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1-Alkoxyamino-4-dimethylaminopyridinium derivatives as new representatives of O-N-N^+ geminal systems and their structure

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Experimental

N-*Methoxy*-N-*(4-dimethylaminopyridin-1-ium-1-yl)urea chloride* **2**. The solution of DMAP (0.159 g, 1.300 mmol) in MeCN (5 ml) was added to the solution of *N*-chloro-*N*-methoxyurea **1**[1] (0.157 g, 1.261 mmol) in MeCN (5 ml) at −25°C. The reaction mixture was slowly heated to 20 °C within 20 h. The precipitate formed was filtered off and washed with CH_2Cl_2 (2 ml), dried *in vacuo* (2 Torr), yielding 0.285 g (92%) urea **2**, colourless crystals, mp 148−149°C (decomp.). ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 3.26 (s, 6H, NMe_2); 3.59 (s, 3H, OMe); 7.05 (d, 2H, C(3)H,C(5)H, ^3J 7.8 Hz); 8.45 (d, 2H, C(2)H,C(6)H, ^3J 7.8 Hz); 10.95(s, 1H, NH); 11.18 (s, 1H, NH). IR (υ, cm^{-1}): 3300, 3230 (NH_2), 1725 (C=O), 1628 ($C=N^+Me_2$). MS (FAB): 211 [M^+] (100). Found (%): C 40.52; H 6.69; N 21.25. Calc. for $C_9H_{15}ClN_4O_2 \cdot H_2O$ (%): C 40.84; H 6.47; N 21.17. N-*Propoxy*-N-*(4-dimethylaminopyridin-1-ium-1-yl)*-N',N'-*dimethylurea chloride* **4a** was similarly obtained from *N*-chloro-*N*-propoxy-*N',N'*-dimethylurea **3**,[2] yield 97%, colourless hygroscopic crystals. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 0.85 (t, 3H, $NOCH_2CH_2\mathit{Me}$, ^3J 7.2 Hz); 1.55 (sex, 2H, $NOCH_2\mathit{CH_2}Me$, ^3J 7.2 Hz); 3.05 (br. s, 6H, $C(O)NMe_2$); 3.29 (s, 6H, $Py\mathit{NMe_2}$); 3.92 (t, 2H, $NOCH_2$, ^3J 7.2 Hz); 7.08 (d, 2H, C(3)H, C(5)H, ^3J 7.8 Hz); 8.46 (d, 2H, C(2)H, C(6)H, ^3J 7.8 Hz). IR (υ, cm^{-1}): 1720 (C=O), 1645 ($C=N^+Me_2$). MS (FAB): 267 [M^+] (100).

N-*Propoxy*-N-*(4-dimethylaminopyridin-1-ium-1-yl)*-N',N'-*dimethylurea perchlorate* **4b** The solution of $AgClO_4$ (0.101 g, 0.488 mmol) in MeCN (3 ml) was added to the solution of urea **4a** (0.148 g, 0.488 mmol) in MeCN (5 ml). The precipitate of AgCl was filtered off, washed with MeCN (2 ml), the filtrate was evaporated *in vacuo*, yielding 0.175 g (97.8 %) urea **4b**, colourless crystals, mp 150−152°C (decomp.) (CH_2Cl_2–C_6H_{14}). ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 0.85 (t, 3H, $NOCH_2CH_2\mathit{Me}$, ^3J 7.2 Hz); 1.54 (sex, 2H, $NOCH_2\mathit{CH_2}Me$, ^3J 7.2 Hz); 3.04 (br. s, 6H, $C(O)NMe_2$); 3.29 (s, 6H, $Py\mathit{NMe_2}$); 3.92 (t, 2H, $NOCH_2$, ^3J 7.2 Hz); 7.07 (d, 2H,

C(3)H,C(5)H, ^3J 7.8 Hz); 8.46 (d, 2H, C(2)H, C(6)H, ^3J 7.8 Hz). Found (%): C 42.31; H 6.57; N 15.19. Calc. for $C_{13}H_{23}ClN_4O_6\cdot$(%): C 42.57; H 6.32; N 15.27.

