

4,6-Dimethyl-5-nitro-1*H*-pyridin-2-one

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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.043
 wR factor = 0.111
 Data-to-parameter ratio = 12.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_7\text{H}_8\text{N}_2\text{O}_3$, molecules form centrosymmetrical dimers *via* $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

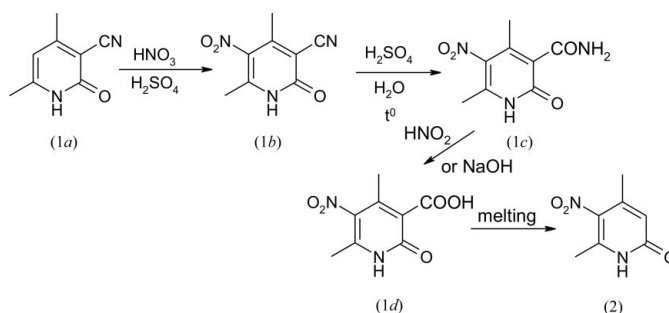
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Comment

Previously, we have reported the crystal structure determination of Guareschi pyridone (*1a*) (Rybakov *et al.*, 2004). Now we have investigated the crystal structure of a related compound, (*2*), which can be obtained from Guareschi pyridone. A search of Cambridge Structural Database (CSD, Version of November 2002; Allen, 2002) does not give any hits for 4,6-disubstituted 5-nitro-pyridin-2-ones. The multistep synthesis of (*2*) has been performed previously (Mariella *et al.*, 1955) by nitration of Guareschi pyridone (*1a*) and further stepwise hydrolysis of the nitro derivative (*1b*) to amide (*1c*) and carboxylic acid (*1d*), followed by decarboxylation. To obtain compound (*2*), we simplified the earlier multistep procedure and, after obtaining the crude intermediate product (*1b*), converted it to the target compound (*2*) by prolonged reflux in sulfuric acid.



The structure of the six-membered heterocycle has a well defined diene-like fragment (Fig. 1); bond distances $\text{C}3-\text{C}4$ and $\text{C}5-\text{C}6$ are shorter than the $\text{C}2-\text{C}3$ and $\text{C}4-\text{C}5$ distances. The $\text{C}-\text{C}$ bonds of the methyl groups, $\text{C}4-\text{C}41$ [$1.499(3)\text{ \AA}$] and $\text{C}6-\text{C}61$ [$1.501(3)\text{ \AA}$], are almost equal in length. The nitro group is twisted away from the attached ring; the dihedral angle between the heterocyclic ring and the $\text{O}51/\text{O}52/\text{N}5/\text{C}5$ plane is $39.36(12)^\circ$. An intramolecular $\text{C}61-\text{H}61\text{B}\cdots\text{O}52$ interaction is observed in the molecular structure. In the crystal structure, an $\text{N}1-\text{H}1\cdots\text{O}2(1-x, -y, 1-z)$ intermolecular hydrogen bond links the molecules into centrosymmetric dimers (see Fig. 2 and Table 2 for details).

Experimental

To a solution of pyridone (*1a*) (40 g, 0.22 mol) in 150 ml of 98% H_2SO_4 a mixture of fuming nitrous acid (13 ml) and sulfuric acid (14 ml) was carefully added dropwise, keeping the temperature in the

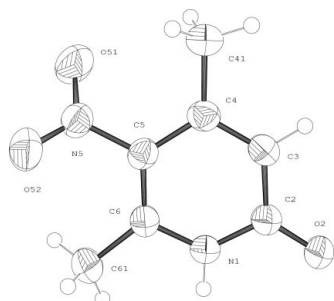


Figure 1
ORTEP-3 (Farrugia, 1997) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

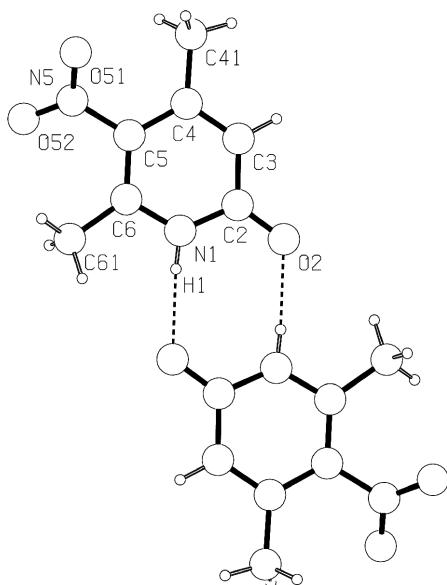


Figure 2
PLUTON97 (Spek, 1997) plot showing a N—H···O hydrogen bonded dimer.

