SYNTHESIS AND STRUCTURE OF NEW N-ALKOXY-N-(1-PYRIDINIUM)UREA CHLORIDES

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New N-[1-(4-amino)pyridinium]-N-methoxyurea chloride, N-[1-(2-amino)pyridinium]-N-methoxyurea chloride and their analogs were synthesized by N-alkoxy-N-chloroureas reaction with the proper pyridines in acetonitrile or ether solution by improved procedure. XRD study of N-[1-(4-amino)pyridinium]-N-methoxyurea and N-[1-(2-amino)pyridinium]-N-methoxyurea revealed the elongation of N-N^+ bonds and some shortening of MeO-N bonds, qunonoid deformation of pyridine rings compare to it unsubstituted analog. The substantial pyramidality of central nitrogen atom in O-N-N^+ moiety and N-C carbamoyl bonds difference were established too. The structure summary of N-alkoxy-N-(1-pyridinium)ureas salts and other derivatives of 1-(N-alkoxyamino)pyridinium salts has been done.

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Introduction

1-(N-alkoxyamino)pyridinium salts were first synthesized by the interaction of N-chloro-N-methoxy-N-tert-alkylamines with pyridine.[1] The hygroscopic 1-(N-alkoxyamino)pyridinum chlorides are easily converted in the unhygroscopic perchlorates. These compounds may be regarded as a kind of N-alkoxyhydrazines. Usually such N-alkoxyhydrazines are labile due to destabilization by $n_{N'} \rightarrow \sigma^*_{N\text{-}O(R)}$ orbital interaction or anomeric effect.[2] But the 1-(N-alkoxyamino)pyridinum chlorides are relatively stable compounds due to impossibility of the orbital interaction caused by the absence of lone electron pair (LP) on nitrogen N'.

XRD study of the structure of perchlorate of 1-(N-methoxy-N-tert.alkyl)aminopyridinium[3] revealed a high degree of pyramidality of central nitrogen atom in the O−N−N^+ geminal system. The sum of bond angles centered on this nitrogen atom (∑β) is 322.8°. But the pyramidality of O−N−O central nitrogen atom in acyclic N,N-dialkoxyamine and in perhydro-1,3,2-dioxazepine is somewhat higher.[4] However, it was found by an XRD study[5] that in 1-(N-methoxy-N-tert.alkyl)amino-4-dimethylamino-pyridinium perchlorate, LP of central nitrogen is situated in pyridine plane (TaLPPy is 18°), its ∑β is 325.7°, the N−N^+ (1.445(2) Å) is shorter, and the N−OMe bond (1.425(2) Å) is longer. These structure changes reflect decreasing of action of $n_{O(Me)} \rightarrow \sigma^*_{N\text{-}N+}$ anomeric effect and stabilization of N−N^+ bond, respectively. These data are consistent with observed "quinonoid" deformation of pyridine ring in this compound. This phenomenon causes some difference in chemical properties of these classes of compounds. But reported structural data of N-alkoxy-N-(1-pyridinium)urea salts[5,6] are not sufficient for the complete understanding of this novel kind of anomeric urea salts. So, this work was undertaken to synthesize new N-alkoxy-N-(1-pyridinium)urea salts and to study of their structure.

Experimentals

^{1}H and ^{13}C NMR spectra were recorded on Varian VXP-300 spectrometer (300 and 75 MHz, respectively) and Varian JEMINI 2000 (400 and 100 MHz, respectively). Solvents were DMSO and CD_3OD with TMS as internal standard and expressed as δ ppm. IR spectra were recorded on UR-20 in KBr pellets. Mass spectra were recorded on VG 70-70EQ mass spectrometer in fast atom bombardment (FAB) mode. XRD structural study was performed on Xcalibur 3 automatic four-circle diffractometer (MoKα-radiation, graphite monochromator, Sapphire-3 CCD-detector, ω-scanning). Elemental analysis for C, H and N was performed on Carlo Erba analyzer.

4-Dimethylaminopyridine (DMAP), 4-aminopyridine and 2-aminopyridine were sublimated under vacuum (3 Torr). The solvents were purified and dried according to standard procedures.