N-*Chloro*-N-*methoxybenzamide* **5** was prepared by general procedure of *N*-chloro-*N*-alkoxyamides synthesis[3] as viscous pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 3.92 (s, 3H, OMe); 7.51 (t, 2H, C(3)H, C(5)H, ^3J 7.2 Hz), 7.62 (t, 1H, C(4)H, ^3J 7.2 Hz); 8.12 (d, 2H, C(2)H, C(6)H, ^3J 7.2 Hz). N-*Methoxy*-N-*(4-dimethylaminopyridin-1-ium-1-yl)benzamide chloride* **7**. The solution of DMAP (0.123 g, 1.095 mmol) in Et_2O (7 ml) was added to the solution of *N*-chloro-*N*-methoxybenzamide **5** (0.191 g, 1.027 mmol) in Et_2O (2 ml) at −20˚C. The reaction mixture was kept at 22˚C for 20 h, the precipitate was filtered off, washed with Et_2O (5 ml), dried *in vacuo*, yielding 0.310 g (98%) of benzamide **7**, colourless hygroscopic crystals, unstable. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 3.33 (s, 6H, NMe_2); 3.91 (s, 3H, OMe); 7.22 (d, 2H, C(3)H, C(5)H (Py), ^3J 8.1 Hz); 7.63 (t, 2H, C(3)H, C(5)H, ^3J 7.35 Hz); 7.74 (t, 1H, C(4)H, ^3J 7.35 Hz); 7.88 (d, 2H, C(2)H, C(6)H, ^3J 7.35 Hz); 8.73 (d, 2H, C(2)H, C(6)H (Py), ^3J 8.1 Hz). IR (υ, cm^{-1}): 1709 (C=O), 1643 (C=N^+Me_2). Found (%): Cl 11.25. Calc. for $C_{15}H_{18}ClN_3O_2$ (%): Cl 11.52. In a similar way, N-*ethoxy*-N-*(4-dimethylaminopyridin-1-ium-1-yl)benzamide chloride* **8** was obtained in 65% yield, colourless hygroscopic crystals, unstable. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 1.11 (t, 3H, $NOCH_2$*Me*, ^3J 7.2 Hz); 3.32 (s, 6H, NMe_2); 4.23 (q, 2H, NO*CH*$_2$Me, ^3J 7.2 Hz); 7.19 (d, 2H, C(3)H, C(5)H (Py), ^3J 8.4 Hz); 7.64 (t, 2H, C(3)H, C(5)H, ^3J 7.2 Hz); 7.73 (t, 1H, C(4)H, ^3J 7.2 Hz); 7.87 (d, 2H, C(2)H, C(6)H, ^3J 7.2 Hz); 8.72 (d, 2H, C(2)H, C(6)H (Py), ^3J 8.4 Hz). MS (FAB): 286 [M^+] (8.0); 182 (100).

*Methyl 3-[*N-*methoxy*-N-*(4-dimethylaminopyridin-1-ium-1-yl)amino]-3-methylbutanoate chloride* **10a**. The solution of DMAP (0.387 g, 3.166 mmol) in MeCN (5 ml) was added to the solution of methyl 3-(*N*-chloro-*N*-methoxyamino)-3-methylbutanoate **9**[17] (0.619 g, 3.166 mmol) in MeCN (5 ml) at - 27˚C, the reaction mixture was slowly warmed to 17°C within 17 h, then it was concentrated *in vacuo* to 3 ml volume, Et_2O (25 ml) was then added. The obtained precipitate was filtered off, dried at 1 Torr, extracted with CH_2Cl_2 (4 ml). To the CH_2Cl_2-extract hexane (5 ml) was added, the precipitated oil was separated, dried at 1 Torr, yielding 0.728 g (72%) of the product **10a**, viscous colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): 1.26 (br. s, 6H, Me_2C); 2.55 (br. s, 2H, CH_2); 3.40 (s, 6H, NMe_2); 3.54 (s, 3H, OMe); 3.70 (s, 3H, CO_2Me); 7.30 – 7.40 (m, 2H, C(3)H, C(5)H); 8.28 – 8.42 (m, 2H, C(2)H, C(6)H). MS (FAB): 282 [M^+] (100). Found (%): Cl 10.85. Calc. for $C_{14}H_{24}ClN_3O_3\cdot$(%): Cl 11.16. *Methyl 3-[*N-*methoxy*-N-*(4-dimethylaminopyridin-1-ium-1-yl)amino]-3-methylbutanoate perchlorate* **10b**. The solution of $AgClO_4$ (0.0982 g, 0.474 mmol) in MeOH (4 ml) was added to the solution of chloride **10a** (0.151 g, 0.474 mmol) in MeOH (4 ml), AgCl was filtered out, washed by MeOH (10 ml). The combined MeOH filtrate was evaporated *in vacuo*, dried at 2 Torr, yielding 0.165 g (91%)

