

Synthesis, structure and properties of *N*-alkoxy-*N*-(1-pyridinium)urea salts, *N*-alkoxy-*N*-acyloxyureas and *N,N*-dialkoxyureas†

Vasiliy G. Shtamburg,^a Oleg V. Shishkin,^b Roman I. Zubatyuk,^b Svetlana V. Kravchenko,^a
 Alexander V. Tsygankov,^a Victor V. Shtamburg,^c Vitaliy B. Distanov^c and Remir G. Kostyanovsky^{*d}

^a Department of Chemistry, Dnepropetrovsk National University, 49050 Dnepropetrovsk, Ukraine.

E-mail: heterocycle@ff.dsu.dp.ua

^b STC 'Institute for Single Crystals', National Academy of Sciences of Ukraine, 61001 Kharkov, Ukraine.

E-mail: shishkin@xray.isc.kharkov.com

^c Department of Chemistry, National Technical University, Kharkov Polytechnic Institute, 61002 Kharkov, Ukraine. E-mail: vitalius2002@ukr.net

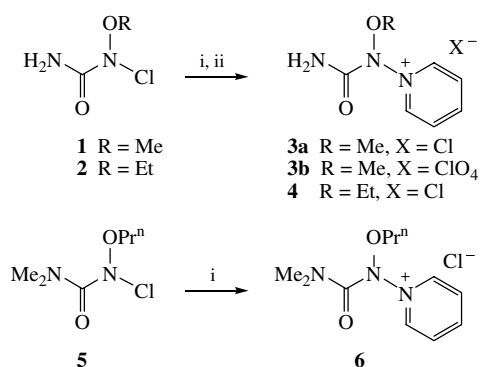
^d N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 137 8284; e-mail: kost@chph.ras.ru

DOI: 10.1016/j.mencom.2007.05.016

N-Alkoxy-*N*-(1-pyridinium)urea salts **3**, **4** have been prepared, the conversions of *N*-acetoxy-*N*-methoxyurea **7** into *N,N*-dimethoxyurea **8** and of *N*-*n*-propyloxy-*N*-(1-pyridinium)-*N',N'*-dimethylurea chloride **6** into *N,N*-dimethoxy-*N',N'*-dimethylurea **11** were carried out. A high pyramidalicity of the amide nitrogen in O–N–X groups [X = N⁺C₅H₅, OMe, OC(O)C₆H₄Cl-*p*] has been revealed by XRD studies of ureas **3b**, **8** and *N*-*p*-chlorobenzoyloxy-*N*-*n*-butyloxyurea **9**.

The pyramidalicity of amide nitrogen was found earlier in acyclic anomeric amides² such as *N,N*-dialkoxy-*N',N'*-dimethylureas by the DNMR method³ and XRD studies in *N*-acyloxy-*N*-alkoxybenzamides,⁴ *N,N'*-diacyl-*N,N'*-dialkoxyhydrazines,⁵ *N*-acyloxy-*N*-alkoxyureas,^{6(a)} *N*-acyloxy-*N*-alkoxycarbamates^{6(a)} and *N*-chloro-*N*-alkoxyureas.¹ However, *N*-alkoxy-*N*-(1-pyridinium)urea salts have never been regarded as a kind of anomeric amides and the pyramidalicity parameters of unsubstituted *N,N*-dialkoxyureas were unknown.

We have synthesised salts **3**, **4**[‡] and **6** by nucleophilic substitution at nitrogen in *N*-chloro-*N*-alkoxyureas **1**, **2**, **5**^{1,7} and performed an XRD study of **3b** (Figure 1, Tables 1, 2).



Scheme 1 Reagents and conditions: i, Py, Et₂O, room temperature; ii, AgClO₄, MeCN.

In order to investigate the structure of the simplest *N,N*-dialkoxyurea by methanolysis of *N*-acetoxy-*N*-methoxyurea **7**, crystalline *N,N*-dimethoxyurea **8**¹ was obtained (Scheme 2) and studied by XRD analysis (Figure 2, Tables 1, 2).

