

Synthesis and structure of *N*-alkoxyhydrazines and *N*-alkoxy-*N',N',N'*-trialkylhydrazinium salts[†]

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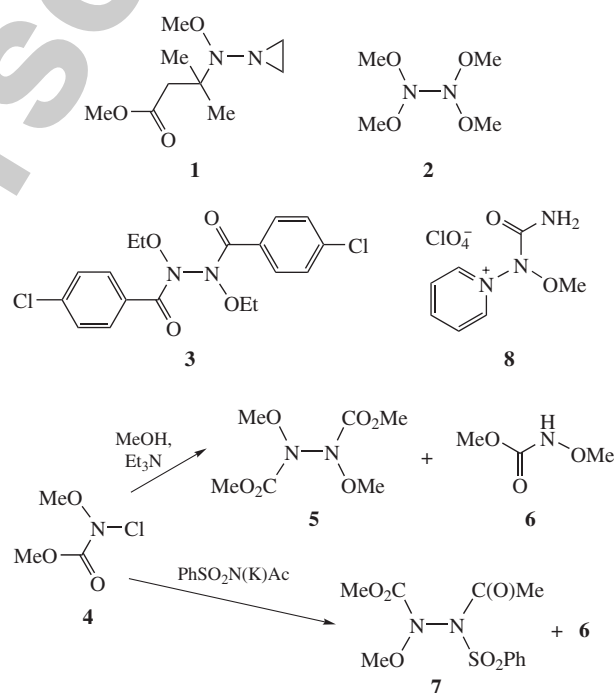
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New types of 1,1,1-trialkyl-2-alkoxyhydrazinium chlorides and *N*-alkoxyhydrazines were obtained by reactions of *N*-chloro-*N*-alkoxyureas with trimethylamine or 1,4-diaza[2.2.2]bicyclooctane and by reactions of methyl *N*-chloro-*N*-methoxycarbamate with potassium salt of *N*-acetylbenzenesulfonylamide. The XRD studies of *N,N'*-bis(methoxycarbonyl)-*N,N'*-dimethoxyhydrazine, *N'*-methoxy-*N'*-methoxycarbonyl-*N*-acetylbenzenesulfonylhydrazide and 1,1,1-trimethyl-2-methoxyhydrazinium perchlorate revealed the pyramidal configuration of the central nitrogen atoms in O–N–N geminal system, unusual elongation of N–N⁺ bond and shortening of N–OMe bond in 1,1,1-trimethyl-2-methoxyhydrazinium perchlorate.

N-Alkoxyhydrazines represent an interesting example of O–N–N geminal systems.^{1–10} Usually, *N*-alkoxyhydrazines are very unstable due to $n_N \rightarrow \sigma_{N-O(Alk)}^*$ orbital interaction within the N–OAlk bond.¹¹ Only one compound of this type 1 is known,¹¹ in which the donor capacity of nitrogen is decreased owing to its participation in aziridine cycle (Scheme 1). Tetramethoxyhydrazine 2 easily dissociates into two dimethoxyaminyl radicals on heating since its N–N bond is weakened by $n_{O(Me)} \rightarrow \sigma_{N-N}^*$ anomeric effect.^{3,4} The other *N*-alkoxy-*N*-alkylhydrazines are postulated as unstable primary intermediates in nucleophilic substitution at nitrogen atom in the reactions of *N*-chloro-*N*-alkoxy-*N*-*tert*-alkylamines with *N*-nucleophiles^{9,11} and in the reactions of *N*-acyloxy-*N*-alkoxybenzamides with anilines.^{12,13}

However, *N*-alkoxyhydrazines with electron-withdrawing substituents at both nitrogen atoms, such as *N,N'*-dialkoxy-*N,N'*-bis(alkoxycarbonyl)hydrazines¹⁴ and *N,N'*-diacyl-*N,N'*-dialkoxyhydrazines^{8,15,16} are relatively stable compounds. Among them, structure of *N,N'*-bis(4-chlorobenzoyl)-*N,N'*-diethoxyhydrazine 3 has been studied by XRD.⁸ For the further XRD studies of *N*-alkoxyhydrazines structures we selected *N,N'*-bis(methoxycarbonyl)-*N,N'*-dimethoxyhydrazine 5 and *N*-methoxyhydrazine 7. Compound 5 is major product of methanolysis of methyl *N*-chloro-*N*-methoxycarbamate 4 in the presence of Et₃N.¹⁷ Compound 7 was synthesized by the reaction of compound 4 with potassium salt of *N*-acetylbenzenesulfonylamide in MeCN (see Scheme 1).[‡]