perchlorate **10b** as oil, after CH_2Cl_2–C_6H_{14} crystallization as colourless crystals, mp 78−80°C. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 1.22 (br. s, 6H, Me_2C); 2.63 (br. s, 2H, CH_2); 3.27 (s, 6H, NMe_2); 3.52 (s, 3H, OMe); 3.66 (s, 3H, CO_2Me); 7.02 (d, 2H, C(3)H, C(5)H, ^3J 7.2 Hz); 8.43 (d, 2H, C(2)H, C(6)H, ^3J 7.2 Hz). MS (FAB): 282 [M^+] (100). *Attempted methanolysis of* **10b**. The solution of perchlorate **10b** (0.0338 g, 0.0885 mmol) and AcONa (0.030g, 0.3658 mmol) in MeOH (3 ml) was kept at 20−23°C for 144 h, then it was evaporated *in vacuo*, the residue was extracted with CH_2Cl_2 (15 ml), the extract was evaporated *in vacuo* yielding 0.0328 g (97%) of the unconverted compound **10b**.

1,1,1-Trimethyl-2-methoxyhydrazinium perchlorate **13**. A solution of 3-*N*-chloro-*N*-methoxyurea **1** (0.338 g, 2.714 mmol) in MeCN (6 ml) was added to a solution of trimethylamine (2.24 g, 37.64 mmol) and $AgClO_4$·3MeCN (0.896 g, 2.712 mmol) in MeCN (10 ml) at −29°C, the reaction mixture was allowed to slowly warm up to 17 °C within 19 h, AgCl was filtered off, the filtrate was evaporated *in vacuo*, the residue was stirred with $NaHCO_3$/MeCN−H_2O, the solvent was then evaporated *in vacuo*, the residue was extracted with MeCN (10 ml), the extract was evaporated *in vacuo* and dried at 1 Torr to yield 0.305 g (55%) of the product **13**, colourless crystals. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): 2.995 (s, 9H, Me_3N^+), 3.773 (s, 3H, NOMe), 9.168 (s, 1H, NH). MS (FAB, H^+): 311 [$2M^+ \cdot ClO_4^-$] (5), 309 [$2M^+ \cdot ClO_4^-$] (13), 105 [M^+] (100), 58(26). Found (%): N 13.20. Calc. for $C_4H_{13}ClN_2O_5$·(%): N 13.69.

Crystal data

Data were measured using an Xcalibur 3 diffractometer [298 K, graphite-monochromated MoK_α radiation, $2\theta/\theta$ scan, $2\theta_{max}$=60° (**2**), 55° (**4b**), 55° (**10b**)]. The structures were solved by direct method using the SHELXTL PLUS program package.[4] Refinement against F^2 in an anisotropic approximation (the hydrogen atoms isotropic in the riding model) by a full matrix least-squares method for 3701 reflections was carried out to wR_2=0.1335 [R_1=0.0490 for 2640 reflections with $F>4\sigma(F)$, S=1.031] for **2**, and for 4246 reflections was carried out to wR_2=0.207 [R_1=0.060 for 2576 reflections with $F>4\sigma(F)$, S=1.00] for **4b**, and for 4218 reflections was carried out to wR_2=0.087 [R_1=0.041 for 2182 reflections with $F>4\sigma(F)$, S=0.99] for **10b**.

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