Chlorides **3a**, **4** are stable at room temperature for 12 h and decompose at long-duration storage at –5 °C (10 weeks). Chloride **6** can be stored without decomposition at –5 °C for

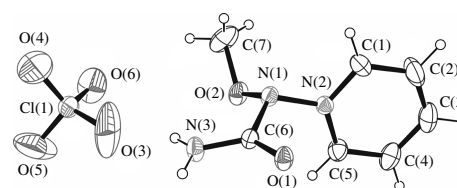
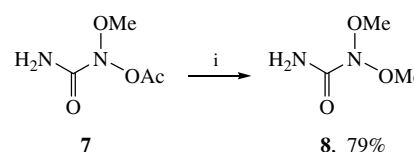


Figure 1 Molecular structure of **3b**. Selected bond lengths (Å) and bond angles (°): N(1)–C(6) 1.4515(19), N(3)–C(6) 1.3234(18), O(1)–C(6) 1.2218(17), N(1)–N(2) 1.4254(18), O(2)–N(1) 1.3999(17), O(2)–C(7) 1.442(3), N(2)–C(1) 1.341(2), N(2)–C(5) 1.341(2); O(2)–N(1)–N(2) 109.03(12), O(2)–N(1)–C(6) 113.03(12), N(2)–N(1)–C(6) 111.72(11), N(1)–O(2)–C(7) 108.94(18), C(5)–N(2)–N(1) 120.44(13), C(5)–N(2)–C(1) 123.61(16), C(1)–N(2)–N(1) 115.95(15).

more than one year, but it is very hygroscopic. Chloride **3a** was converted into more stable perchlorate **3b**. This allowed us to perform an XRD study⁸ at room temperature without any decomposition of the crystal. The results revealed that amide nitrogen in the O–N–N⁺ system has a pyramidal configuration (Figure 1, Tables 1, 2). The nitrogen pyramidalicity parameters as the sum of bond angles centered at this atom ($\Sigma\beta$) and the deviation of N(1) from the plane of three atoms it is bonded with (h_N) are given in Table 1. In *N*-alkoxy-*N*-(1-pyridinium)urea salt **3b**, the N pyramidalicity degree is less as it was found for *N*-alkoxy-*N*-(1-pyridinium)-*N*-*tert*-alkylamine salts,⁸ but it is closer to N pyramidalicity in *N*-acetoxy-*N*-ethoxyurea^{6(a)} and methyl *N*-4-chlorobenzoyloxy-*N*-methoxycarbamate.^{6(a)} The decreasing nitrogen pyramidalicity degree in salt **3b** against the *N*-alkoxy-*N*-(1-pyridinium)-*N*-*tert*-alkylamine salt⁸ can be explained by stabilization of the planar configuration of amide



Scheme 2 Reagents and conditions: i, MeOH, room temperature.

† Asymmetric Nitrogen, Part 100. Geminal Systems, Part 57. Previous communication, see ref. 1.

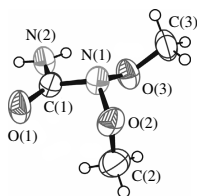


Figure 2 Molecular structure of **8**. Selected bond lengths (Å) and bond angles (°): N(1)–C(1) 1.438(2), N(2)–C(1) 1.320(3), O(1)–C(1) 1.220(2), O(2)–N(1) 1.397(2), O(3)–N(1) 1.401(2), O(2)–C(2) 1.431(3), O(3)–C(3) 1.429(2), O(2)–N(1)–O(3) 110.33(13), O(2)–N(1)–C(1) 111.37(16), O(3)–N(1)–C(1) 110.07(14), O(1)–C(1)–N(2) 125.61(19), O(1)–C(1)–N(1) 118.78(16), N(2)–C(1)–N(1) 115.2(2), N(1)–O(2)–C(2) 114.17(16), N(1)–O(3)–C(3) 109.19(16).