range 313–318 K. Increasing the temperature to 338 K during the addition causes a violent explosion. The reaction mixture was kept for 5 d, and it was periodically heated to the temperature 333–343 K (and then even up to 373 K). When the TLC control displayed complete absence of the starting pyridone, the reaction mixture was poured into a fivefold excess of ice-cold water. The yellow precipitate was filtered and dried. The resulting material was dissolved in 50% H₂SO₄ and refluxed for 2 d. The reaction mixture was poured on to a fourfold excess of cold water, and the precipitate was filtered, washed with water (2 × 150 ml) and dried. The resulting nitropyridone (2) (12.5 g, 19%) has a melting point of 518 K, compared to 523 K reported by Mariella *et al.* (1955). ¹H NMR spectra (DMSO-*d*₆, δ): 6.20 (H-3, s, 1H), 3.42 (NH, s, 1H), 2.35 (6-Me, s, 3H), 2.21 (4-Me, s, 3H).

Crystal data

C₇H₈N₂O₃
M_r = 168.15
Monoclinic, P2₁/n
a = 9.7677 (15) Å
b = 5.875 (3) Å
c = 13.7295 (15) Å
β = 100.760 (10)°
V = 774.0 (4) Å³
Z = 4

D_x = 1.443 Mg m⁻³
Cu Kα radiation
Cell parameters from 25 reflections
θ = 28–31°
μ = 0.98 mm⁻¹
T = 293 (2) K
Needle, colourless
0.30 × 0.10 × 0.03 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: none
1524 measured reflections
1462 independent reflections
999 reflections with I > 2σ(I)
R_{int} = 0.037

θ_{max} = 69.9°
h = -11 → 11
k = 0 → 7
l = 0 → 16
1 standard reflection every 200 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.043
wR(F²) = 0.111
S = 0.98
1462 reflections
113 parameters

H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(F_o²) + (0.0554P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.13 e Å⁻³
Δρ_{min} = -0.15 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1—C6	1.343 (2)	C4—C41	1.499 (3)
N1—C2	1.379 (2)	C5—C6	1.375 (3)
N1—H1	0.84 (2)	C5—N5	1.454 (3)
C2—O2	1.242 (2)	N5—O52	1.216 (2)
C2—C3	1.426 (3)	N5—O51	1.226 (2)
C3—C4	1.353 (3)	C6—C61	1.501 (3)
C4—C5	1.431 (3)		
C6—N1—C2	126.17 (19)	C6—C5—C4	121.33 (18)
C6—N1—H1	118.4 (13)	C6—C5—N5	118.52 (17)
C2—N1—H1	114.7 (13)	C4—C5—N5	120.14 (18)
O2—C2—N1	120.11 (19)	O52—N5—O51	122.6 (2)
O2—C2—C3	125.47 (18)	O52—N5—C5	119.40 (19)
N1—C2—C3	114.41 (19)	O51—N5—C5	117.95 (18)
C4—C3—C2	123.15 (19)	N1—C6—C5	117.41 (17)
C3—C4—C5	117.44 (19)	N1—C6—C61	115.33 (18)
C3—C4—C41	119.59 (18)	C5—C6—C61	127.25 (18)
C5—C4—C41	122.91 (19)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2 ⁱ	0.84 (2)	1.94 (2)	2.776 (2)	176 (2)
C61—H61B···O52	0.96	2.44	2.809 (3)	102

Symmetry code: (i) 1 - x, -y, 1 - z.

The H atom bonded to N atom was located in a difference map and refined isotropically [N—H = 0.84 (2) Å]. The H atoms bonded to C atoms were included in calculated positions (C—H = 0.93–0.96 Å) and refined as riding atoms, with U_{iso}(H) set equal to 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C3) for H3.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLUTON97 (Spek, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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References

- Allen, H. F. (2002). *Acta Cryst.* **B58**, 380.
- Enraf–Nonius (1994). *CAD-4 EXPRESS Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Mariella, R. P., Callahan, J. J. & Jibril, A. O. (1955). *J. Org. Chem.* **20**, 1721–1728.
- Rybakov, V. B., Bush, A. A., Babaev, E. V., & Aslanov, L. A. (2004). *Acta Cryst.* **E60**, o160–o161.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *PLUTON97*. University of Utrecht, The Netherlands.