N-[1-(4-Dimethylamino)pyridinium]-N-methoxyurea chloride (1)

A solution of DMAP (327 mg, 2.674 mmol) in Et_2O (30 mL) was added to a solution of N-chloro-N-methoxyurea (**2**)[7] (350 mg, 2.868 mmol) in Et_2O (5 mL) at -10 °C, the reaction mixture was maintained for 10 min at -10 °C, then 70 h at 5°C. The white precipitate was filtered off, washed with Et_2O (10 mL), then dried for 2 h under

vacuum (2 Torr), yielding **1** as white crystals (607 mg, 92 %). m.p. 168–169 °C (decomp.). which was identified by ^{1}H NMR spectroscopy and mass spectrometry.[5] ^{1}H NMR (300 MHz, CD_3OD) δ = 3.35 (6H, s, NMe_2), 3.88 (3H, s, NOMe) 7.07 (2H, d, ^3J = 7.8, H Py), 8.30 (2H, d, ^3J = 7.8, H Py). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 3.28 (6H, s, NMe_2), 3.78 (3H, s, NOMe), 7.06 (2H, d, ^3J = 7.8, H Py), 7.96 (2H, br.s, $C(O)NH_2$), 8.44 (2H, d, ^3J = 7.8, H Py). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 40.4 (NMe_2), 63.1 (NOMe), 107.5, 142.1, 156.6, 157.0 (C-2, C-3, C-4, C-5, C-6 Py), 255.8 (C=O). IR 1628 (C=N), 1725 (C=O), 3230 (N–H), 3300 (N–H) cm^{-1}. MS, *m/z* (%) = 211 [M+]$^+$ (100), 180 (27), 168 (8), 122 (14).

N-[1-(4-Amino)pyridinium]-N-methoxyurea chloride (3)

A solution of 4-aminopyridine (186 mg, 1.976 mmol) in MeCN (16 mL) was added to a solution of **2** (242 mg, 1.947 mmol) in MeCN (5 mL) at -30 °C. The reaction mixture was heated to 18 °C during 18 h, maintained for 2 h at 18°C, the precipitate was filtered off, washed with MeCN (4 mL), then CH_2Cl_2 (5 mL), dried under vacuum (2 mmHg), yielding **3** as yellowish-white hygroscopic crystals (408 mg, 95 %). m.p. 124–125 °C (decomp.)(i-PrOH). ^{1}H NMR (300 MHz, CD_3OD) δ = 3.88 (3H, s, NOMe), 6.93 (2H, d, ^3J = 7.5, H Py), 8.25 (d, 2H, ^3J = 7.5, H Py). ^{13}C NMR (75 MHz, CD_3OD) δ = 64.2 (NOMe), 110.7 (C-3, C-5 Py), 144.5 (C-2, C-6 Py), 162.5 (C-4 Py), 232.1 (C=O). IR 1660 (C=N), 1747 (C=O), 3310 ((N–H)$_2$), 3380 ((N–H) cm^{-1}. MS, *m/z* (%) = 183 M$^+$ (100). Anal. Calcd. for $C_7H_{11}ClN_4O_2$: C 38.45, H 5.07, N 25.62. Found: C 38.29, H 5.32, N 25.46.

N-[1-(2-Amino)pyridinium]-N-methoxyurea chloride (4).