‡ *N*-Methoxy-*N*-(1-pyridinium)urea chloride **3a**. A solution of pyridine (95 mg, 1.206 mmol) in Et₂O (2 ml) was added to a solution of *N*-chloro-*N*-methoxyurea **1**¹ (135 mg, 1.085 mmol) in Et₂O (3 ml) at –30 °C. During 3 h, the reaction mixture was heated to 5 °C and kept at this temperature for 40 h. The obtained solid was filtered off, washed with Et₂O and dried *in vacuo*, yielding 198 mg (89%) of urea **3a**, white crystals, mp 97–98 °C (decomp.). ¹H NMR (300 MHz, [D₆]DMSO) δ: 3.90 (s, 3H, OMe), 8.31 (br. s, 2H, NH₂), 8.32 [t, 2H, C(3)H, C(5)H, ³J 7.5 Hz], 8.83 [t, 1H, C(4)H, ³J 7.5 Hz], 9.40 [d, 2H, C(2)H, C(6)H, ³J 5.7 Hz]. IR (ν/cm⁻¹): 3285 (NH), 1745 (C=O). MS (FAB, H⁺), *m/z* (%): 168 (M⁺, 100). Found (%): C, 41.18; H, 5.02; N, 20.75; Cl, 17.32. Calc. for C₇H₁₀N₃O₂Cl (%): C, 41.29; H, 4.95; N, 20.64; Cl, 17.41.

In a similar manner, *N*-ethoxy-*N*-(1-pyridinium)urea chloride **4** was obtained from *N*-chloro-*N*-ethoxyurea **2**,⁷ colourless crystals, yield 73%, mp 124–125 °C (decomp.). ¹H NMR (300 MHz, [D₆]DMSO) δ: 1.21 (t, 3H, NOCH₂Me, ³J 7.2 Hz), 3.98 (q, 2H, NOCH₂Me, ³J 7.2 Hz), 8.22 [t, 2H, C(3)H, C(5)H, ³J 7.8 Hz], 8.65 [t and br. s, 3H, NH₂, C(4)H, ³J 7.8 Hz], 9.25 [d, 2H, C(2)H, C(6)H, ³J 7.8 Hz]. IR (ν/cm⁻¹): 3270 (NH), 1750 (C=O). Found (%): N, 19.12; Cl, 16.05. Calc. for C₈H₁₂N₃O₂Cl (%): N, 19.31; Cl, 16.29.

In a similar manner, *N*-*n*-propyloxy-*N*-(1-pyridinium)-*N*,*N*'-dimethylurea chloride **6** was obtained from *N*-chloro-*N*-*n*-propyloxy-*N*,*N*'-dimethylurea **5**,⁷ colourless crystals, yield 77%, mp 83–84 °C (decomp.). ¹H NMR (300 MHz, CDCl₃) δ: 0.95 (t, 3H, NOCH₂CH₂Me, ³J 7.2 Hz), 1.68 (sext, 2H, NOCH₂CH₂Me, ³J 7.2 Hz), 3.09 (s, 3H, NMe), 3.35 (s, 3H, NMe), 4.17 (t, 2H, NOCH₂CH₂Me, ³J 7.2 Hz), 8.42 [t, 2H, C(3)H, C(5)H, ³J 7.8 Hz], 8.78 [t, 1H, C(4)H, ³J 7.8 Hz], 9.59 [d, 2H, C(2)H, C(6)H, ³J 7.8 Hz]. IR (ν/cm⁻¹): 1745 (C=O). Found (%): N, 16.01; Cl, 13.74. Calc. for C₁₁H₁₈ClN₃O₂ (%): N, 16.18; Cl, 13.65.

N-Methoxy-*N*-(1-pyridinium)urea perchlorate **3b**. A solution of AgClO₄ (139 mg, 0.670 mmol) was added to a solution of urea **3a** (137 mg, 0.670 mmol) in a mixture of MeCN (5 ml) and MeOH (2 ml). The AgCl precipitate was filtered off; the filtrate was evaporated *in vacuo*. The obtained residue was washed by THF and crystallised from MeCN–CH₂Cl₂ at –20 °C, yielding 159 mg (88%) of urea **3b**, colourless crystals, mp 128–130 °C (decomp.). ¹H NMR (300 MHz, [D₆]DMSO) δ: 3.90 (s, 3H, OMe), 8.29 (br. s, 2H, NH₂), 8.32 [t, 2H, C(3)H, C(5)H, ³J 7.5 Hz], 8.83 [t, 1H, C(4)H, ³J 7.5 Hz], 9.39 [d, 2H, C(2)H, C(6)H, ³J 5.7 Hz]. MS (FAB, H⁺): 168 (M⁺, 100). Found (%): C, 31.23; H, 3.92; N, 15.45. Calc. for C₇H₁₀N₃O₆Cl (%): C, 31.42; H, 3.77; N, 15.70.