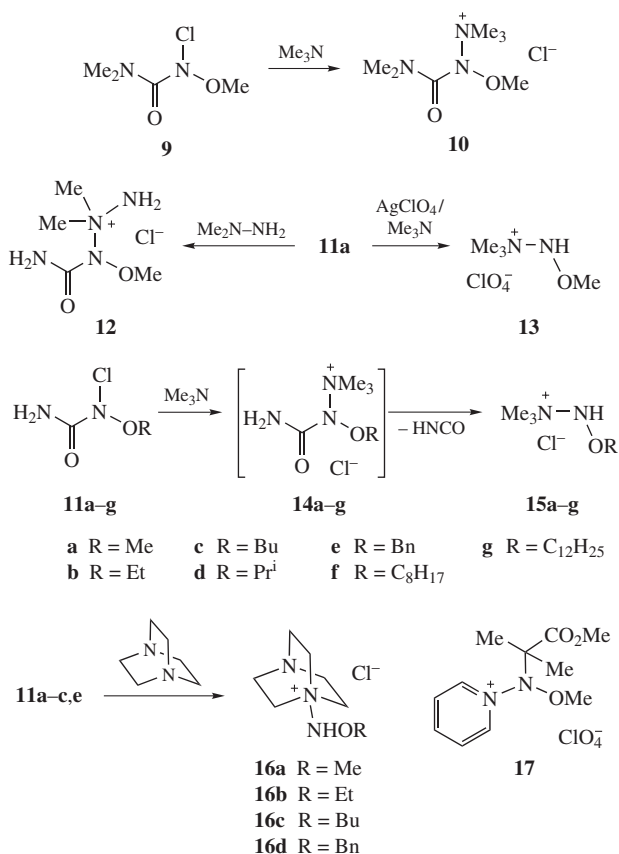
Scheme 1

[†] Geminal Systems. Part 63. For the previous communication, see ref. 1.

[‡] *N,N'*-Bis(methoxycarbonyl)-*N,N'*-dimethoxyhydrazine 5:¹⁷ the colourless crystals, mp 52–53 °C (hexane). ¹H NMR (400 MHz, CDCl₃) δ: 3.902 (s, 6H, NOME), 3.916 (s, 6H, CO₂Me). MS (FAB, NaI) *m/z* (%): 439 [2M+Na]⁺ (12), 231 [M+Na]⁺ (100).

N'-Methoxy-*N'*-methoxycarbonyl-*N*-acetylbenzenesulfonylhydrazide 7. The solution of methyl *N*-chloro-*N*-methoxycarbamate 4¹⁷ (0.541 g, 3.877 mmol) in MeCN (8 ml) was added to the mixture of (1.187 g, 4.996 mmol) potassium salt of *N*-acetylbenzenesulfonylamide and MeCN (11 ml). The reaction mixture was stirred at 20 °C for 32 h, the precipitate was filtered off and washed with MeCN (8 ml). The combined MeCN filtrate was evaporated *in vacuo*, the residue was extracted with benzene (20 ml), the extract was evaporated *in vacuo*, the residue was washed with

 Et₂O (6 ml) and dried *in vacuo* (2 Torr), yielding 0.53 g (45%) of the product 7, the colourless crystals, mp 114–115 °C (C₆H₆–C₆H₁₄). ¹H NMR (300 MHz, CDCl₃) δ: 2.28 [s, 3H, C(O)Me], 3.91 (s, 3H, NOME), 3.97 (br. s, 3H, CO₂Me), 7.57 (t, 2H, C³H, C⁵H, ³J 7.5 Hz), 7.68 (t, 1H, C⁴H, ³J 7.5 Hz), 8.12 (d, 2H, C²H, C⁶H, ³J 7.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 22.115 [C(O)Me], 55.101 (NOME), 62.338 (CO₂Me), 128.557, 129.439, 129.674, 134.205, 138.212 (C_{ip}⁶), 155.845 (C_{ip}⁶), 168.540 [C(O)Me], 183.442 (CO₂Me). MS (FAB, NaI) *m/z* (%): 325 [M+Na]⁺ (100). Found (%): C, 43.64; H, 4.72; N, 9.15; S, 11.02. Calc. for C₁₁H₁₄N₂O₄S (%): C, 43.70; H, 4.67; N, 9.27; S, 10.61. The ethereal extract was evaporated *in vacuo* to half volume and hexane (10 ml) was added. The formed precipitate was filtered off to give 0.161 g (14%) of product 7. The C₆H₁₄–Et₂O filtrate was evaporated *in vacuo*, yielding 0.110 g (27%) of compound 6.¹⁷