A solution of 2-aminopyridine (194 mg, 2.055 mmol) in MeCN (6 mL) was added to a solution of **2** (253 mg, 2.035 mmol) in MeCN (6 mL) at -22 °C, the reaction mixture was heated to 9 °C for 16 h, maintained for 100 h at 12 °C, the white precipitate was filtered off, washed by benzene (4 mL), dried for 2 h under vacuum (5 Tor), yielding **4** as colourless hygroscopic crystals (288 mg, 65 %). m.p. 142–144 °C (decomp.)(i-PrOH). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ, = 3.86 (3H, s, NOMe), 6.84 (1H, t, ^3J = 6.8 H Py), 7.40 (1H, d, ^3J = 8.4, H, Py), 7.83 (1H, t, ^3J = 8.0, H Py), 7.93 (1H, d, ^3J = 8.0 H Py), 7.96 (2H, s, $C(O)NH_2$), 9.04 (1H, s, NH_2 Py), 10.00 (1H, s, NH_2 Py). ^{1}H NMR (300MHz, CD_3OD) δ = 3.94 (3H, s, NOMe), 6.95 (1H, t, ^3J = 6.9 H Py), 7.17 (1H, d, ^3J = 9.0 H Py), 7.91 (1H, t, ^3J = 7.8 H Py), 8.01 (1H, d, ^3J = 7.2 H Py). ^{13}C NMR (75 MHz, CD_3OD) δ = 64.6 (NOMe), 115.3, 116.5, 137.6, 144.9 (C-3, C-4, C-5, C-6 Py), 158.0 (C-4 Py), 232.1 (C=O). MS, *m/z* (%): 183 M$^+$ (100). Anal. Calcd. for $C_7H_{11}ClN_4O_2 \cdot H_2O$: C 35.53, H 5.54, N 23.67. Found: C 35.44, H 5.65, N 23.46.

XRD structural study of compounds 3 and 4

Crystals, suitable for X-ray structural analysis, were grown from a solution in i-PrOH–MeOH mixture of **3** and from a solution of **4** in i-PrOH. The structure was solved by conjugate gradient technique with the SHELXD[8] software and refined by full matrix method of least squares in anisotropic approximation for non-hydrogen atoms SHELXL[8] software. The atomic coordinates, molecular geometry parameters, and crystallographic data of compounds **3** and **4** have been deposited in the Cambridge Crystallographic Data Center (deposits CCDC 1457353 (**3**) and 1457354 (**4**)).

N-[1-(4-Methyl)pyridinium]-N-methoxyurea chloride (5)

A solution of 4-methylpyridine (170 mg, 1.825 mmol) in Et_2O (4 mL) was added to a solution of **2** (167 mg, 1.341 mmol) in Et_2O (5 mL) at -34 °C, the reaction mixture was heated to 12 °C for 22 h, the white precipitate was filtered off, washed by Et_2O (6 mL), dried under vacuum (5 Torr) giving **5** as colorless hygroscopic crystals (163 mg, 56 %). m.p. 84–85 °C ($CHCl_3$) (decomp.). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 2.72 (3H, s, Me,; 3.87 (3H, s, NOMe), 8.06 (2H, d, ^3J = 6.5, H Py,), 8.28 (2H, s, $C(O)NH_2$), 9.25 (2H, d, ^3J = 6.5, H Py,). ^{1}H NMR (300 MHz, CD_3OD) δ = 2.80 (3H, s, Me), 3.98 (3H, s, NOMe), 8.14 (2H, d, ^3J = 6.6, H Py,), 9.10 (2H, d, ^3J = 6.6, H Py). ^{13}C NMR (75 MHz, CD_3OD) δ = 22.9 (Me), 65.2 (NOMe), 130.5 (C-3, C-5 Py), 144.5 (C-2, C-6 Py), 158.9 (C-4 Py), 165.6 (C=O). MS *m/z* (%): 182 M$^+$ (100). Anal. Calcd. for $C_8H_{12}ClN_3O_2$: C 44.15, H 5.56, N 19.31. Found: C 43.98, H 5.82, N 18.65.

N-[1-(4-Dimethylamino)pyridinium]-N-ethoxyurea chloride (6a)