N,N-Dimethoxyurea **8**. *N*-Acetoxy-*N*-methoxyurea **7**¹ (87 mg, 0.598 mmol) was dissolved in MeOH (2 ml), and the solution was kept at 22 °C for 74 h. Then, it was evaporated *in vacuo*; the residue was kept at 2 Torr and crystallised from Et₂O–hexane, yielding 57 mg (79%) of urea **8**, colourless crystals, mp 47–48 °C, identified by ¹H NMR with a sample¹ obtained from *N*-chloro-*N*-methoxyurea **1**¹. MS (FAB, H⁺), *m/z*: 121 ([M + H]⁺, 100).

Methanolysis of N-n-propyloxy-N-(1-pyridinium)-N',N'-dimethylurea chloride **6**. A solution of salt **6** (199 mg, 0.766 mmol) in MeOH (3 ml) was refluxed for 3 h; then, it was evaporated *in vacuo*. The residue was extracted by Et₂O (10 ml), the extract was evaporated *in vacuo*. By NMR, the residue is a mixture of *N,N*-dimethoxyurea **11**³ (main component) with trace *N-n*-propyloxy-*N*-methoxyurea **10**.⁷ After distillation *in vacuo*, 11 mg (10%) of *N,N*-dimethoxy-*N',N'*-dimethylurea **11** was obtained and identified by ¹H NMR spectroscopy.^{3,7} ¹H NMR (300 MHz, CDCl₃) δ: 3.00 (s, 6H, NMe₂), 3.75 [s, 6H, N(OMe)₂].

Table 1 Parameters of nitrogen atom pyramidalicity in Y–N(X)OR compounds.

| Y | X | R | $h_N/\text{Å}$ | $\Sigma\beta/^\circ$ |
|--|--|--|----------------|----------------------|
| H ₂ NC(O) | OMe | Me (8) | 0.444 | 331.8 |
| H ₂ NC(O) | Cl ¹ | Me | 0.500 | 329.0 |
| O ₂ NC ₆ H ₄ HNC(O) | Cl ¹ | CMe ₂ CO ₂ Me | 0.533 | 325.8 |
| H ₂ NC(O) | OAc ^{6(a)} | Et | 0.431 | 333.6 |
| H ₂ NC(O) | OC(O)C ₆ H ₄ Cl- <i>p</i> | Bu ⁿ (9) | 0.511 | 323.8 |
| H ₂ NC(O) | N ⁺ C ₅ H ₅ | Me (3b) | 0.429 | 333.9 |
| MeO ₂ CMe ₂ C | N ⁺ C ₅ H ₅ ⁸ | Me | 0.531 | 322.8 |
| Bz | OBz ⁴ | CH ₂ C ₆ H ₄ Bu ^t - <i>p</i> | 0.508 | 324.14 |
| <i>p</i> -Bu ^t C ₆ H ₄ C(O) | OC(O)C ₆ H ₄ Bu ^t - <i>p</i> ⁴ | CH ₂ C ₆ H ₄ Bu ^t - <i>p</i> | 0.513 | 323.51 |
| MeOC(O) | OC(O)C ₆ H ₄ Cl- <i>p</i> ^{6(a)} | Me | 0.426 | 334.1 |

nitrogen due to conjugation with the carbonyl group. The nitrogen pyramidalicity parameters in different O–N–X geminal systems are given in Table 1. Earlier, we believed that *N*-acyloxy-*N*-alkoxybenzamides are most strongly pyramidal at nitrogen.⁴ But, as we have found by means of XRD study, in *N-p*-chlorobenzoyloxy-*N-n*-butyloxyurea **9**^{6(b)} the nitrogen pyramidalicity parameters h_N and $\Sigma\beta$ were close to those of *N*-acyloxy-*N*-alkoxybenzamides⁴ (Table 1). The conformation of urea **9** (Figure 3) is similar to the conformation of *N*-acyloxy-*N*-alkoxybenzamides.⁴ In urea **9**, the nitrogen pyramidalicity degree is higher than that in the Kirby ‘most twisted’ amide (1-aza-2-adamantanone⁹). We suppose that the high degree of nitrogen pyramidalicity in urea **9** is caused by the *O*-butyl group.

