deg	102.38(3)	94.65(1)
Space group	$P2_1/a$	$P2_1/c$
Z	4	4
V, Å^3	1200.2(7)	1496.8(4)
Formula weight	244.25	343.70
ρ (calcd), g/cm^3	1.352	1.525
μ, mm^{-1}	0.098	0.294
$\theta_{min}/\theta_{max}$, deg	2.55/25.97	1.80/26.97
Experimental range	$-11 \le h \le 11$ $-6 \le k\ 15$ $-5 \le l \le 12$	$-14 \le h \le 14$ $0 \le k \le 15$ $0 \le l \le 13$
F_{000}	512	708
Total number of reflections	2578	3416
Number of reflections with $I > 2\sigma(I)$	2304	3238
Number of refined parameters	212	257
GOF (F^2)	0.973	1.055
R_1 ($I > 2\sigma(I)$)	0.0708	0.0500
wR_2($I > 2\sigma(I)$)	0.1479	0.1035
R_1 (all data)	0.1885	0.0960
wR_2 (all data)	0.2057	0.1213
$\Delta\rho_{max}$, e/A^3	0.289	0.359
$\Delta\rho_{min}$, e/A^3	−0.213	−0.259

IR spectrum (ν, cm^{-1}): 1662 ν(NC=O), 1760 ν(CC=O).

The ^{1}H NMR spectra were recorded on a Bruker AM-400 instrument; and IR spectra, on a UR-20 spectrophotometer (suspension in mineral oil; samples of **IX** as pallets with CaF_2).

X-ray diffraction analysis of compounds **VIII** and **IX** was carried out using a CAD-4 automated diffractometer [8] (MoK_α radiation, graphite monochromator, ω scan mode). The unit cell parameters and crystal systems of **VIII** and **IX** were determined and refined from 24 reflections over the θ angle interval of 12°–13°. Diffraction data were preliminarily processed using the WinGX-98 program package [9].

The coordinates of non-hydrogen atoms in both compounds were determined by the direct method and refined by the full-matrix least-squares method (SHELX97 [10]) in anisotropic approximation. Hydrogen atoms were located from difference synthesis and refined by the least-squares method in isotropic approximation. An attempt to locate the proton in compound **IX** was a failure.

The crystallographic data and the details of data collection for compounds **VIII** and **IX** are summarized in Table 1; coordinates of atoms and their thermal parameters U_{equiv}/U_{iso} are given in Table 2; and bond lengths and angles, in Table 3 (C–H distances and HCH bond angles are not indicated). The selected torsion angles in the molecules are listed in Table 4. The geometry of the atoms in the molecules and their numbering are shown in Figs. 1 and 2. The schematic representation of molecules was obtained using the ORTEP-3 program [11].

Table 2. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters U_{eq}/U_{iso} ($\times 10^3$) for structures **VIII** and **IX**