Scheme 2

Earlier,¹⁸ it was found that *N*-chloro-*N*-methoxy-*N*',*N*'-dimethylurea **9** on treatment with Me₃N yields hydrazonium derivative **10** (Scheme 2). *N*-Chloro-*N*-methoxyurea **11a** reacts with 1,1-dimethylhydrazine to form unstable salt **12**. However, on using excess of Me₃N in the presence of AgClO₄ compound **11a** is converted into 1,1,1-trimethyl-2-methoxyhydrazinium perchlorate **13**.² Similarly, reaction of *N*-chloro-*N*-alkoxyureas **11a-g** with Me₃N affords 1,1,1-trimethyl-2-alkoxyhydrazinium chlorides **15a-g**. Probably, the primary unstable intermediates **14a-g** eliminate HNCO yielding compounds **15a-g**. Analogously, *N*-chloro-*N*-alkoxyureas **11a-c,e** react with 1,4-diazabicyclo[2.2.2]octane giving 1-alkoxyamino-1-azonia-4-aza[2.2.2]bicyclooctanes chlorides **16a-d**.⁸ The structures of compounds **12**, **15a-g** and **16a-d** were characterized by ¹H NMR and MS spectra, the structure of compound **13** has been studied by XRD.

¹H NMR spectra of salts **15b,c,e** showed significant non-equivalence of geminal N-OCH₂R protons [²*J* = 32.8 (**15b**), 27.3 (**15c**) and 55.0 Hz (**15e**)]. The signals of N-OCH₂R protons appear as doublet of quartets (**15b**), doublet of triplets (**15c**), doublet of doublets (**15e**) and doublet of multiplets (**15f,g**).

XRD studies of compound **5**[†] (Figure 1) revealed that N(1) and N(1') atoms had the same pyramidal configuration. The sum

[§] 1,1,1-Trimethyl-2-methoxyhydrazinium perchlorate **13** was obtained from *N*-chloro-*N*-methoxyurea **11a** and AgClO₄ solution in Me₃N.²

For synthesis and characteristics of compounds **12**, **15** and **16**, see Online Supplementary Materials.

[†] Crystal data for **5**: C₆H₁₂N₂O₆ (from hexane, *M* = 208.18), monoclinic, space group *C2/c*, *a* = 14.3113(13), *b* = 8.5900(5) and *c* = 9.1538(7) Å, β = 118.918(11)°, *V* = 984.99(13) Å³, *F*(000) = 440, *d*_{calc} = 1.404 g cm⁻³, *Z* = 4, μ = 0.126 mm⁻¹.

Crystal data for **7**: C₁₁H₁₄N₂O₆S (from benzene-hexane, *M* = 302.30) monoclinic, space group *C2/c*, *a* = 12.7416(10), *b* = 6.9567(4), *c* = 30.729(2) Å, β = 92.436(7)°, *V* = 2721.4(3) Å³, *F*(000) = 1264, *d*_{calc} = 1.476 g cm⁻³, *Z* = 8, μ = 0.265 mm⁻¹.

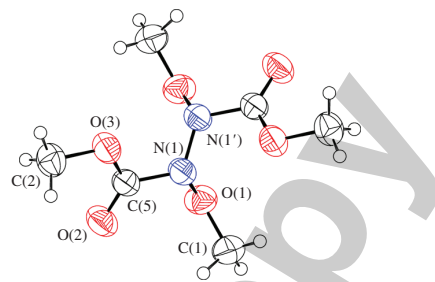


Figure 1 Molecular structure of compound **5**. Selected bond lengths (Å): N(1)–N(1') 1.366(2), N(1)–O(1) 1.4233(16), N(1)–C(5) 1.408(2), O(1)–C(1) 1.4340(19), C(2)–O(5) 1.1937(18), O(3)–C(2) 1.4507(18), O(3)–C(5) 1.3171(19); selected bond angles (°): N(1')–N(1)–O(1) 111.92(9), N(1')–N(1)–C(5) 116.59(15), C(5)–N(1)–O(1) 111.50(12).