In urea **3b**, the lone electron pair (Lp) of N(1) is oriented in the pyridine ring plane [the torsion angle C(1)–N(2)–N(1)–Lp(N1) is equal to 0.2°] similarly to *N*-methoxy-*N*-(1-pyridinium)-*N-tert*-alkylamine perchlorate.⁸ It is interesting to note some differences in amide N–C bonds in urea **3b**. The N(1)–C(6) bond is much longer than the N(3)–C(6) bond (see Table 2). It is probably the sequence of different degrees of carbonyl C(6)=O(1) conjugation with *sp*²-hybridized N(3) and *sp*³-

§ *Crystal data for 3b*: crystals were grown from MeCN–CH₂Cl₂ at –20 °C, [C₇H₁₀N₃O₂]⁺[ClO₄]⁻, monoclinic, space group *P2₁/m*, *a* = 9.733(2), *b* = 0.330(2) and *c* = 11.929(3) Å, β = 103.77(2)°, *V* = 1164.9(4) Å³, *F*(000) = 552, *d*_{calc} = 1.526 g cm⁻³, *Z* = 4, μ = 0.35 mm⁻¹.

Crystal data for 8: crystals were grown from Et₂O–hexane at –20 °C, C₃H₈N₂O₃, rhombic, space group *Fdd2*, *a* = 24.358(9), *b* = 18.941(6) and *c* = 5.199(2) Å, *V* = 2399(1) Å³, *F*(000) = 1024, *d*_{calc} = 1.330 g cm⁻³, *Z* = 16, μ = 0.118 mm⁻¹.

Crystal data for 9:^{6(b)} crystals were grown from CH₂Cl₂–hexane at –20 °C, C₁₂H₁₅N₂O₄Cl, monoclinic, space group *C2/c*, *a* = 17.362(2), *b* = 20.000(2) and *c* = 9.7443(8) Å, β = 121.10(1)°, *V* = 2897.1(4) Å³, *F*(000) = 1200, *d*_{calc} = 1.315 g cm⁻³, *Z* = 8, μ = 0.275 mm⁻¹.

Data were measured using an Xcalibur 3 diffractometer (*T* = 298 (**3b**), 100 K (**8** and **9**), graphite-monochromated MoKα radiation, 2θ/θ scan, 2θ_{max} = 70° (**3b**), 55° (**8**), 60° (**9**)). The structures were solved by a direct method using the SHELXTL PLUS program package.¹² Refinement against *F*² in an anisotropic approximation (the hydrogen atoms isotropic in the riding model, except for H atoms of amino groups, those were free refined) by a full matrix least-squares method for 5054 reflections was carried out to *wR*₂ = 0.252 [163 parameters, *R*₁ = 0.076 for 3368 reflections with *F* > 4σ(*F*), *S* = 1.01] for **3b**, for 1065 reflections were carried out to *wR*₂ = 0.067 [82 parameters, *R*₁ = 0.029 for 675 reflections with *F* > 4σ(*F*), *S* = 1.00] for **8** and 4090 reflections out to *wR*₂ = 0.159 [181 parameters, *R*₁ = 0.058 for 3430 reflections with *F* > 4σ(*F*), *S* = 1.08] for **9**.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 624636, 624635 and 632716 for **3b**, **8** and **9**, respectively. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.

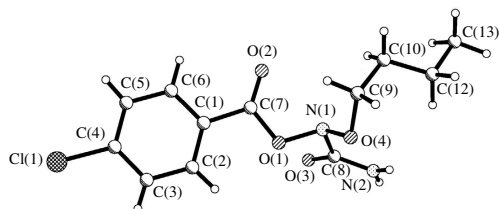
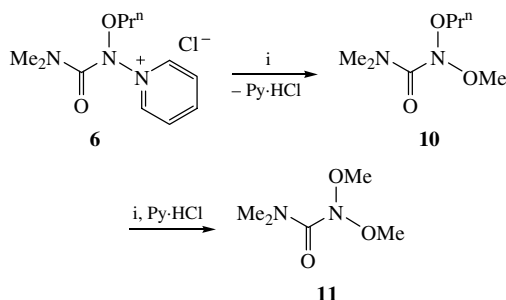


