# The Structures of the Intermediates Formed in the Ring-Opening Reaction of 2-chloro-3-nitropyridine

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Compound 3-pentenenitrile, 2-nitro-5-oxo, ion(-1), sodium

**Table S1. Crystal data**

| | |
|---|---|
| $Na^{1+}.C_5H_3N_2O_3^{1-}.H_2O$ | $V$ = 357.98 (14) Å$^3$ |
| $M_r$ = 180.10 | $Z$ = 2 |
| Triclinic, $P$-1 | $D_x$ = 1.671 Mg m$^{-3}$ |
| $a$ = 3.5647 (8) Å | Mo $K\alpha$ radiation |
| $b$ = 10.192 (2) Å | Cell parameters from 1846 reflections |
| $c$ = 10.679 (2) Å | θ = 2.4–28.3° |
| α = 109.196 (4)° | μ = 0.19 mm$^{-1}$ |
| β = 98.770 (4)° | $T$ = 93 (2) K |
| γ = 95.216 (4)° | Plate, yellow |

**Table S2. Data collection**

| | |
|---|---|
| CCD area detector diffractomer | 1263 reflections with $I > 2\sigma(I)$ |
| phi and ω scans | $R_{int}$ = 0.030 |
| Absorption correction: multi-scan (based | $\theta_{max}$ = 28.3° |
| on symmetry-related measurements) | |
| $T_{min}$ = 0.679, $T_{max}$ = 0.970 | $h$ = -4 → 4 |
| 3150 measured reflections | $k$ = -12 → 13 |
| 1726 independent reflections | $l$ = -13 → 14 |

**Table S3. Refinement**

| | |
|---|---|
| Refinement on $F^2$ | Mixture of independent and constrained H-atom refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.053$ | Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.1324P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.136$ | $(\Delta/\sigma)_{max} < 0.0001$ |
| $S = 1.07$ | $\Delta\rho_{max} = 0.35$ e Å$^{-1}$ |
| 1726 reflections | $\Delta\rho_{min} = -0.35$ e Å$^{-1}$ |
| 124 parameters | Extinction correction: none |

**Table S4. Geometric parameters (Å, °)**

| | | | |
|---|---|---|---|
| N1—C1 | 1.150 (3) | C3—C4 | 1.361 (3) |
| N1—Na1 | 2.463 (2) | C4—C5 | 1.421 (3) |
| C1—C2 | 1.418 (3) | O5—C5 | 1.249 (3) |
| C2—N2 | 1.378 (3) | O5—Na1$^{i}$ | 2.4022 (19) |
| C2—C3 | 1.408 (3) | O5—Na1$^{ii}$ | 2.4047 (19) |
| N2—O2B | 1.246 (2) | O5—Na1$^{iii}$ | 2.519 (2) |
| N2—O2A | 1.264 (3) | Na1—O1W | 2.379 (2) |

| | | | |
|---|---|---|---|
| N2—C2—C3 | 120.97 (19) | O2A—N2—C2 | 118.74 (18) |
| N2—C2—C1 | 114.7 (2) | C4—C3—C2 | 125.8 (2) |
| C3—C2—C1 | 124.2 (2) | C3—C4—C5 | 117.4 (2) |
| O2B—N2—O2A | 120.42 (19) | O5—C5—C4 | 125.1 (2) |
| O2B—N2—C2 | 120.8 (2) | | |

| | | | |
|---|---|---|---|
| C3—C2—N2—O2B | 0.8 (4) | C1—C2—C3—C4 | 1.8 (4) |
| C1—C2—N2—O2B | 178.1 (2) | C2—C3—C4—C5 | 179.2 (2) |
| C3—C2—N2—O2A | -179.6 (2) | Na1$^{i}$—O5—C5—C4 | 162.83 (19) |
| C1—C2—N2—O2A | -2.3 (3) | C3—C4—C5—O5 | -179.8 (2) |
| N2—C2—C3—C4 | 178.8 (2) | | |

Symmetry codes: (i) x, y, -1+z; (ii) -x, 1-y, 1-z; (iii) 1-x, 1-y, 1-z.