A solution of DMAP (92 mg, 0.753 mmol) in Et_2O (20 mL) was added to a solution of N-chloro-N-ethoxyurea (**7a**)[9] (115 mg, 0.828 mmol) in Et_2O (5 mL) at – 23 °C. The reaction mixture was heated to 13 °C for 20 h, maintained for 1 h at 17 °C, the precipitate was filtered off, washed with Et_2O (15 mL), dried under vacuum (3 Torr), giving **6a** as colorless crystals (187 mg, (5 %). M.p. 167–168°C (decomp.). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ = 1.24 (3H, t, ^3J = 6.9, $NOCH_2\underline{Me}$), 3.29 (6H, s, NMe_2), 4.02 (2H, q, ^3J = 6.9, $NO\underline{CH_2}Me$,), 7.04 (2H, d, ^3J = 7.8, H Py), 7.28 (1H, br. s, $C(O)\underline{NH_2}$), 7.99 (1H, br. s, $C(O)NH_2$), 8.48 (2H, d, ^3J = 7.8, H Py). ^{1}H NMR (300 MHz, CD_3OD) δ = 1.32 (3H, t, ^3J = 6.9, $NOCH_2\underline{Me}$), 3.34 (6H, s, NMe_2), 4.12 (2H, q, ^3J = 6.9, $NO\underline{CH_2}Me$,), 7.06 (2H, d, ^3J = 7.8, H Py), 8.30 (2H, d, ^3J = 7.8, H Py). ^{13}C NMR (75 MHz, CD_3OD) δ = 13.8 ($NOCH_2\underline{Me}$), 41.3 (NMe_2), 73.0 ($NOCH_2$), 109.0 (C-3, C-5 Py), 143.2 (C-2, C-6 Py), 159.0; 160.1 (C-4 Py), 232.1 (C=O). MS *m/z* (%) 225 M$^+$ (100), 180 (41), 164 (6). Anal. Calcd. for $C_{10}H_{17}ClN_4O_2$: C 46.07, H 6.57, N 21.49. Found: C 45.97, H 6.71, N 21.23.

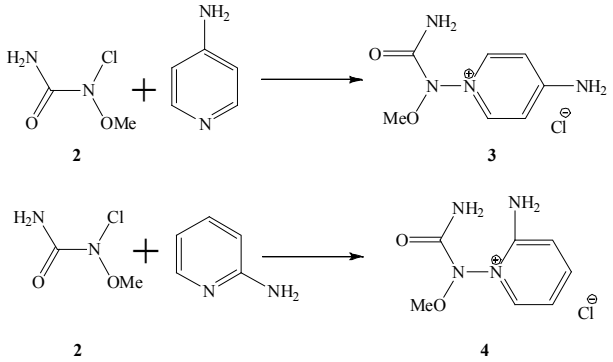
N-[1-(4-Dimethylamino)pyridinium]-N-n-butyloxyurea chloride (6b)

A solution of DMAP (94 mg, 0.769 mmol) in Et_2O (18 mL) was added to a solution of N-n-butyloxy-N-chlorourea (**7b**)[6,10] (135 mg, 0.810 mmol) in Et_2O (5 mL) at 23 °C, The reaction mixture was maintained at 5°C for 22 h, the white precipitate was then filtered off, washed with Et_2O (6 mL), then with CH_2Cl_2 (15 mL), dried under vacuum (3 mmHg), giving **6b** as colorless crystals (141 mg, 63 %). m.p. 56–58 °C (decomp.). ^{1}H NMR (300 MHz, CD_3OD) δ = 0.91 (3H, t ^3J = 7.2, $NOCH_2CH_2CH_2\underline{Me}$), 1.37 (2H, sex, ^3J = 7.2, $NOCH_2CH_2\underline{CH_2}Me$), 1.69 (2H, quint, ^3J = 7.2,

$NOCH_2\underline{CH_2}CH_2Me$), 3.35 (6H, s, NMe_2); 4.09 (2H, t, ^3J = 7.2, $NO\underline{CH_2}CH_2CH_2Me$); 7.07 (2H, d, ^3J = 7.8, H Py), 8.31 (2H, д, ^3J = 7.8, H Py). ^{13}C NMR (75 MHz, CD_3OD, recorded in APT mode) δ = 14.1 ($NO(CH_2)_3\underline{Me}$), 41.0 (NMe_2), 108.9 (C-3, C-5 Py), 141.3 (C-2, C-6 Py), 19.9, 30.8 ($NOCH_2(\underline{CH_2})_2Me$), 77.2 ($NOCH_2$), 159.0 (C-4 Py), 232.2 (C=O). MS *m/z* (%): 253 M^+ (100), 210 (10), 179 (37), 124 (34). Anal. Calcd. for $C_{12}H_{21}ClN_4O_2$: C 49.91, H 7.33, N 19.40. Found: C 49.86, H 7.55, N 19.25.