Figure 3 Molecular structure of **9**. Selected bond lengths (Å) and bond angles (°): N(1)–O(1) 1.447(2), N(1)–O(4) 1.397(2), N(1)–C(8) 1.441(2), N(2)–C(8) 1.321(2); O(4)–N(1)–O(1) 106.4(1), O(4)–N(1)–C(8) 111.5(1), O(1)–N(1)–C(8) 105.9(1).

hybridized N(1) nitrogen atoms. In urea **3b**, the N(1)–N(2) bond is shorter [1.4254(18) Å] than the corresponding bond in *N*-alkoxy-*N*-(1-pyridinium)-*N*-*tert*-alkylamine salts⁸ [1.466(2) Å]. It may cause a lower mobility of the pyridine group in reactions of ureas **3**, **4**, **6** with nucleophiles.

However, the N(1)–N(2) bond is much longer than the N–N bonds of carboxylic acid hydrazides (1.400 Å).¹⁰ As it follows from quantum-chemical calculations,¹¹ the N–N bond in anomeric *N*-dimethylamino-*N*-methoxyformamide should be 1.385 Å, whereas the N–OMe bond is longer (1.426 Å). It is a sequence of an $n_{\text{NMe}_2} - \sigma_{\text{N-OMe}}^*$ anomeric effect. In the cases of *N*-alkoxy-*N*-(1-pyridinium)-*N*-*tert*-alkylamines and *N*-alkoxy-*N*-(1-pyridinium)urea salts, the opposite $n_{\text{O}} - \sigma_{\text{N-N}^+}^*$ anomeric effect takes place, and the N(1)–N(2) bond is destabilised. Probably, this is the reason why at boiling in methanol *N*-*n*-propyloxy-*N*-(1-pyridinium)urea chloride **6** is converted (with a moderate yield) into *N,N*-dimethoxyurea **11** via intermediate urea **10** (Scheme 3).



Scheme 3 Reagents and conditions: i, MeOH, reflux, 3 h.

XRD studies of *N,N*-dimethoxyurea **8** have revealed that amide O–N–O nitrogen N(1) had a pyramidal configuration (Figure 2, Tables 1, 2). The pyramidal parameters h_{N} and $\sum\beta$ are close to those of *N*-acetoxy-*N*-ethoxyurea^{6(a)} (see Table 1). The carbamoyl nitrogen N(2) has a planar trigonal configuration; the sum of bond angles is 358.2°. Similarly to urea **3b**, big differences in the amide N–C bond are observed for urea **8**. The N(1)–C(1) bond is much longer than the N(2)–C(1) bond (see Table 2). It is also a sequence of a bigger conjugation degree of carbonyl C(1)=O(1) with the sp^2 -hybridized N(2) nitrogen atom comparing with sp^3 -hybridized N(1). The total picture of N–C and N–O bond deformation in anomeric ureas is given in Table 2. The carbonyl stretch frequencies of ureas **3b** (1745 cm^{-1}) and **8** (1720 cm^{-1})¹ are appreciably higher than those of *N*-methoxyurea (1685 cm^{-1}). The same fact was predicted and found by Glover and Rauk² for different kinds of anomeric benzamides.

In *N,N*-dimethoxyurea **8**, the methoxy groups C(2)–O(2) and C(3)–O(3) have *ap*- and *sp*-orientations, respectively, in reference to Lp(N1) [the torsion angle Lp(N1)–N(1)–C(2)–O(2) is 174°, and Lp(N1)–N(1)–C(3)–O(3) is –29°]. However, the N–O bond lengths are close (see Table 2). The lengths of C–O bonds are

Table 2 The lengths of N–O bonds and amide N–C bonds in anomeric ureas $\text{H}_2\text{N}^{(2)}\text{C}^{(1)}(\text{O})\text{N}^{(1)}(\text{X})\text{O}^{(1)}\text{R}$ (Å).

