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# 4-Amino-1-(5-nitro-2-pyridyloxy)pyridinium Chloride

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**Abstract.** $C_{10}H_9N_4O_3^+.Cl^-$, $M_r = 268{\cdot}7$, orthorhombic, $Pna2_1$, $a = 12{\cdot}7974$ (8), $b = 11{\cdot}8401$ (8), $c = 7{\cdot}7697$ (6) Å, $V = 1177{\cdot}3$ (2) Å$^3$, $Z = 4$, $D_x = 1{\cdot}516$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 30{\cdot}0$ cm$^{-1}$, $F(000) = 552$, $T = 293$ K, $R = 0{\cdot}0343$ for 1269 reflections. The title compound is a condensation product of 2-chloro-5-nitropyridine with 4-aminopyridine 1-oxide. The dihedral angle between the two pyridine planes is 80·3 (1)°; the N(1)—O(1) and O(1)—C(6) bonds connecting the pyridine rings lie almost in the nitropyridine plane. The $Cl^-$ ions are hydrogen bonded to the aminopyridine N—H and C—H atoms of adjacent molecules.

**Experimental.** As part of an investigation into the chemistry of ambident nucleophiles we have studied the reaction of 4-aminopyridine 1-oxide with some electrophiles. The title compound was formed by condensation of 2-chloro-5-nitropyridine with 4-aminopyridine 1-oxide under the conditions described previously (Kalinowski, Rykowski & Nantka-Namirski, 1984). Since chemical and spectroscopic data were inconclusive as regards the structure of the molecule, a crystallographic study of the compound was undertaken.

Colorless prismatic crystals were grown by slow evaporation from methanol solution. $D_m$ was not measured. A crystal 0·22 × 0·30 × 0·15 mm was used for diffractometer measurements. Data were collected with an Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation and graphite monochromator; $\omega$–$2\theta$ scan method. Unit-cell parameters were refined from the setting angles of 25 reflections having $20 < \theta < 29°$. 1433 reflections were measured with $2 < \theta < 75°$; index ranges: $h$ 0/16, $k$ 0/14, $l$ 0/9; no significant intensity variation for three standard reflections; no absorption correction. Systematic absences: $0kl$ for $k + l$ odd, $h0l$ for $h$ odd indicated the space groups $Pna2_1$ or $Pnam$ ($Pnma$ reoriented); successful refinement in non-centrosymmetric space group; 1294 unique reflections of which 1275 had $F > 3\sigma(F)$. Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined with *SHELX*76 (Sheldrick, 1976) programs; full-matrix least-squares refinement on $F$ with anisotropic thermal parameters for non-H atoms. All H atoms were located from difference maps and refined with isotropic thermal parameters. Six reflections with max. $\Delta F/\sigma(F)$ were omitted in the last cycles. Weighting scheme $w = 0{\cdot}6759/[\sigma^2(F) + 0{\cdot}002450F^2]$; empirical extinction correction $F_{\rm corr} = F(1 - xF^2/\sin\theta)$, $x = 1{\cdot}09\ (7) \times 10^{-5}$. Final $R = 0{\cdot}0343$ for 1299 reflections and 199 variables, $wR = 0{\cdot}0416$, $S = 0{\cdot}9182$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}021$ in final cycle; max. and min. heights in final difference Fourier map 0·19 and −0·31 e Å$^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Refinement using $-x$, $-y$, $-z$ coordinates gave an identical $R$ value, so the absolute structure of the particular crystal used cannot be determined from the available data. Calculations performed using

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$ × 10$^4$) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Cl | −0·00435 (4) | −0·29876 (5) | 0·7107* | 445 (2) |
| O(1) | −0·0083 (1) | −0·0257 (2) | 0·4645 (3) | 448 (6) |
| O(2) | −0·2808 (2) | −0·3357 (2) | 0·0113 (5) | 719 (8) |
| O(3) | −0·1407 (2) | −0·4363 (1) | 0·0278 (4) | 561 (6) |
| N(1) | 0·1007 (1) | −0·0225 (2) | 0·4572 (4) | 386 (5) |
| N(2) | 0·0095 (1) | −0·1766 (2) | 0·2736 (3) | 388 (6) |
| N(11) | 0·4166 (2) | −0·0022 (2) | 0·4536 (4) | 464 (6) |
| N(21) | −0·1915 (2) | −0·3522 (2) | 0·0631 (4) | 448 (6) |
| C(1) | 0·1455 (2) | 0·0571 (2) | 0·3562 (4) | 402 (7) |
| C(2) | 0·2512 (2) | 0·0652 (2) | 0·3531 (4) | 395 (7) |
| C(3) | 0·3133 (2) | −0·0088 (2) | 0·4543 (4) | 374 (7) |
| C(4) | 0·2607 (2) | −0·0892 (2) | 0·5581 (4) | 399 (7) |
| C(5) | 0·1550 (2) | −0·0948 (2) | 0·5567 (4) | 406 (7) |
| C(6) | −0·0519 (2) | −0·1098 (2) | 0·3612 (3) | 362 (5) |
| C(7) | −0·1610 (2) | −0·1119 (2) | 0·3646 (4) | 413 (7) |
| C(8) | −0·2083 (2) | −0·1924 (2) | 0·2647 (4) | 426 (7) |
| C(9) | −0·1442 (2) | −0·2653 (2) | 0·1717 (3) | 376 (7) |
| C(10) | −0·0372 (2) | −0·2565 (2) | 0·1779 (3) | 412 (7) |

* Fixed coordinate to define the origin.