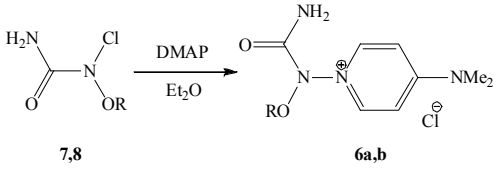
Results and Discussion

We have synthesized novel amino-substituted pyridinium derivatives **3** and **4** by an interaction of **2** with 4-aminopyridine and 2-aminopyridine, respectively (Scheme 1).



Scheme 1. Synthesis of compounds **3** and **4**.

This reaction has been carried out in MeCN solution, in which the products **3** and **4** are insoluble. In ether solution, **2** reacts with 4-methylpyridine to give **5**. N-alkoxy-N-chlorourea **7** and **8** yield **6a** and **6b** with DMAP (Scheme 2). Products **5**, **6a** and **6b** are insoluble in ether and appear as precipitates. As it analog **1** is sensitive to the presence of base,[11] N-alkoxy-N-chlorourea, **7** and **8** were used in excess in the syntheses of **6a** and 6**b**. This procedure avoids partial decomposition of the products. The known compound **1** can also be synthesized by this method.



Scheme 2. Synthesis of compounds **6a** and **6b**. R = Et (**6a**, **7**), Bu (**6b**, **8**).

The structure of N-alkoxy-N-(1-pyridinium)urea chlorides **3, 4**, **5**, **6a** and **6b** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, MS, and in the case of compounds **3** and **4** by XRD study also (Figure 1).

In the crystal, cations of compound **3** are linked in centrally symmetric dimmers by hydrogen bonds N1-H1a…O1^i [i: -x,1-y,-z] (H…O 2.09(2) Å, N-H…O 173.0(19)°). The dimmers are linked by intermolecular hydrogen bonds with Cl^- anions participating N1-H1b…Cl1^{ii} [-x,-y,-z] (H…Cl 2.74(3) Å, N-H…Cl 158(2)°), N4-H4a…Cl1^{iii} [iii: 1/2+x,1/2-y,-1/2+z] (H…Cl 2.39(3) Å, N-H…Cl 159(2)°), N4-H4b…Cl1^{iv} [iv: 1-x,-y,-z] (H…Cl 2.33(3) Å, N-H…Cl 170(2)°), C3-H3…Cl1^v [v: 1/2-x,1/2+y,-1/2-z] (H…Cl 2.68 Å, C-H…Cl 139°) and C7-H7…Cl1 (H…Cl 2.63 Å, C-H…Cl 155°). In compound **4** all intermolecular hydrogen bonds are formed with the participation of water and Cl^- anions: N1-H1b…O3^i [i: x,1/2-y,-1/2+z] (H…O 1.96(3) Å, N-H…O 173(2)°), O3-H3b…O1 (H…O 2.06(3) Å, O-H…O 162(3)°), N1-H1a…Cl1 (H…Cl 2.51(2) Å, N-H…Cl 157.2(18)°), O3-H3a…Cl1^{ii} [ii: -1+x,1/2-y,1/2+z] (H…Cl 2.28(4) Å, O-H…Cl 176(3)°), N4-H4a…Cl1^{iii} [iii: x,y,1+z] (H…Cl 2.34(2) Å, N-H…Cl 165(2)°), N4-H4b…Cl1^{iv} [iv: x,1/2-y,1/2+z] (H…Cl 2.53(3) Å, N-H…Cl 161(3)°) and C5-H5…O1^v [v: 1-x,-y,2-z] (H…O 2.55 Å, C-H…O 146°).