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}, Å^2	*x*	*y*	*z*	U_{eq}/U_{iso}, Å^2
	VIII				**IX**			
N(1)	−878(1)	9393(1)	1389(1)	51(1)	7377(1)	9940(1)	−529(1)	43(1)
C(2)	−2349(2)	9539(1)	677(2)	54(1)	6347(1)	10377(1)	−1018(1)	42(1)
O(2)	−3163(1)	8782(1)	367(1)	84(1)	5950(1)	10033(1)	−2115(1)	58(1)
C(3)	−2733(2)	10595(1)	392(2)	63(1)	5795(1)	11140(1)	−304(1)	55(1)
C(4)	−1802(2)	11370(1)	832(2)	70(1)	6287(1)	11419(1)	849(1)	69(1)
C(5)	−387(2)	11177(1)	1597(2)	76(1)	7347(1)	10977(1)	1317(1)	73(1)
C(6)	42(2)	10200(1)	1856(2)	65(1)	7868(1)	10242(1)	631(1)	61(1)
C(7)	−353(2)	8346(1)	1689(2)	55(1)	7913(1)	9082(1)	−1217(1)	49(1)
C(8)	−431(2)	8006(1)	3045(2)	48(1)	7483(1)	7996(1)	−811(1)	40(1)
O(8)	−989(1)	8505(1)	3781(1)	62(1)	6930(1)	7890(1)	100(1)	56(1)
C(9)	265(2)	6949(1)	3404(2)	61(1)	7821(1)	7072(1)	−1603(1)	46(1)
N(10)	6(1)	6562(1)	4626(1)	46(1)	7583(1)	6049(1)	−1019(1)	39(1)
C(11)	−1399(2)	6186(1)	4588(2)	65(1)	6506(1)	5577(1)	−1258(1)	46(1)
O(11)	−2326(1)	6207(1)	3563(2)	99(1)	5755(1)	6064(1)	−2012(1)	65(1)
C(12)	−1533(2)	5817(2)	5980(2)	93(1)	6337(1)	4598(1)	−654(1)	61(1)
C(13)	−338(3)	5907(2)	6972(2)	91(1)	7179(1)	4178(1)	176(1)	66(1)
C(14)	984(3)	6292(2)	6855(2)	106(1)	8243(1)	4711(1)	427(1)	64(1)
C(15)	1140(2)	6610(2)	5702(2)	81(1)	8427(1)	5628(1)	−170(1)	52(1)
H(3)	−3760(15)	10756(10)	−146(12)	49(4)	5102(10)	11414(9)	−614(10)	59(3)
H(4)	−2145(15)	12051(10)	641(12)	53(4)	5963(13)	11839(12)	1278(14)	98(5)
H(5)	316(19)	11683(13)	2027(15)	91(6)	7704(13)	11161(11)	2010(13)	91(5)
H(6)	848(18)	10020(12)	2309(15)	76(5)	8498(12)	9921(10)	872(12)	80(4)
H(7*A*)	634(16)	8304(11)	1607(13)	59(4)	7780(9)	9201(9)	−2084(10)	53(3)
H(7*B*)	−982(16)	7899(11)	1101(12)	56(4)	8734(10)	9107(10)	−982(11)	60(3)
H(9*A*)	−197(18)	6422(12)	2610(14)	77(5)	7352(11)	7114(9)	−2455(11)	66(4)
H(9*B*)	1200(20)	7035(14)	3447(15)	90(6)	8656(10)	7133(9)	−1723(10)	60(3)
H(12)	−2348(13)	5591(8)	5294(10)	18(3)	5663(11)	4312(10)	−814(11)	69(4)
H(13)	−300(20)	5700(15)	7901(18)	117(7)	7047(11)	3573(11)	567(12)	77(4)
H(14)	2060(20)	6392(15)	7683(18)	128(7)	8838(11)	4482(11)	944(12)	78(4)
H(15)	1990(30)	6870(18)	5520(20)	146(8)	9110(9)	6023(8)	−61(10)	51(3)
Cl(1)					595(1)	7875(1)	1433(1)	43(1)
O(1*a*)					119(1)	6958(1)	2007(1)	61(1)
O(1*b*)					1845(1)	7893(1)	1672(1)	74(1)
O(1*c*)					112(1)	8822(1)	1949(1)	82(1)
O(1*d*)					283(1)	7845(1)	111(1)	81(1)

For convenience, the geometrical fragments of molecules have a common numbering of atoms.

RESULTS AND DISCUSSION

An analysis of the geometry and structures of related compounds **VIII** and **IX** allows one to draw an indirect conclusion that the proton in cation **IX** is most likely bound to the amide oxygens O(2) and O(11) rather than to the ketone oxygen O(8) because the C(8)–O(8) distance in both structures is virtually the same (1.195(2) Å in molecule **VIII** and 1.203(1) Å in cation **IX**), whereas the C(2)–O(2) and C(11)–O(11) distances markedly increase when changing over from **VIII** to **IX**: from 1.231(2) to 1.288(1) Å and from 1.211(2) to 1.275(1) Å, respectively. This change in the

