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Structure of 3-Nitro-4-oxopyrido[1,2-a]pyrimidin-1-ium-2-olate and its Ammonium Salt

By Ole Simonsen

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

Abstract. $C_8H_5N_3O_4$ (N-acid), $M_r = 207 \cdot 15$, monoclinic, $P2_1/c$, $a = 4 \cdot 7663$ (6), $b = 13 \cdot 825$ (1), $c = 12 \cdot 205$ (2) Å, $\beta = 96 \cdot 45$ (1)°, $V = 799 \cdot 1$ (5) Å^3, $Z = 4$, $D_m = 1 \cdot 71$ (1), $D_x = 1 \cdot 722$ (1) Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0 \cdot 71073$ Å, $\mu = 0 \cdot 132$ mm^{-1}, $F(000) = 424$, $T = 295$ K, $R = 0 \cdot 039$ for 1727 unique observed reflections. $NH_4^+.C_8H_4N_3O_4^-$ (NH$_4^+$-salt), $M_r = 224 \cdot 18$, monoclinic, $P2_1/c$, $a = 7 \cdot 489$ (1), $b = 7 \cdot 524$ (2), $c = 16 \cdot 401$ (4) Å, $\beta = 94 \cdot 37$ (1)°, $V = 921 \cdot 5$ (8) Å^3, $Z = 4$, $D_m = 1 \cdot 62$ (1), $D_x = 1 \cdot 616$ (1) Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0 \cdot 71073$ Å, $\mu = 0 \cdot 124$ mm^{-1}, $F(000) = 464$, $T = 295$ K, $R = 0 \cdot 056$ for 1517 unique observed reflections. The nitro group is out of plane with the ring system both in the N-acid and the NH$_4^+$-salt. Introduction of a nitro group between the two C—O groups does not change the H-tautomeric form of the molecule, but induces a shortening of the C—O bonds and an elongation of the C—C bonds in α position to the nitro group. Formation of the NH$_4^+$-salt causes delocalization of negative charge from N to O through four bonds. The N-acid packs with centrosymmetric hydrogen-bonded dimers. The NH$_4^+$-salt structure contains layers of cations.

Introduction. The structure determinations of 3-nitro-4-oxopyrido[1,2-a]pyrimidin-1-ium-2-olate and its ammonium salt are parts of a study of structural changes associated with the steps in the series: compound, nitro compound, anion of nitro compound.

Experimental. N-acid, prepared as described by Tschitschibabin (1924). Yellow-brown needles (a-direction needle axis) were obtained from the slow cooling of a solution in boiling water. D_m by flotation in a mixture of $CHCl_3$ and $CHBr_3$. NH$_4^+$-salt, yellow needles (b-direction needle axis) separated from an NH_3–H_2O solution of the N-acid. D_m by flotation in a mixture of CCl_4 and CH_2BrCl.

Crystals: $0 \cdot 4 \times 0 \cdot 2 \times 0 \cdot 1$ mm (both N-acid and NH$_4^+$-salt), Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from Guinier–Hägg photographs with Cu $K\alpha_1$ ($\lambda = 1 \cdot 54051$ Å), N-acid, 30 reflections with $4 \cdot 85 < \theta < 40 \cdot 41°$, NH$_4^+$-salt, 25 reflections with $5 \cdot 40 < \theta < 19 \cdot 69°$, Si used as an internal standard. N-acid, 2415 unique reflections ($h\ -6 \rightarrow 6$, $k\ 0 \rightarrow 19$, $l\ 0 \rightarrow 17$) with $2 \cdot 0 < \theta < 30 \cdot 0°$, 1727 with $I > 2 \cdot 5\sigma(I)$ used in refinement process. NH$_4^+$-salt, 2681 unique reflections ($h\ 0 \rightarrow 10$, $k\ 0 \rightarrow 10$, $l\ -22 \rightarrow 22$) with $2 \cdot 0 < \theta < 30 \cdot 0°$, 1517 with $I > 2 \cdot 5\sigma(I)$ used in refinement process together with 'less-than' reflections $[I < 2 \cdot 5\sigma(I)]$ with calculated values greater than the observed (2306 contributing reflections). Mixed $\omega/2\theta$ scan technique, scan angle (N-acid: $1 \cdot 00° + 0 \cdot 35°$ tan θ, NH$_4^+$-salt: $1 \cdot 40° + 0 \cdot 35°$ tan θ), standard reflections (N-acid: 153 and $3\overline{1}\overline{3}$, NH$_4^+$-salt: $\overline{2}32$, $20\overline{8}$ and $10\overline{6}$) used for orientation control every 100 reflections, intensity check every 10 800 s of exposure time by using (N-acid: 006, NH$_4^+$-salt: $\overline{2}3\overline{3}$), standard intensity variations