of bond angles centered at these nitrogen atoms ($\Sigma\beta$) is 340.0(4)°, the deviation of N(1) atom from the plane of bonded with N(1) atoms (h_N) is 0.368(2) Å. In *N*-methoxy-*N*-(1-pyridinium)urea perchlorate **8**¹⁹ and its analogues² the pyramidity degree of such nitrogen atoms is higher [in **8** $\Sigma\beta$ is 333.9(3)° and h_N is 0.429(3) Å¹⁹]. In *N,N'*-diethoxyhydrazine **3** the nitrogen atoms have different and some smaller pyramidity degrees ($\Sigma\beta$ are 341.1° and 343.2°, h_N are 0.358 Å and 0.334 Å⁸).

In the crystal, the molecule of hydrazine **5** is situated in the particular site at the second order rotation axis, which continued from N(1)–N(1') bond center. The methoxy group C(1)–O(1) bond is parallel oriented to lone pair (Lp) of N(1) atom [the C(1)–O(1)–N(1)–LpN(1) torsion angle is 16°]. The MeOC(O) substituent is oriented perpendicular to LpN(1) [the O(2)–C(5)–N(1)–LpN(1) torsion angle is 95°]. The LpN(1) and LpN(1') are mutually turned [the LpN(1)–N(1)–N(1')–LpN(1') torsion angle is 77°]. Thus, the hydrazine **5** molecule has *sc*-conformation along the lines of N(1)–N(1') bond. *N,N'*-Bis(4-chlorobenzoyl)-*N,N'*-diethoxyhydrazine **3**⁸ and *N,N'*-dimesyl-*N,N'*-dimethoxyhydrazine²⁰ have the similar conformations.

The N(1)–N(1') bond is substantially shortened [1.366(2) Å] and O(1)–N(1) bond is some elongated [1.4233(16) Å] relative to the similar bonds in salt **8**¹⁹ [1.4254(18) Å for N–N⁺ bond and 1.3999(17) Å for N–O(Me) bond], and in *N*-methoxy-*N*-[1-(4-dimethylamino)pyridinium]urea chloride² [1.413(2) Å for N–N⁺ bond and 1.411(2) Å for N–O(Me) bond].

XRD studies of compound **7**[†] (Figure 2) revealed that the N(1) and N(2) atoms had different configurations. Atom N(1) atom has pyramidal configuration [$\Sigma\beta$ is 341.7(9)°, h_N is 0.351(4) Å], whereas atom N(2) has planar configuration [$\Sigma\beta$ is 360.0°]. The pyramidity degree of N(1) is similar to that in compound **3**.⁸ The lengths of N(1)–N(2) [1.379(4) Å] and N(1)–O(3)Me [1.414(4) Å] bonds are mediate to these parameters in compounds **5** and **3**⁸ [N–N, 1.389(3) Å; N–O(Et), 1.403(2) and 1.411(3) Å].

Crystal data for **13**: C₄H₁₃N₂O·ClO₄ (from CH₂Cl₂, *M* = 204.61), monoclinic, space group *P2₁/c*, *a* = 5.8068(5), *b* = 12.2167(8) and *c* = 13.6451(9) Å, β = 94.405(6)°, *V* = 965.13(12) Å³, *F*(000) = 432, *d*_{calc} = 1.408 g cm⁻³, *Z* = 4, μ = 0.387 mm⁻¹.

Data were measured using an Xcalibur 3 diffractometer (*T* = 298 K, graphite-monochromated MoKα radiation), 2θ/θ scan, 2θ_{max} = 57.6° (**5**), 56.24° (**7**), 58.0° (**13**). The structures were solved by direct method using the SHELXTL PLUS program package.²³ Refinement against *F*² in an anisotropic approximation (the hydrogen atoms isotropic in the riding model) by a full matrix least-squares method was carried out for 3784 reflections to *wR*₂ = 0.136 [*R*₁ = 0.041 for 788 reflections with *F* > 4σ(*F*), *S* = 1.05] for **5**, 3101 reflections to *wR*₂ = 0.171 [*R*₁ = 0.071 for 1887 reflections with *F* > 4σ(*F*), *S* = 1.07] for **7**, and 2337 reflections to *wR*₂ = 0.175 [*R*₁ = 0.054 for 1696 reflections with *F* > 4σ(*F*), *S* = 1.04] for **13**.