Table 3. Bond lengths and angles in structures **VIII** and **IX**

Bond	*d*, Å		Angle	ω, deg	
	VIII	**IX**		**VIII**	**IX**
Cl(1)–O(1*b*)		1.4184(9)	O(1*b*)Cl(1)O(1*c*)		109.05(6)
Cl(1)–O(1*d*)		1.4205(9)	O(1*d*)Cl(1)O(1*c*)		109.17(6)
Cl(1)–O(1*a*)		1.4234(9)	O(1*a*)Cl(1)O(1*c*)		109.22(6)
Cl(1)–O(1*c*)		1.4295(9)	C(2)N(1)C(6)	122.3(1)	120.8(1)
N(1)–C(2)	1.405(2)	1.354(1)	C(2)N(1)C(7)	118.5(1)	119.0(1)
N(1)–C(6)	1.363(2)	1.364(2)	C(6)N(1)C(7)	119.2(1)	120.0(1)
N(1)–C(7)	1.447(2)	1.455(2)	O(2)C(2)N(1)	119.3(1)	116.1(1)
C(2)–O(2)	1.231(2)	1.288(1)	O(2)C(2)C(3)	126.8(2)	125.4(1)
C(2)–C(3)	1.425(2)	1.397(2)	N(1)C(2)C(3)	113.9(1)	118.4(1)
C(3)–C(4)	1.332(2)	1.350(2)	C(4)C(3)C(2)	122.5(2)	119.9(1)
C(4)–C(5)	1.391(2)	1.378(2)	C(3)C(4)C(5)	120.8(2)	120.5(1)
C(5)–C(6)	1.332(2)	1.338(2)	C(6)C(5)C(4)	119.0(2)	119.3(1)
C(7)–C(8)	1.490(2)	1.514(2)	C(5)C(6)N(1)	121.3(2)	121.0(1)
C(8)–O(8)	1.195(2)	1.203(1)	N(1)C(7)C(8)	113.4(1)	111.0(1)
C(8)–C(9)	1.520(2)	1.495(2)	O(8)C(8)C(9)	122.9(2)	122.9(1)
C(9)–N(10)	1.429(2)	1.454(1)	O(8)C(8)C(7)	123.9(1)	121.9(1)
N(10)–C(11)	1.369(2)	1.360(1)	C(9)C(8)C(7)	113.2(1)	115.3(1)
N(10)–C(15)	1.353(2)	1.366(1)	N(10)C(9)C(8)	113.0(1)	111.8(1)
C(11)–O(11)	1.211(2)	1.275(1)	C(11)N(10)C(15)	126.3(2)	121.7(1)
C(11)–C(12)	1.551(3)	1.400(2)	C(11)N(10)C(9)	115.6(1)	119.7(1)
C(12)–C(13)	1.337(3)	1.350(2)	C(15)N(10)C(9)	118.1(2)	118.4(1)
C(13)–C(14)	1.339(4)	1.385(2)	O(11)C(11)N(10)	119.8(2)	116.9(1)
C(14)–C(15)	1.302(3)	1.332(2)	O(11)C(11)C(12)	130.1(2)	126.5(1)
Angle	ω, deg		N(10)C(11)C(12)	110.2(1)	116.5(1)
	VIII	**IX**	C(13)C(12)C(11)	118.2(2)	121.5(1)
O(1*b*)Cl(1)O(1*d*)		110.04(6)	C(12)C(13)C(14)	124.9(2)	119.9(1)
O(1*b*)Cl(1)O(1*a*)		110.10(5)	C(15)C(14)C(13)	118.7(2)	119.2(1)
O(1*d*)Cl(1)O(1*a*)		109.23(6)	C(14)C(15)N(10)	121.8(2)	121.1(1)

Table 4. Selected torsion angles in structures **VIII** and **IX**

Angle	φ, deg	
	VIII	**IX**
C(7)–N(1)–C(2)–O(2)	2.1(3)	−4.0(1)
C(2)–N(1)–C(7)–C(8)	−97.8(2)	−90.6(1)
N(1)–C(7)–C(8)–O(8)	6.3(2)	−11.0(1)
O(8)–C(8)–C(9)–N(10)	7.8(2)	−9.8(1)
C(8)–C(9)–N(10)–C(11)	75.9(2)	89.2(1)
C(9)–N(10)–C(11)–O(11)	−0.4(3)	0.9(2)

NC–O bond lengths corresponds to the decrease in their multiplicity upon protonaton of the O atom and agrees with the general trend in the changing of the length for other bonds in the pyridine rings when going over from the neutral molecule to the cation. The pyridone fragments of the nonprotonated molecule **VIII** are characterized by alternating ordinary and double bonds. Obviously, cation **IX** with protonated amide oxygen atom can be represented not only by the resonance structure with alternating bond lengths (**A**) but also by the structure with equalized bond lengths in the six-membered ring (**B**). Such a change (elongation

