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

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.

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 \( \text{C} \cdots \text{C} \) bonds of the methyl groups, \( \text{C}4\text{C}41 \) [1.499 (3) \( \text{Å} \)] and \( \text{C}6\text{C}61 \) [1.501 (3) \( \text{Å} \)], 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)°. 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 centrosymmetrical 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% \( \text{H}_2\text{SO}_4 \) a mixture of fuming nitrous acid (13 ml) and sulfuric acid (14 ml) was carefully added dropwise, keeping the temperature in the
Crystal data

\[ \begin{align*}
\text{C}_7\text{H}_8\text{N}_2\text{O}_3 & \text{H}_2\text{SO}_4 \\
M_r & = 293 (2) \text{ K} \\
\text{Needle, colourless} & \text{with water (2\,150\,ml) and dried. The resulting nitropyridone (2) (12.5 g, 19\%) has a melting point of 518 K, compared to 523 K.}
\end{align*} \]

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

Data collection

\[ \begin{align*}
\text{Enraf-Nomius CAD-4} & \text{ diffractometer} \\
\theta_{\text{max}} & = 69.9^\circ \\
\text{Non-profiled } \omega \text{ scans} & \text{ } \\
\text{Absorption correction: none} & \text{ } \\
1524 \text{ measured reflections} & \text{ } \\
1462 \text{ independent reflections} & \text{ } \\
999 \text{ reflections with } I > 2\sigma(I) & \text{ } \\
R_{\text{int}} & = 0.037 \\
\end{align*} \]

Refinement

\[ \begin{align*}
\text{Re\text{finement on } F^2} & \text{ } \\
R(F^2) & = 0.043 \\
S & = 0.98 \\
1462 \text{ reflections} & \text{ } \\
113 \text{ parameters} & \text{ } \\
\text{H atoms treated by a mixture of independent and constrained refinement} & \text{ } \\
\text{where } P = (F^2 + 2F'^2)/3 & \text{ } \\
(\Delta/\sigma)_{\text{max}} & < 0.001 \\
\Delta \rho_{\text{max}} & = 0.13 e \, \text{Å}^{-3} \\
\Delta \rho_{\text{min}} & = -0.15 e \, \text{Å}^{-3} \\
\end{align*} \]

Table 1

\begin{tabular}{cccc}
\hline
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 & C2 & 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 & 1.591 (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 (3) & C4 & C5 & N5 & 120.14 (18) \\
O2 & C2 & N1 & 120.11 (19) & O52 & N5 & O51 & 122.6 (2) \\
O2 & C2 & C3 & 124.47 (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 & C3 & 117.44 (19) & N1 & C6 & C61 & 115.33 (18) \\
C3 & C4 & C41 & 119.59 (18) & C3 & C6 & C61 & 127.25 (18) \\
C5 & C4 & C41 & 122.91 (19) & \\
\hline
\end{tabular} \]

Table 2

\begin{tabular}{cccccc}
\hline
D & H & \cdots & A & D & H & \cdots & A & D & A & D & H & \cdots & A \\
\hline
N1 & H1 & \cdots & O2 & 0.84 (2) & 1.94 (2) & 2.776 (2) & 176 (2) \\
C61 & H61B & \cdots & O52 & 0.86 & 2.44 & 2.809 (3) & 102 (3) \\
\hline
\end{tabular} \]

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

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References