< (N-acid: 3·1%, NH₄⁺-salt: 4·1%). Absorption ignored. N-acid structure solved by direct methods. The NH₄⁺-salt and Rb⁺-salt are isomorphous. The heavy-atom method was applied to solve the Rb⁺-salt structure, coordinates from this used as basis for refinement of the NH₄⁺-salt structure. Full-matrix least-squares refinement of anisotropic non-H atoms. Positional H parameters from $\Delta\rho$ maps. Refinements of H(x,y,z) with $\sin\theta/\lambda < 0.40$ Å⁻¹, fixed isotropic H temperature factor. $\sum w(\Delta|F|)^2$ minimized, N-acid: final $R = 0.039$, $wR = 0.049$, NH₄⁺-salt: final $R = 0.056$, $wR = 0.050$.* Average $(w\Delta|F|)^2$ was almost independent of $|F_o|$ by using $w = 1/\{1 + [(F_o - 6.0)/12.0]^2\}$ for N-acid and for NH₄⁺-salt $w = 1$ when $|F_o| < 40$ else $w = (40/F_o)^2$. $S = 1.83$, $(\Delta/\sigma)_{max} = 0.001$ (N-acid). $S = 1.00$, $(\Delta/\sigma)_{max} = 0.005$ (NH₄⁺-salt). Minimum and maximum in final $\Delta\rho$ map: −0·3 and 0·3 e Å⁻³ for both compounds. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs from *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The positional and thermal parameters are given in Table 1.

Discussion. The ten atoms which constitute the bicyclic system show only small deviations from a least-squares plane (I) defined by these atoms. Maximum deviations from the plane are, N-acid: 0·02 (1) Å [C(3)] and NH₄⁺-salt: 0·07 (4) Å [C(2)].

Introduction of a nitro group at C(3) (Fig. 1) does not change the tautomeric form of the molecule. The electrophilic nitro group induces shortenings of the C—O bonds and elongations of the adjacent C—C bonds (Table 2). The C—NO₂ bonding distances [1·441 (2) Å, N-acid; 1·428 (2) Å, NH₄⁺-salt] are between the corresponding distances observed in nitroacetamide [1·481 (3) Å] (Thorup, Drier & Simonsen, 1981) and nitromalonamide [1·397 (4) Å] (Simonsen & Thorup, 1979). This corresponds to the possibility of π-overlap in the compounds: nitromalonamide is a planar system (Simonsen & Thorup, 1979); in nitroacetamide the angle between the least-squares planes O₂N—C and C—CON is 83·1 (5)° (Thorup *et al.*, 1981) and for the N-acid and NH₄⁺-salt the angle between the least-squares planes (I) and O₂N—C is 31·4 (5) and 23·6 (5)° respectively.

The material from Table 2 shows that release of a proton from N(1) in N-acid has a drastic effect on the molecule as seven bond distances are changed significantly and three angles changed by more than 3° (Fig. 1, Table 2). C(10)—N(5) becomes elongated and N(1)—C(10) shorter when the ammonium salt is

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters of* non-H *atoms with e.s.d.'s in parentheses*

N(11) is the N atom in the NH₄⁺ ion.