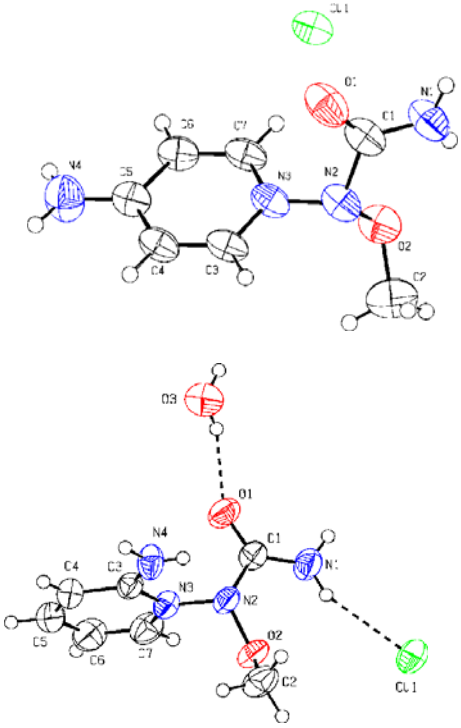


Figure 1. Molecular structure of **3** and **4** (monohydrate) with non-hydrogen atoms represented by thermal vibration ellipsoids of 50% probability.

In **3** and **4** central nitrogen atom of O–N–N^+ geminal system has trigonal-pyramidal configuration. In all cases its LP is situated in the plane of the pyridine circle. In compound **3** TaLPPy is equal to -1°, in compound **4** TaLPPy is 11°, the lengths of characteristic bonds are given in the Table 1.

In compounds **3** and **4** the carbamoyl moiety is oriented perpendicular to LP of N3 atom (the torsion angle O1-C1-N2-LP(N2) is -79° (**3**), -85° (**4**)), C-O bond of methoxy group is close to *sp*-orientation toward to LP of N3 atom (the torsion angle C2-O2-N2-LP(N2) is 22°(**3**), 18° (**4**)). In compounds **3** and **4** the weak intramolecular hydrogen bond N1-H1b…O2 takes place (H…O 2.20(2) Å (**3**), 2.28(2) Å (**15**), N-H…O 106(2)° (**3**), 102(2)° (**4**)). In compound **4,** N4 amino group is oriented to LP of N2 atom and forms a weak intramolecular hydrogen bond N4-H4b…N2 (H…N 2.39(3) Å, N-H…N 104(2)°).

Table 1. Structural parameters in N-alkoxy-N-(1-pyridinium)urea salts.

Compounds	∑β °	Bond lengths, Å			
		N−N$^+$	N−OMe	N−C(O)	R_2N'−C(O)
9[6]	333.9 (3)	1.425 (2)	1.400 (2)	1.452 (2)	1.323 (2)
1[5]	332.7	1.413 (2)	1.411 (2)	1.450 (2)	1.310 (2)
10[5]	324.22	1.425 (3)	1.429 (3)(Pr)	1.465 (3)	1.324 (3)
3	332.8 (4)	1.410 (2)	1.413 (2)	1.438 (2)	1.315 (3)
4	336.6 (4)	1.415 (2)	1.408 (2)	1.432 (2)	1.313 (2)

Note: **9** = 1-(N-methoxy-N-carbamoyl)aminopyridinium perchlorate, **10** = 1-(N-propoxy-N-dimethylcarbamoyl)amino-4-dimethylamino-pyridinium perchlorate

Table 2. Pyridinium ring deformation in N-alkoxy-N-(1-pyridinium)ureas salts **1**, **3, 4** and **10**.

Compounds	Bond lengths, Å			
	N1-C2, N1-C6	C2-C3, C5-C6	C3-C4, C4-C5	C4-NMe_2, C-NH_2
9[6]	1.341(2), 1.341(2)	1.385(3), 1.385(3)	1.349(5), 1.387(4)	-
1[5]	1.361(2), 1.345(2)	1.353(3), 1.341(3)	1.425(2), 1.426(2)	1.324(2)
10[5]	1.366(3), 1.346(3)	1.349(3), 1.334(3)	1.430(3), 1.413(3)	1.333(3)
3*	1.353(2), 1.356(2)	1.342(3), 1.343(3)	1.405(3), 1.421(3)	1.320(3)
4*	1.357(2), 1.374(3)	1.411(3), 1.336(3)	1.346(3), 1.402(3)	1.308(3)
Py[16]	1.337	1.380	1.379	C=N, 1.316

*Standard numeration of pyridine ring atoms has been used.