**Table S5. Hydrogen-bond parameters (Å, °)**

| | *D*—H | H...*A* | D...A | *D*—H...*A* |
|---|---|---|---|---|
| O1W—H1W...O2A$^{i}$ | 0.86 (3) | 2.02 (3) | 2.860 (2) | 165 (3) |
| O1W—H2W...O2B$^{ii}$ | 0.84 (3) | 2.60 (3) | 3.358 (3) | 152 (3) |
| O1W—H2W...O2A$^{ii}$ | 0.84 (3) | 2.10 (3) | 2.876 (3) | 154 (3) |

Symmetry codes: (i) -1+x, y, z; (ii) 1-x, 2-y, 2-z.

***Table S6. Atomic site parameters***

| | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| N1 | 0.2550 (6) | 0.6387 (2) | 0.7036 (2) | 0.0163 (5) |
| C1 | 0.3925 (7) | 0.7190 (2) | 0.6630 (2) | 0.0121 (5) |
| C2 | 0.5615 (7) | 0.8186 (2) | 0.6135 (2) | 0.0119 (5) |
| N2 | 0.7406 (6) | 0.9435 (2) | 0.7119 (2) | 0.0132 (4) |
| O2B | 0.9085 (5) | 1.03800 (18) | 0.68141 (18) | 0.0186 (4) |
| O2A | 0.7297 (6) | 0.96090 (19) | 0.83400 (17) | 0.0195 (4) |
| C3 | 0.5674 (7) | 0.7936 (2) | 0.4761 (2) | 0.0113 (5) |
| H3 | 0.697 (8) | 0.871 (3) | 0.461 (3) | 0.014 |
| C4 | 0.4065 (7) | 0.6736 (3) | 0.3714 (2) | 0.0130 (5) |
| H4 | 0.272 (8) | 0.598 (3) | 0.388 (3) | 0.016 |
| O5 | 0.3064 (5) | 0.56725 (17) | 0.13302 (17) | 0.0144 (4) |
| C5 | 0.4392 (7) | 0.6692 (2) | 0.2391 (2) | 0.0122 (5) |
| H5 | 0.583 (8) | 0.757 (3) | 0.234 (3) | 0.015 |
| Na1 | 0.2437 (3) | 0.61108 (10) | 0.92366 (9) | 0.0139 (3) |
| O1W | -0.1806 (5) | 0.77795 (19) | 0.98655 (19) | 0.0155 (4) |
| H1W | -0.223 (9) | 0.820 (3) | 0.928 (3) | 0.019 |
| H2W | -0.074 (9) | 0.844 (3) | 1.057 (3) | 0.019 |

***Table S7. Anistropic atomic displacement parameters***

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0174 (11) | 0.0156 (10) | 0.0147 (11) | -0.0009 (8) | 0.0028 (9) | 0.0047 (9) |
| C1 | 0.0123 (11) | 0.0130 (11) | 0.0090 (11) | 0.0017 (9) | 0.0013 (9) | 0.0015 (9) |
| C2 | 0.0125 (12) | 0.0099 (10) | 0.0120 (12) | -0.0005 (9) | 0.0029 (9) | 0.0025 (9) |
| N2 | 0.0135 (10) | 0.0116 (10) | 0.0137 (11) | 0.0021 (8) | 0.0020 (8) | 0.0035 (8) |
| O2B | 0.0195 (9) | 0.0123 (8) | 0.0226 (10) | -0.0039 (7) | 0.0020 (8) | 0.0068 (7) |
| O2A | 0.0279 (10) | 0.0160 (9) | 0.0100 (9) | -0.0004 (8) | 0.0005 (8) | 0.0009 (7) |
| C3 | 0.0094 (11) | 0.0122 (11) | 0.0154 (12) | 0.0022 (9) | 0.0046 (9) | 0.0076 (10) |
| C4 | 0.0132 (12) | 0.0124 (11) | 0.0132 (12) | 0.0008 (9) | 0.0019 (9) | 0.0049 (9) |
| O5 | 0.0158 (9) | 0.0138 (8) | 0.0118 (9) | 0.0002 (7) | 0.0031 (7) | 0.0024 (7) |
| C5 | 0.0089 (11) | 0.0129 (11) | 0.0153 (12) | 0.0003 (9) | 0.0030 (9) | 0.0053 (10) |
| Na1 | 0.0143 (5) | 0.0140 (5) | 0.0131 (5) | 0.0000 (4) | 0.0041 (4) | 0.0045 (4) |
| O1W | 0.0181 (9) | 0.0120 (8) | 0.0123 (9) | 0.0000 (7) | -0.0006 (7) | 0.0011 (7) |