| X | R | N(1)–C(1) | N(2)–C(1) | N(1)–O(1)R |
|---|----|-----------|-----------|--------------|
| OAc ^{6(a)} | Et | 1.426 | 1.330 | 1.398 |
| O ₂ CC ₆ H ₄ Cl- <i>p</i> (9) | Bu | 1.441 | 1.321 | 1.397 |
| Cl ¹ | Me | 1.446 | 1.319 | 1.397 |
| OMe (8) | Me | 1.438 | 1.320 | 1.397, 1.401 |
| N ⁺ C ₅ H ₅ (3b) | Me | 1.452 | 1.323 | 1.3999 |

almost similar [O(2)–C(2), 1.431(3) Å; O(3)–C(3), 1.429(2) Å]. A carbamoyl substituent is perpendicular to the direction of Lp(N1) [the torsion angle Lp(N1)–N(1)–C(1)–O(1) is 88°].

Thus, by means of XRD data, the nitrogen pyramidality in the O–N–O geminal systems of *N,N*-dialkoxyureas and in the O–N–N⁺ geminal systems of *N*-alkoxy-*N*-(1-pyridinium)urea salts has been proved. It is caused by the presence of two electronegative substituents at the nitrogen atom and by the $n_{\text{O}} - \sigma_{\text{N-X}}^*$ anomeric effects (X = Oalk, N⁺C₅H₅). In *N*-acyloxy-*N*-alkoxyureas, the nitrogen pyramidality degree depends on the nature of *O*-alkyl substituents.

This work was supported by the Russian Academy of Sciences and the Russian Foundation for Basic Research (grant no. 06-03-32840).

References

- V. G. Shtamburg, O. V. Shishkin, R. I. Zubatyuk, S. V. Kravchenko, A. V. Tsygankov, A. V. Mazepa, E. A. Klots and R. G. Kostyanovsky, *Mendeleev Commun.*, 2006, 323.
- (a) S. A. Glover and A. Rauk, *J. Org. Chem.*, 1996, **61**, 2337; (b) S. A. Glover, *Tetrahedron*, 1998, **54**, 7229; (c) S. A. Glover and A. Rauk, *J. Org. Chem.*, 1999, **64**, 2340.
- I. I. Chervin, V. S. Nosova, V. F. Rudchenko, V. I. Shevchenko and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1148 (in Russian) (*Chem. Abstr.*, 1986, **105**, 2082129q).
- A.-M. E. Gillson, S. A. Glover, D. J. Tucker and P. Turner, *Org. Biomol. Chem.*, 2003, **1**, 3430.
- S. A. Glover, G. Mo, A. Rauk, D. J. Tucker and P. Turner, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2053.
- (a) O. V. Shishkin, R. I. Zubatyuk, V. G. Shtamburg, A. V. Tsygankov, E. A. Klots, A. V. Mazepa and R. G. Kostyanovsky, *Mendeleev Commun.*, 2006, 222; (b) V. G. Shtamburg, A. V. Tsygankov, E. A. Klots and R. G. Kostyanovsky, *Mendeleev Commun.*, 2004, 208.
- V. G. Shtamburg, E. A. Klots, A. P. Pleshkova, V. I. Avramenko, S. P. Ivonin, A. V. Tsygankov and R. G. Kostyanovsky, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 2132 (*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2251).
- V. G. Shtamburg, A. V. Tsygankov, E. A. Klots, I. I. Fedyanin, K. A. Lyssenko and R. G. Kostyanovsky, *Mendeleev Commun.*, 2006, 85.
- (a) A. J. Kirby, I. V. Komarov, P. D. Wothers and N. Feeder, *Angew. Chem., Int. Ed.*, 1998, **37**, 785; (b) A. J. Kirby, I. V. Komarov, K. Kowski and P. Rademacher, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1313; (c) A. J. Kirby, I. V. Komarov and N. Feeder, *J. Chem. Soc., Perkin Trans. 2*, 2001, 522.
- L. H. Jensen, *J. Am. Chem. Soc.*, 1956, **78**, 3993.
- S. A. Glover, G. Mo and A. Rauk, *Tetrahedron*, 1999, **55**, 3413.
- G. M. Sheldrick, *SHELXTL PLUS. PC Version. A System Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data*. Rev. 5.1.

Received: 19th October 2006; Com. 06/2798