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1-Alkoxyamino-4-dimethylaminopyridinium salts: synthesis and structure

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In molecule of compound **5a** Lp of N(2) atom lies in the plane of pyridine ring [the torsion angle Lp(N2)–N(2)–N(1)–C(5) is -4°]. Such an LpN orientation is typical of 1-(*N*-alkoxyamino)pyridium salts **1**,**2**.[1-3] Methoxy moiety is in –*sc*-conformation towards the N(1)–C(1) bond [the torsion angle C(1)–N(1)–N(2)–O(1) is -57.4(2)°], methyl group has orthogonal orientation to N(1)–N(2) bond [the torsion angle C(6)–O(1)–N(2)–N(1) is 92.0(1)°], and dimethylamino group is slightly turned round the cycle plane [the torsion angle C(7)–N(3)–C(3)–C(2) is 8.0(2)°].

In the crystal the cation and anion are bonded *via* strong intermolecular hydrogen bond N(2)–H…Cl(1)’ (1.5-x, -0.5+y, 0.5-z) H…Cl 2.31 Å, N–H…Cl 178°, as well as weak hydrogen bond C(2)–H…Cl(1)’ (0.5+x, 1.5-y, 0.5+z) H…Cl 2.90 Å, C–H…Cl 134°.

In molecule of compound **5b** Lp(N2) somewhat deviates from the plane of pyridine ring [the torsion angle Lp(N2)–N(2)–N(1)–C(1) is 17°]. Ethoxy group has –*ac*-orientation towards the N(1)–C(1) bond [the torsion angle C(1)–N(1)–N(2)–O(1) is -111.2(1)°]. The ethyl group is orthogonally oriented in respect to the N(2)–N(1) bond [the torsion angle C(6)–O(1)–N(2)–N(1) is 90.48(9)°]. The C(6)–C(7) bond has *ap*-orientation toward the N(2)–O(1) bond [the torsion angle N(2)–O(1)–C(6)–C(7) is 168.38(9)°].

Dimethylamino group lies in the plane of pyridine ring [the torsion angle C(8)–N(3)–C(3)–C(2) is 0.5(2)°], whereas some steric repulsion between Me_2N group atoms and C_{arom} and H_{arom} atoms occurs (the shortened intramolecular contacts H(9c)…C(4) 2.75 Å, H(8a)…C(2) 2.72 Å, H(4)…C(9) 2.48 Å, and H(2)…C(8) 2.55 Å (the van der Waals radius sum is 2.87 Å[4]). In the molecule of 5**b** the cation and anion are bonded by strong intermolecular hydrogen bond N(2)–H…Cl(1)’ H…Cl 2.24 Å, N–H…Cl 173°.

Experimental

N-*(4-Dimethylaminopyridin-1-ium-1-yl)*-N-*methoxybenzamide chloride* **3a**.
^{1}H NMR (300 MHz, (CD$_3$)$_2$SO): 3.33 (s, 6H, NMe$_2$); 3.91 (s, 3H, NOMe); 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 7.2 Hz); 7.74 (t, 1H, C(4)H, ^3J 7.2 Hz); 7.88 (d, 2H, C(2)H, C(6)H, ^3J 7.2 Hz); 8.72(d, 2H, C(2)H,C(2H Py, ^3J 8.1 Hz). ^{13}C NMR (75 MHz, (CD$_3$)$_2$SO, APT regime): 40.6 (NMe$_2$); 62.3 (NOMe); 108.1 (C-3,5 Py); 128.6, 128.9 (C-2,3,5,6 Ph);130.5 (C-1 Ph); 133.4 (C-4 Ph); 142.3 (C-2,6 Py); 156.8 (C-4 Py); 171.5 (C=O). MS (FAB, m/z, I$_{rel.}$(%)): 272 M$^+$ (100), 241 [M-MeO]$^+$ (17), 168 (8), 123(15), 122(17).

1-Isopropyloxyamino-4-dimethylaminopyridinium chloride **5c**.
Yield 81%, colorless crystals, mp175–177 °C (MeCN – Et$_2$O) (decomp.). ^{1}H NMR (300 MHz, (CD$_3$)$_2$SO): 1.13 (d, 6H, NOCH*Me*$_2$, ^3J 5.7 Hz); 3.25 (s, 6H, NMe$_2$); 4.04 (sept, 1H, NO*CH*Me$_2$, ^3J 5.7 Hz); 7.01 (d, 2H, C(3)H, C(5)H, ^3J 7.5 Hz); 8.43 (d, 2H, C(2)H, C(6)H, ^3J 7.5 Hz); 10.58 (s, 1H, NHO). ^{13}C NMR (75 MHz, CDCl$_3$): 21.12 (NOCH*Me*$_2$); 40.70 (NMe$_2$); 75.15 (NO*C*HMe$_2$); 107.24 (C(3), C(5)); 142.26 (C(2), C(6)); 156.81 (C(4)). MS (FAB, m/z, I$_{rel.}$(%)): 429 [2M$^+\cdot$Cl$^-$] (2), 427 [2M$^+\cdot$Cl$^-$] (5), 196 M$^+$ (100), 137 (10), 123 (14). Found (%): N 18.01; Cl 15.25. Calc. for $C_{10}H_{18}ClN_3O$ (%): N 18.13; Cl 15.30.

1-Butyloxyamino-4-dimethylaminopyridinium chloride (monohydrate) **5d**·H$_2$O.
Yield 46%, hygroscopic colorless crystals, mp 49–51 °C (monohydrate). ^{1}H NMR (300 MHz, (CD$_3$)$_2$SO):0.86 (t, 3H, NOCH$_2$CH$_2$CH$_2$*Me*, ^3J 7.5 Hz); 1.27 (sex, 3H, NOCH$_2$CH$_2$*CH*$_2$Me, ^3J 7.5 Hz); 1.51 (quint, 3H, NOCH$_2$*CH*$_2$CH$_2$Me, ^3J 7.5 Hz); 3.25 (s, 6H, NMe$_2$); 3.79 (t, 2H, NOCH$_2$, ^3J 6.3 Hz); 7.05 (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); 11.00 (s, 1H, NHO). ^{13}C NMR (75 MHz, CDCl$_3$): 13.52 (NO(CH$_2$)$_3$*Me*); 18.76 (NO(CH$_2$)$_2$$\underline{C}H_2$Me); 30.12 (NOCH$_2$$\underline{C}H_2CH_2$Me); 40.68 (NMe$_2$); 73.27 (NO*C*H$_2$Pr); 107.30 (C(3), C(5)); 142.37 (C(2), C(6)); 156.97 (C(4)). Found (%): N 15.98; Cl 13.16. Calc. for $C_{11}H_{20}ClN_3O$ H_2O (%): N 15.93; Cl 13.44.

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