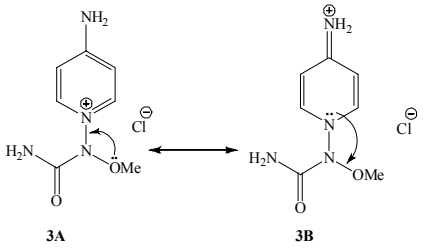
In the family of N-alkoxy-N-(1-pyridinium)ureas **1**, **3**, **4, 9** and **10** the largest degree of pyramidality of central nitrogen atom in O−N−N$^+$ germinal system is observed in compound **10.** Probably, it is caused by the presence of weak electronegative dimethylcarbamoyl substituent[2] at the nitrogen in contrast with the carbamoyl moiety present in other compounds. In compounds **1** and **3,** the nitrogen pyramidality degrees are similar (Table 1).

It must noted that N−C bond lengths in the family of N-alkoxy-N-(1-pyridinium)urea salts, **1**, **3, 4**, **9** and **10** are somewhat different (Table 1). The (AlkO)N−C(=O) bond is much longer, than N−C in urea[12] (1.350(1) Å) and in amides[13] (1.359 Å). But H_2N'−C(O) bond (or Me_2N'−C(O) bond in compound **10** is very short (Table 1). It results from different degrees of C=O conjugation with sp^3 hybridized nitrogen atom, N, and sp^2 hybridized nitrogen atom N'.[5]

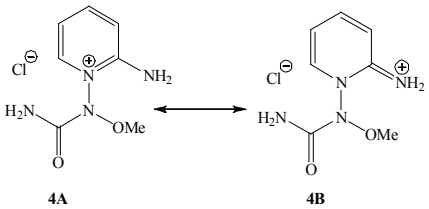
The same difference of N−C carbamoyl bonds has been established for N-alkoxy-N-chlorourea,[7,14,15] N-acyloxy-N-alkoxyureas[6,9,13] and N,N-dialkoxyureas.[6,15]

In compound **3,** the presence of 4-amino group causes some N−OMe bond elongation and some N−N$^+$ bond shortening relatively to compound **9** (Table 1) and the known[5] quinonoid deformation of pyridine ring relatively to pyridine[16] and compound **9**[6] is established (Table 2). Thus it may be supposed that resonance form **3B** (Scheme 3) makes certain contribution to the structure of compound **14**. In form **3B** $n_N \rightarrow \sigma^*_{N\text{-}OMe}$ anomeric effect becomes possible. Its action is opposite to that of $n_{O(Me)} \rightarrow \sigma^*_{N\text{-}N+}$ anomeric effect, which dominate in resonance form **3A**.

In compound **4** a quinonoid deformation of pyridine ring is somewhat different, C4-C5 bond is shortened, C3-C4 bond is elongated, that is correspond with qinonoid form **4B** (Scheme 4).



Scheme 3. Resonance in compound **3.**

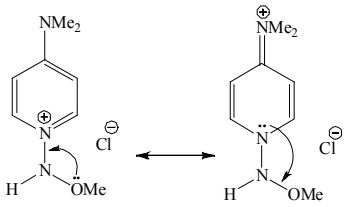


Scheme 4. Resonance in compound **4.**

Presence of 2-amino group in the pyridinium moiety causes some N−OMe elongation and any N−N$^+$ shortening relatively to compound **9** (Table 1). Probably, it is the concurrence of the sequence of $n_N \rightarrow \sigma^*_{N\text{-}OMe}$ and $n_{O(Me)} \rightarrow \sigma^*_{N\text{-}N+}$ anomeric effects.

In the case of both **3** and **4** C-NH_2, bond is shortened and its length is close to length of C=N$^+$H$_2$ bond.

It must be noted that quinonoid deformation of pyridine ring, similar to that observed in compound **3**, also takes place in 1-N-alkoxyamino-4-dimethylaminopyridinium salts[11] (Scheme 5).



Scheme 5. Quininoid deformation in 1-N-alkoxyamino-4-dimethylaminopyridinium salts.

