Z. Kristallogr. NCS 221 (2006) 183-184 / DOI 10.1524/ncrs.2006.0031

Crystal structure of 3,5-dinitro-2-pyridone, $C_5H_3NO(NO_2)_2$

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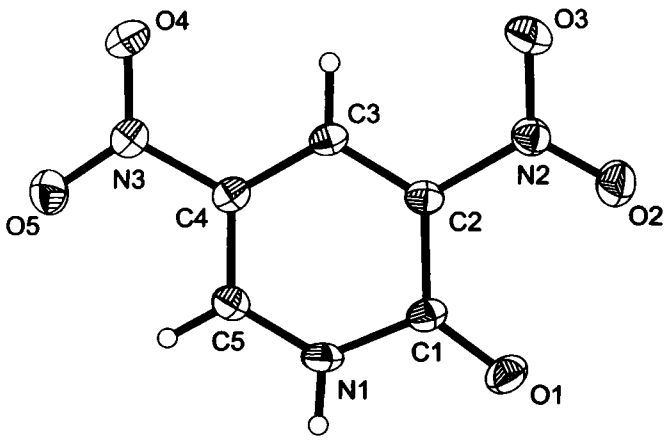
Received April 3, 2006, accepted and available on-line April 22, 2006; CCDC no. 1267/1757



Abstract

$C_5H_3N_3O_5$, orthorhombic, $Pna2_1$ (no. 33), a = 12.335(4) Å, b = 9.636(3) Å, c = 5.738(2) Å, V = 682.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.031, $wR_{ref}(F^2)$ = 0.085, T = 298 K.

Source of material

Under stirring, 1.4 g (0.01 mol) 2-hydroxy-3-nitropyridine was dissolved in 2 ml fuming H_2SO_4 (50 % SO_3 content). 1.5 ml mixture ® = 1.6 g/ml) of oleum with fuming HNO_3 was added slowly and kept below 40 °C. The solution was stirred at RT for 1 h and slowly rised to 90 °C in 2 h, followed by keeping at 90 °C for additional 4 h. The solution was cooled to RT and poured on 20 g ice. 1.05 g (75 %) pale yellow needles were obtained. Single crystals suitable for X-ray diffraction analysis were isolated after several weeks from aqueous solution (m.p. 175-176 °C).

Discussion

Pyridone and hydroxypyridine are tautomeric organic molecules. The calculation of two tautomeric forms of unsubstituted hydroxypyridine, benzoid and quinoid structures, resulted in the difference of energies. The benzoid form is slightly more preferable than the quinoid form [1]. Nitropyridine and its derivatives have been paid much attention due to their practical applications: 2-hydroxy-3,5-dinitropyridine is extremely important as an intermediate for oxidative dyestuffs, medicines or agrochemicals [2]. Also some derivatives of the nitropyridine have nonlinear optics property [3]. A variety of substituted nitropyridine compounds are used as herbicidal chemicals to control the growth of undesired plants [4]. 2-Hydroxyl-3,5-dinitropyridine and its metal complexes have higher explosion temperature and lower sensitivity. So, they are used as energetic catalysts for solid propellants in order to adjust and improve their trajectory properties [5].

The atoms of nitropyridone moiety (including N3, O4, O5) display an almost coplanar configuration with a mean deviation to the least-squares plane of 0.0134 Å. The plane through N2, O2 and O3 has a dihedral angle of 12.5° with the above-mentioned plane. The C2—N2, C2—C3 and C4—C5 distances are 1.462(3) Å, 1.363(4) Å and 1.360(3) Å, respectively, which agree well with the corresponding distance in compound 3-nitro-2-pyridone [6]. The distances 1.456(3) Å for C1—C2 and 1.390(4) Å for C3—C4 are slightly longer than the respective distances in 3-nitro-2-pyridone (1.439(3) Å and 1.371(4) Å, respectively), while the distances of 1.223(3) Å for C1—O1 and 1.325(4) Å for C5—N1 are slightly shorter than the corresponding distances in the same compound (1.236(3) Å and 1.339(4) Å, respectively) [6].

Table 1. Data collection and handling.

Crystal:	yellowish block, size 0.31 × 0.43 × 0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.65 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3404, 666
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 616
$N(param)_{refined}$:	118
Programs:	SHELXS-97 [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4a	0.5043	0.0685	0.7750	0.045
H(3)	4a	0.2724	0.4289	0.7369	0.037
H(5)	4a	0.5254	0.2151	0.4888	0.042

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4a	0.4605(2)	0.1378(2)	0.7735(5)	0.034(1)	0.029(1)	0.050(2)	0.0092(9)	0.000(1)	0.000(1)
N(2)	4a	0.2263(2)	0.2839(2)	1.0999(5)	0.032(1)	0.039(1)	0.038(1)	0.0006(9)	–0.001(1)	0.000(1)
N(3)	4a	0.4135(2)	0.4304(2)	0.3891(5)	0.037(1)	0.035(1)	0.038(1)	–0.0046(9)	–0.003(1)	0.002(1)

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Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*a*	0.3873(2)	0.0581(2)	1.1099(4)	0.040(1)	0.046(1)	0.062(2)	0.0085(9)	0.003(1)	0.021(1)
O(2)	4*a*	0.2289(2)	0.2200(2)	1.2821(4)	0.053(1)	0.059(1)	0.039(1)	0.001(1)	0.004(1)	0.007(1)
O(3)	4*a*	0.1560(2)	0.3690(3)	1.0539(5)	0.047(1)	0.077(2)	0.060(2)	0.030(1)	0.011(1)	0.014(1)
O(4)	4*a*	0.3511(2)	0.5279(2)	0.3720(5)	0.058(1)	0.048(1)	0.054(1)	0.0143(9)	0.000(1)	0.017(1)
O(5)	4*a*	0.4848(2)	0.4048(2)	0.2463(4)	0.059(1)	0.052(1)	0.048(1)	−0.001(1)	0.016(1)	0.007(1)
C(1)	4*a*	0.3852(2)	0.1449(2)	0.9544(5)	0.029(1)	0.029(1)	0.044(2)	0.0004(9)	−0.004(1)	0.004(1)
C(2)	4*a*	0.3118(2)	0.2622(2)	0.9272(5)	0.026(1)	0.032(1)	0.037(2)	0.0004(9)	−0.004(1)	−0.002(1)
C(3)	4*a*	0.3204(2)	0.3548(3)	0.7488(5)	0.030(1)	0.029(1)	0.035(2)	0.0015(9)	−0.006(1)	0.002(1)
C(4)	4*a*	0.4021(2)	0.3369(2)	0.5848(5)	0.034(1)	0.027(1)	0.034(2)	−0.004(1)	−0.005(1)	−0.001(1)
C(5)	4*a*	0.4712(2)	0.2273(2)	0.5996(6)	0.032(1)	0.033(1)	0.040(1)	0.000(1)	0.003(1)	−0.003(1)

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