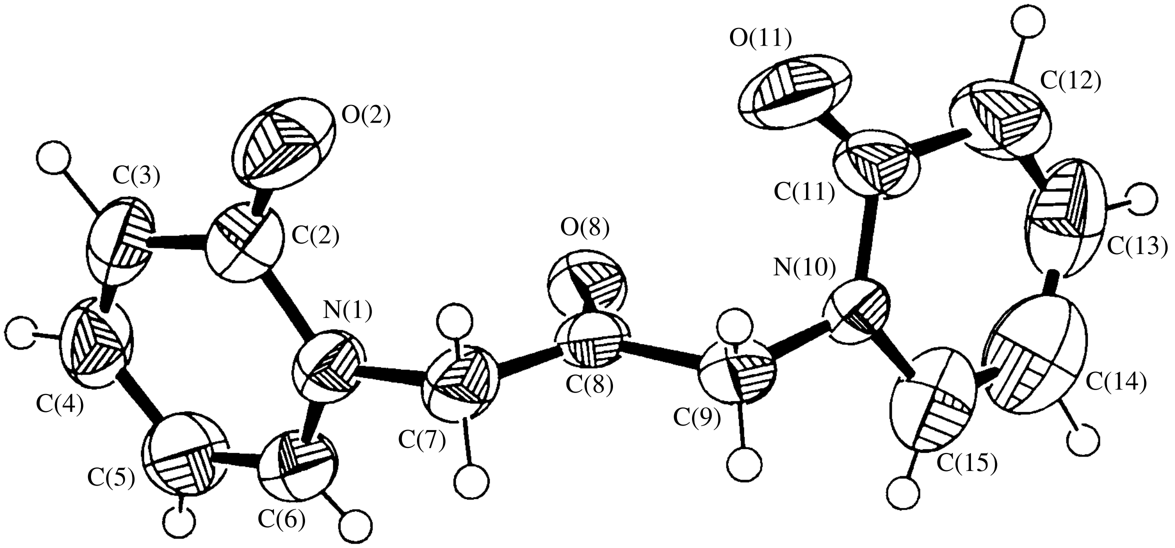


Fig. 1. Structure, numeration, and thermal vibrations of atoms (50%) in compound **VIII**.

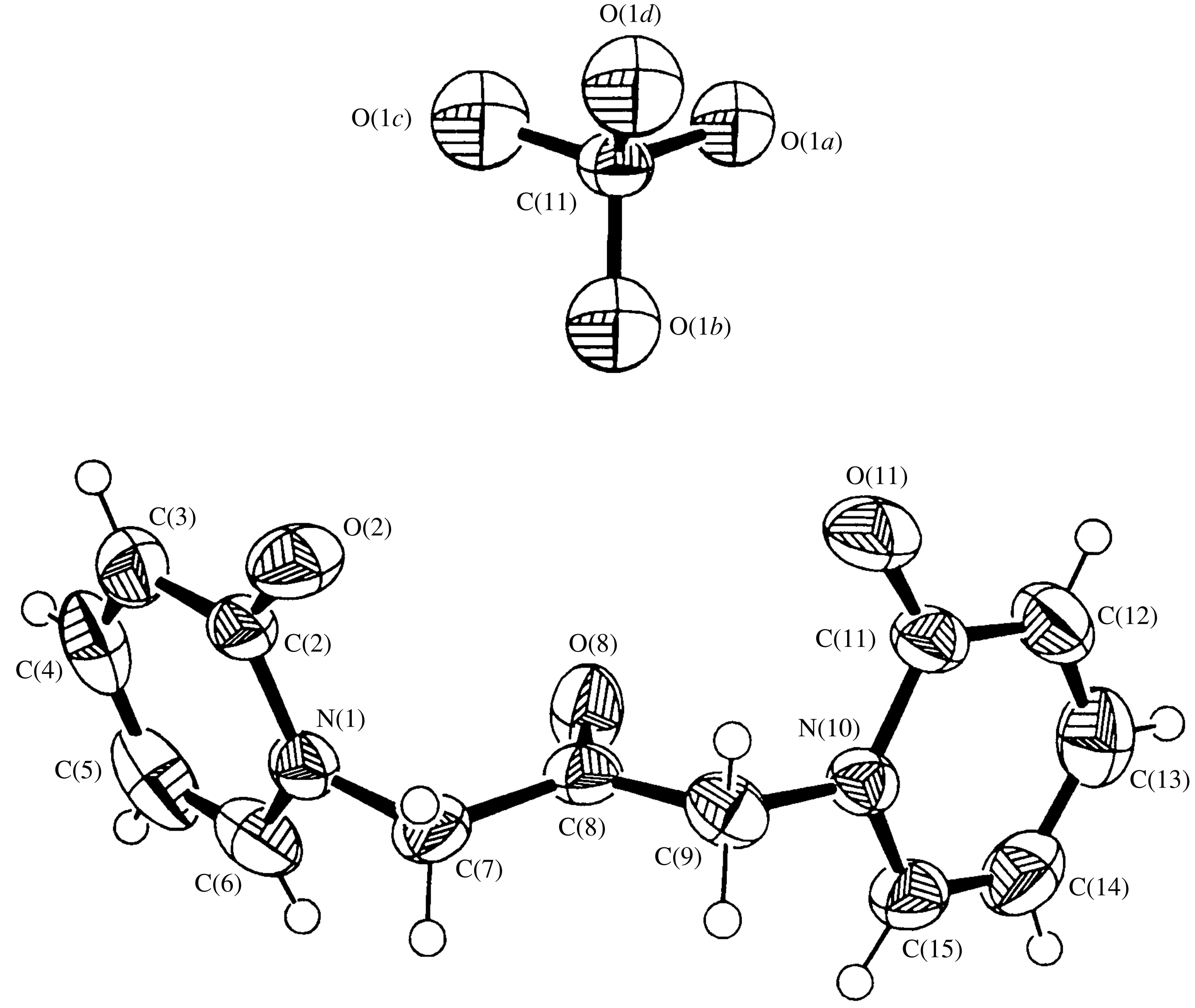
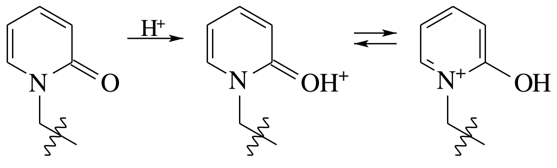