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	$B_{eq}(\text{Å}^2)$
N-acid				
O(2)	2892 (2)	5556 (1)	3933 (1)	2·8 (1)
O(4)	−4428 (3)	3420 (1)	2503 (1)	3·3 (1)
O(31)	−3252 (3)	5081 (1)	1478 (1)	3·8 (1)
O(32)	−1839 (3)	6165 (1)	2686 (1)	3·1 (1)
N(1)	2426 (3)	4050 (1)	4595 (1)	2·1 (1)
N(3)	−2069 (3)	5319 (1)	2387 (1)	2·3 (1)
N(5)	−1052 (3)	2960 (1)	3893 (1)	1·9 (1)
C(2)	1536 (3)	4792 (1)	3875 (1)	2·0 (1)
C(3)	−904 (3)	4572 (1)	3128 (1)	1·9 (1)
C(4)	−2318 (3)	3674 (1)	3073 (1)	2·1 (1)
C(6)	−2338 (3)	2067 (1)	3903 (1)	2·4 (1)
C(7)	−1377 (4)	1390 (1)	4649 (2)	2·7 (1)
C(8)	975 (4)	1595 (1)	5415 (1)	2·6 (1)
C(9)	2274 (3)	2473 (1)	5401 (1)	2·3 (1)
C(10)	1220 (3)	3170 (1)	4627 (1)	1·8 (1)
NH₄⁺-salt				
O(2)	960 (2)	8167 (1)	5303 (1)	4·4 (1)
O(4)	3230 (1)	2432 (1)	6023 (1)	3·2 (1)
O(31)	1314 (2)	4340 (1)	7007 (1)	4·0 (1)
O(32)	1643 (2)	7152 (1)	6865 (1)	4·5 (1)
N(1)	2253 (1)	6478 (1)	4390 (1)	2·8 (1)
N(3)	1662 (1)	5635 (1)	6584 (1)	2·7 (1)
N(5)	3171 (1)	3527 (1)	4717 (1)	2·4 (1)
N(11)	−15 (2)	5668 (2)	8566 (1)	3·1 (1)
C(2)	1752 (2)	6752 (2)	5173 (1)	2·6 (1)
C(3)	2101 (2)	5359 (2)	5762 (1)	2·4 (1)
C(4)	2822 (1)	3696 (2)	5573 (1)	2·3 (1)
C(6)	3757 (2)	1873 (2)	4467 (1)	3·2 (1)
C(7)	4135 (2)	1620 (2)	3682 (1)	3·7 (1)
C(8)	3921 (2)	3024 (2)	3116 (1)	3·4 (1)
C(9)	3322 (2)	4626 (2)	3359 (1)	3·1 (1)
C(10)	2894 (1)	4924 (2)	4183 (1)	2·5 (1)

formed. A parallel to these changes has been observed for *p*-nitroaniline hydrochloride → *p*-nitroaniline (Ploug-Sørensen & Andersen, 1982) and for *p*-chloroaniline hydrochloride → *p*-chloroaniline (Ploug-Sørensen & Andersen, 1985) with approximate differences Δ(N—C) −0·1 Å and Δ(C—C) +0·02 Å. An inspection of the fragment N(1), C(10), N(5), C(4), O(4) shows that salt formation induces alternating shortenings and elongations of the bonds between N(1) and O(4), which can be interpreted as an electron-density shift from N(1) to O(4) through the fragment.

The tendency to form N(1)—H(1)···O(2) intermolecular hydrogen bonds in crystals with the 4-oxopyrido[1,2-a]pyrimidin-1-ium-2-olate system seems to be strong, since centrosymmetric dimers with this type of hydrogen bond are observed in the crystal structure of both 4-oxopyrido[1,2-a]pyrimidin-1-ium-2-olate (Thorup & Simonsen, 1985) and N-acid [N(1)···O(2), 2·757 (2) Å] (Fig. 2). The NH₄⁺-salt packs with (100) layers of ammonium ions (Fig. 3). The cations are donors in hydrogen bonds to N and O atoms in the anions (Fig. 3). The N(11)···(O,N) distances range from 2·772 (2) to 3·053 (2) Å.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42670 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
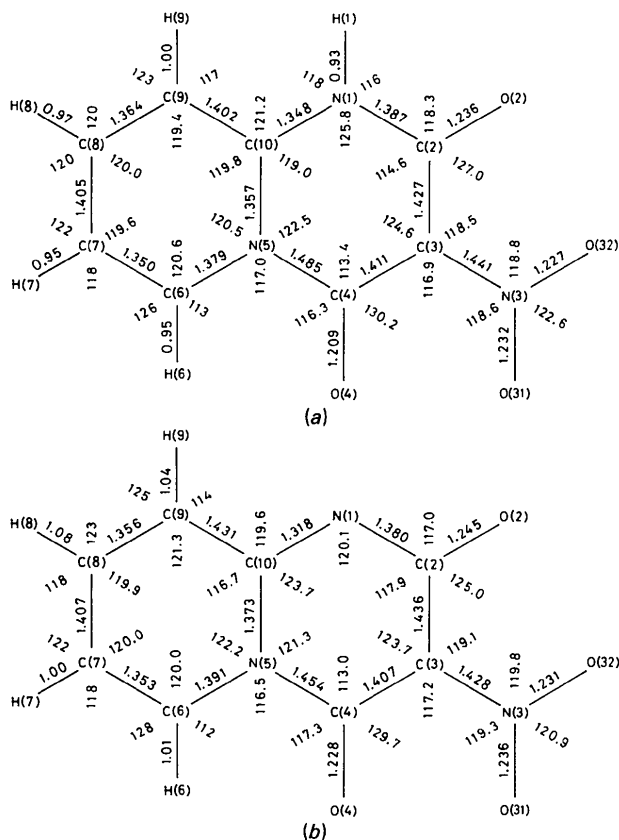
Fig. 1. Bond distances (Å), angles (°) and the atom numbering scheme for (a) N-acid and (b) NH₄⁺-salt. The e.s.d.'s are 0·002 Å and 0·1° when no H atoms are involved, otherwise 0·04 Å and 2°.
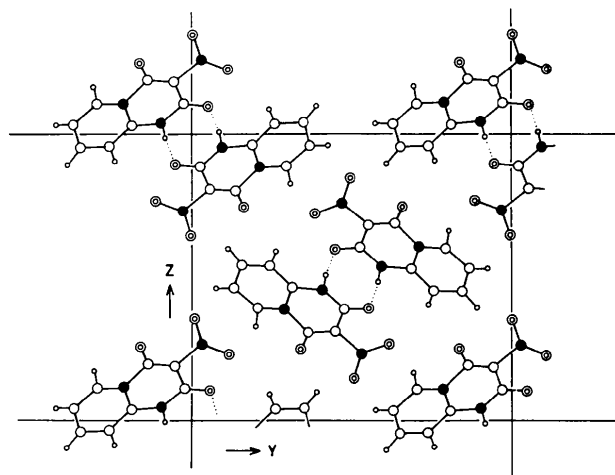