CCDC 942261–942263 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2013.

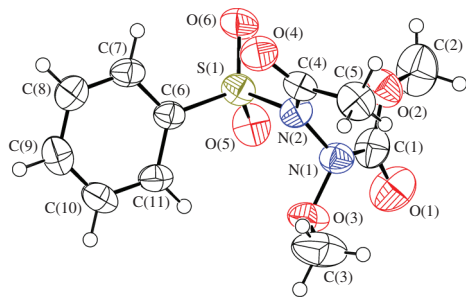


Figure 2 Molecular structure of compound **7**. Selected bond lengths (Å): N(1)–N(2) 1.379(4), N(1)–O(3) 1.414(4), N(1)–C(1) 1.398(5), N(2)–C(4) 1.411(4), C(1)–O(1) 1.196(4), C(4)–O(4) 1.193(4), N(2)–S(1) 1.723(3); selected bond angles (°): N(2)–N(1)–O(3) 112.1(3), N(2)–N(1)–C(1) 118.0(3), O(3)–N(1)–C(1) 111.6(3), N(1)–N(2)–S(1) 119.0(2), N(1)–N(2)–C(4) 120.2(3), C(4)–N(2)–S(1) 120.8(2).

In compound **7** the O(3)–C(3) bond has *sp*-orientation toward LpN(1) [the C(3)–O(3)–N(1)–LpN(1) torsion angle is 17°]. The C(1)=O(1) and C(4)=O(4) carbonyl groups are perpendicular oriented toward adjacent LpN [the O(1)–C(1)–N(1)–LpN(1) torsion angle is 89°, the O(4)–C(4)–N(2)–N(1) torsion angle is 169.1(3)°]. The LpN(1) and LpN(2) have mutual orthogonal orientation [the C(4)–N(2)–N(1)–LpN(1) torsion angle is –8°].

The XRD data for compound **13**^{II} (Figure 3) revealed that N(1)–N(2)⁺ bond is elongated to 1.483(3) Å compared to N–N bond length in hydrazine (1.466 Å)²¹ and N–N⁺ bond length in salt **17** [1.466(2) Å].²² The length of N(1)–N(2)⁺ bond in salt **13** is similar to the N–N bond length in tetramethoxyhydrazine (1.484 Å).⁴ In compound **13** the N(1)–O(1)Me bond is strongly shortened [1.391(3) Å] compared to that in compound **17** [1.4142(16) Å].²² The N(1) atom is strongly pyramidal, $\Sigma\beta$ is 312°. This is in accordance with significant geminal non-equivalence of N–OCH₂R protons in ¹H NMR spectra of hydrazinium salts **15**. The C(1)–O(1)Me bond is parallel oriented towards LpN(1) [the C(1)–O(1)–N(1)–LpN(1) torsion angle is –1.4°].

Thus, the study of structures of compounds **5**, **7** and **13** has revealed the pyramidal configuration of the central nitrogen

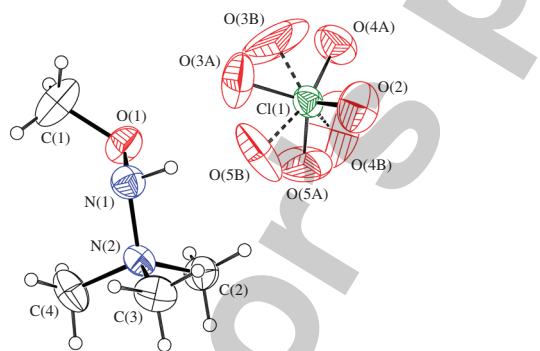


Figure 3 Molecular structure of compound **13**. Selected bond lengths (Å): N(1)–N(2) 1.483(3), O(1)–N(1) 1.391(3), O(1)–C(1) 1.446(4), N(2)–C(2) 1.491(3), N(2)–C(3) 1.500(4), N(2)–C(4) 1.481(4); selected bond angles (°): O(1)–N(1)–N(2) 107.12(19), N(1)–O(1)–C(1) 109.1(3), N(1)–N(2)–C(2) 113.4(2), N(1)–N(2)–C(3) 102.9(2).

atoms in O–N–N geminal system, unusual elongating of N–N⁺ bond and shortening of N–OMe bond in salt **13**.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.09.018.

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