Fig. 2. Structure, numeration, and thermal vibrations of atoms (50%) in compound **IX**.

of double bonds and shortening of ordinary bonds) is really observed in going over from molecule **VIII** to cation **IX**:



(**A**) (**B**)

This pattern of protonation could be experimentally confirmed through the objective location of the proton of one of the amide oxygen atoms. However, it was experimentally established that the proton is delocalized between two positions (O(2) and O(11) atoms), and it was difficult to determine its location because of a small scattering factor. Accurate determination of the proton position could be performed by using the method of neutron diffraction on deuterium nuclei.

One more indirect piece of evidence supporting the protonation of the amide oxygen atoms O(2) and O(11) in structure **IX** is the decrease of the O(2)C(2)N(1) bond angle from 119.3(1)° to 116.1(1)° and the decrease of the O(11)C(11)N(10) bond angle from 119.8(2)° to 116.9(1)°, with the O(8)C(8)C(7) and O(8)C(8)C(9) bond angles remaining virtually unchanged.

The principal difference between the conformation of the O(2)–C(2)–N(1)–C(7)–C(8)–O(8) and O(11)–C(11)–N(10)–C(9)–C(8)–O(8) structural fragments in compounds **VIII** and **IX** cannot be established from the torsion angles (Table 4) because a slight difference can be due to the effect of a balky tetrahedral ClO_4^- anion which "penetrates" into the space between oxygens O(2)···O(8)···O(11) in the organic cation. In this case, the anion slightly turns the heterocycle planes, thus increasing the dihedral angles between them: from 66.75(8)° in molecule **VIII** to 79.35(4)° in cation **IX**.

ACNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 99-03-33076 and 99-07-90133 (for purchasing the license to use the Cambridge Crystallographic Database).

REFERENCES

1. Newton, C.G. and Ramsden, C.A., *Tetrahedron*, 1982, vol. 38, p. 2965.
2. Lawson, A. and Miles, D.H., *J. Chem. Soc.*, 1959, p. 2865.
3. Boyd, G.V. and Wright, P.H., *J. Chem. Soc., Sect. C.*, 1970, p. 1486.
4. Zhukov, S.G., Babaev, E.V., Chernyshev, V.V., *et al.*, *Z. Kristallogr.*, 2000, vol. 215, p. 306.
5. Babaev, E.V. and Orlova, I.A., *Khim. Geterotsikl. Soedin.*, 1997, no. 4, p. 569.
6. Winterfeld, K. and Michael, H., *Chem. Ber.*, 1960, vol. 93, p. 61.
7. Allen, F.H. and Kennard, O., *Chem. Des. Autom. News*, 1993, vol. 8, p. 31.
8. *Enraf-Nonius CAD-4 Software. Version 5.0 Enraf-Nonius*, Delft, the Netherlands, 1989.
9. Farrugia, L.J., *WinGX-98. X-Ray Crystallographic Programs for Windows*, Univ. of Glasgow, UK, 1998.
10. Sheldrick, G.M., *SHELX97. Program for the Solution and Refinement of Crystal Structures*, Univ. of Göttingen, Germany, 1997.
11. Bernett, M.N. and Jahnson, C.K., *ORTEP-3. Report ORNL-6895*, Oak Ridge National Laboratory, 1996.