Conclusion

New N-[1-(4-amino)pyridinium]-N-methoxyurea chloride **3**, N-[1-(2-amino)pyridinium]-N-methoxyurea chloride **4** and their analogs were synthesized by an improved procedure. XRD study of N-[1-(4-amino)pyridinium]-N-methoxyurea and N-[1-(2-amino)pyridinium]-N-methoxyurea revealed the elongation of N-N^+ bonds and some shortening of MeO-N bonds, qunonoid deformation of pyridine rings compare to it unsubstituted analog. The substantial pyramidality of central nitrogen atom in O-N-N^+ moiety and N-C carbamoyl bonds difference was also established. The structural features of N-alkoxy-N-(1-pyridinium)urea salts and other derivatives of 1-(N-alkoxyamino)pyridinium salts has been summarized.

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References

[1]Shtamburg, V. G., Rudchenko, V. F., Nasibov, Sh. S., Chervin I. I., Kostyanovsky, R. G., *Russ. Chem. Bull., Int. Edn.* **1981**, *30*, 1914-1920.

[2]Glover, S. A., *Tetrahedron* **1998**, *54*, 7229-7271.

[3]Shtamburg, V. G., Tsygankov, A. V., Klots, E. A., Fedyanin, I. V., Lyssenko, K. A., Kostyanovsky, R. G., *Mendeleev Commun.* **2006**, *16*, 84-85.

[4]Shtamburg, V. G., Klots, E. A., Gerasimenko, M. V., Shishkin, O. V., Zubatyuk, R. I., Kostyanovsky, R. G., *Mendeleev Commun*. **2011**, *21*, 349-350.

[5]Shtamburg, V. G., Tsygankov, A. V., Shishkin, O. V., Zubatyuk, R. I., Shtamburg, V. V., Gerasimenko, M. V., Mazepa, A. V., Kostyanovsky, R. G., *Mendeleev Commun*. **2012**, *22*, 92-94.

[6]Shtamburg, V. G., Shishkin O. V., Zubatyuk R. I., Kravchenko, S. V., Tsygankov, A. V., Shtamburg, V. V., Distanov, V. B., Kostyanovsky, R. G., *Mendeleev Commun*. **2007**, *17*, 178-180.

[7]Shtamburg, V. G., Shishkin, O. V., Zubatyuk, R. I., Kravchenko, S. V., Tsygankov, A. V.; Mazepa, A. V., Klots, E. A.; Kostyanovsky, R. G., *Mendeleev Commun*. **2006**, *16*, 323-325.

[8]Sheldrick, G. M., *Acta Cryst.* **2008**, *A64***,** 112-122.

[9]Shishkin, O. V., Zubatyuk, R. I., Shtamburg, V. G., Tsygankov, A. V., Klots, E. A., Mazepa, A. V., Kostyanovsky, R. G., *Mendeleev Commun*. **2006**, *16*, 222-223.

[10]Shtamburg, V .G., Klots, E .A., Pleshkova, A. P., Avramenko, V. I., Ivonin, S .P.,; Tsygankov, A. V., Kostyanovsky, R. G., *Russ. Chem. Bull., Int. Edn.* **2003**, *52*, 2251-2260.

[11]Shtamburg, V. G., Shishkina, S. V., Shtamburg, V. V., Mazepa, A. V., Kadorkina, G. K., Kostyanovsky, R. G., *Mendeleev Commun*., **2016**, *26*, 169-171.

[12]Swaminathan, S., Craven, B. M., *Acta Cryst*. **1984**, *B40*, 300-306.

[13]Glover, S. A., White, J. M., Rosser, A. A., Digianantonio, K. M., *J. Org. Chem.* **2011**, *76*, 9757- 9763.

[14]Shishkin, O. V., Shtamburg, V. G., Zubatyuk, R. I., Olefir, D. A., Tsygankov, A. V., Prosyanik, A. V., Mazepa, A. V., Kostyanovsky, R. G., *Chirality*, **2009**, *21*, 642-647.

[15]Shtamburg, V. G., Kostyanovsky, R. G., Tsygankov, A. V.; Shtamburg, V.V., Shishkin, O. V., Zubatyuk, R. I., Mazepa, A. V., Kravchenko, S. V., *Russ. Chem. Bull., Int. Edn.* **2015**, 62-75.

[16]Burgi H.-B., Dunitz J. D., *Structure correlation*. Vol. 2. VCH. Weinheim. 1994, 741-784.

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