Fig. 2. The N-acid crystal structure projected down the x axis. Black circles: N atoms, double circles: O atoms. The dotted lines represent the hydrogen-bonding system.
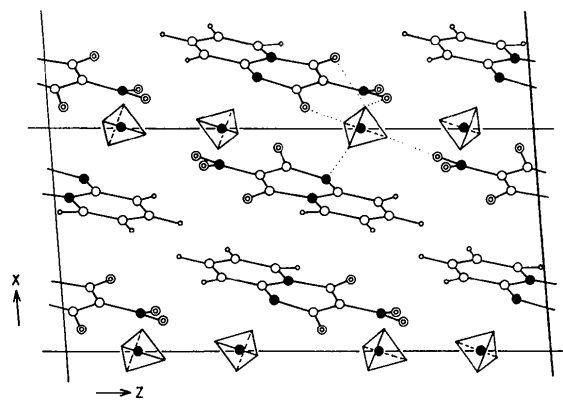

Fig. 3. The NH₄⁺-salt crystal structure projected down the y axis. Black circles: N atoms, double circles: O atoms. Ammonium ions are symbolized by tetrahedra. Only one asymmetric unit of hydrogen bonds is drawn.

Table 2. *A comparison of the bond distances and some of the bond angles for the three compounds 4-oxopyrido[1,2-a]pyrimidin-1-ium-2-olate (A) (Thorup & Simonsen, 1985), N-acid and NH₄⁺-salt*

A bond or angle difference is considered significant if it exceeds 0·01 Å or 0·5° respectively. The e.s.d.'s are 0·002 Å and 0·1° for the quoted bonds and angles.

Distance or angle (Å)/(°)	A	N-acid	NH₄⁺-salt
N(1)–C(2)	1·395	1·387	1·380
O(2)–C(2)	1·251	1·236	1·245
C(2)–C(3)	1·399	1·427	1·436
C(3)–N(3)		1·441	1·428
N(3)–O(31)		1·232	1·236
N(3)–O(32)		1·227	1·231
C(3)–C(4)	1·387	1·411	1·407
O(4)–C(4)	1·228	1·209	1·228
C(4)–N(5)	1·488	1·485	1·454
N(5)–C(6)	1·375	1·379	1·391
C(6)–C(7)	1·359	1·350	1·353
C(7)–C(8)	1·407	1·405	1·407
C(8)–C(9)	1·363	1·364	1·356
C(9)–C(10)	1·410	1·402	1·431
C(10)–N(1)	1·345	1·348	1·318
C(10)–N(5)	1·355	1·357	1·373
C(10)–N(1)–C(2)	123·9	125·8	120·1
N(1)–C(2)–C(3)	116·5	114·6	117·9
C(2)–C(3)–C(4)	124·0	124·6	123·7
C(3)–C(4)–N(5)	114·4	113·4	113·0
C(4)–N(5)–C(10)	121·5	122·5	121·3
N(5)–C(10)–N(1)	119·6	119·0	123·7

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