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Table 2. *Molecular geometry*

Bond distances (Å)

| | | | |
|---|---|---|---|
| O(1)—N(1) | 1·396 (2) | N(21)—C(9) | 1·462 (3) |
| O(1)—C(6) | 1·395 (3) | C(1)—C(2) | 1·356 (3) |
| O(2)—N(21) | 1·227 (3) | C(2)—C(3) | 1·421 (3) |
| O(3)—N(21) | 1·221 (3) | C(3)—C(4) | 1·417 (3) |
| N(1)—C(1) | 1·354 (3) | C(4)—C(5) | 1·355 (3) |
| N(1)—C(5) | 1·346 (3) | C(6)—C(7) | 1·397 (3) |
| N(2)—C(6) | 1·307 (3) | C(7)—C(8) | 1·370 (4) |
| N(2)—C(10) | 1·343 (3) | C(8)—C(9) | 1·393 (3) |
| N(11)—C(3) | 1·324 (3) | C(9)—C(10) | 1·375 (3) |

Bond angles (°)

| | | | |
|---|---|---|---|
| N(1)—O(1)—C(6) | 113·3 (2) | N(11)—C(3)—C(4) | 121·1 (2) |
| O(1)—N(1)—C(5) | 118·4 (2) | C(3)—C(4)—C(5) | 120·2 (2) |
| O(1)—N(1)—C(1) | 117·7 (2) | N(1)—C(5)—C(4) | 119·3 (2) |
| C(1)—N(1)—C(5) | 123·8 (2) | O(1)—C(6)—N(2) | 119·4 (2) |
| C(6)—N(2)—C(10) | 116·6 (2) | N(2)—C(6)—C(7) | 126·9 (2) |
| O(2)—N(21)—O(3) | 123·6 (2) | O(1)—C(6)—C(7) | 113·7 (2) |
| O(3)—N(21)—C(9) | 118·9 (2) | C(6)—C(7)—C(8) | 116·3 (2) |
| O(2)—N(21)—C(9) | 117·6 (2) | C(7)—C(8)—C(9) | 117·7 (2) |
| N(1)—C(1)—C(2) | 118·9 (2) | N(21)—C(9)—C(8) | 119·5 (2) |
| C(1)—C(2)—C(3) | 120·2 (2) | C(8)—C(9)—C(10) | 121·4 (2) |
| N(11)—C(3)—C(2) | 121·3 (2) | N(21)—C(9)—C(10) | 119·1 (2) |
| C(2)—C(3)—C(4) | 117·6 (2) | N(2)—C(10)—C(9) | 121·1 (2) |

Hydrogen-bond parameters (Å, °)

| *A*—H···*B* | *A*—H | H···*B* | *A*···*B* | *A*—H···*B* |
|---|---|---|---|---|
| C(5)—H···Cl$^{i}$ | 0·94 (4) | 2·48 (3) | 3·380 (3) | 159 (4) |
| C(4)—H···Cl$^{ii}$ | 0·88 (5) | 2·73 (4) | 3·494 (3) | 146 (4) |
| N(11)—H(11)···Cl$^{ii}$ | 0·85 (4) | 2·41 (4) | 3·251 (3) | 169 (4) |
| N(11)—H(12)···Cl$^{iii}$ | 1·04 (3) | 2·23 (3) | 3·260 (3) | 172 (3) |

Symmetry code: (i) $x, y, z$; (ii) $x+\frac{1}{2}, -y-\frac{1}{2}, z$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$.

*CRYSRULER* programs (Rizzoli, Sangermano, Calestani, Andreetti, 1986). The final atomic parameters are listed in Table 1,* bond distances, angles and hydrogen bonds in Table 2. Fig. 1 shows a view of the molecule with the numbering of the atoms.

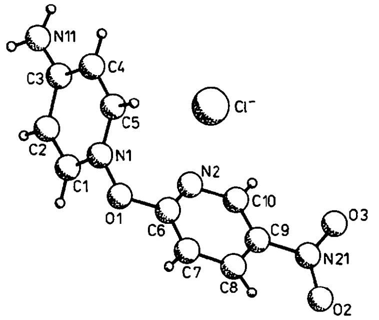

Fig. 1. A view of the molecule with the numbering of the atoms.

**Related literature.** Preparation of similar compounds is given in Kalinowski, Rykowski & Nantka-Namirski (1984).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53490 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Structure of 2,9-Dimethyl-1,10-phenanthroline Hemihydrate

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**Abstract.** $C_{14}H_{12}N_2.\frac{1}{2}H_2O$, $M_r = 217{\cdot}27$, tetragonal, $I4_1/a$, $a = 14{\cdot}258\ (3)$, $c = 22{\cdot}286\ (4)$ Å, $V = 4531\ (3)$ Å$^3$, $Z = 16$, $D_x = 1{\cdot}274\ (1)$ g cm$^{-3}$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}74$ cm$^{-1}$, $F(000) = 1840$, $T = 297$ K, $R = 0{\cdot}041$ for 1196 unique observed reflections with $I > 2\sigma(I)$. Pairs of dimethylphenanthroline molecules related by a twofold axis are bridged by water molecules lying on the