

6-Nitro-1-deazapurine

Jens Müller,* Elisa Gil Bardají
and Fabian-Alexander Polonius

Anorganische Chemie, Universität Dortmund,
Otto-Hahn-Strasse 6, 44227 Dortmund,
Germany

Correspondence e-mail:
mueller@muellerlab.org

Key indicators

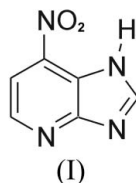
Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.053
wR factor = 0.099
Data-to-parameter ratio = 11.9

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

The title compound, $\text{C}_6\text{H}_4\text{N}_4\text{O}_2$, is a potential nucleobase surrogate. In the crystal structure, molecules are linked by intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds [$\text{H}\cdots\text{N} = 1.88(3) \text{ \AA}$] to form one-dimensional chains in the *b*-axis direction.

Comment

The title purine derivative, (I), was synthesized in the course of our studies of potential ligands for metal-mediated base pairs and models thereof (Müller, Polonius & Roitzsch, 2005; Müller, Böhme *et al.*, 2005). The resulting metal ion-containing oligonucleotides represent promising synthetic targets as they are expected to show interesting physical properties that are difficult to obtain with other compounds (Wagenknecht, 2003).



The molecule of the title compound is essentially planar (Fig. 1), with only the exocyclic nitro group deviating slightly from the least-squares plane of the purine ring system [$7.18(17)^\circ$]. All bond lengths and angles are in the expected ranges. An interesting feature observed in purine and its derivatives is $\text{N}7-\text{H}$ versus $\text{N}9-\text{H}$ tautomerism. For example, in the structure of purine (Watson *et al.*, 1965), the same N atom as in the title compound is protonated, but in solution a solvent-dependent equilibrium between the two tautomers is observed (Gonnella & Roberts, 1982). The present study shows that in the solid state 6-nitro-1-deazapurine exists in the $\text{N}7-\text{H}$ tautomeric form. As in the crystal structure of purine, molecules of (I) are linked by intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds to form one-dimensional chains (Table 2 and Fig. 2). The assignment as the $\text{N}7-\text{H}$ tautomer is based not only on the fact that this H atom could be found in the difference Fourier map but also on the values of the angles $\text{C}8-\text{N}9-\text{C}4$ and $\text{C}8-\text{N}7-\text{C}5$, which are $103.7(2)^\circ$ and $106.4(2)^\circ$, respectively. A comparison with 91 other solid-state structures of purine derivatives (nine of which are reported as $\text{N}7-\text{H}$ tautomers) as retrieved from the Cambridge Structural Database (Version 5.26; Allen, 2002) shows that the respective angle involving the protonated N atom is typically larger by about 3° . In fact, the average values for these angles in the

Received 2 December 2005

Accepted 8 December 2005

Online 14 December 2005

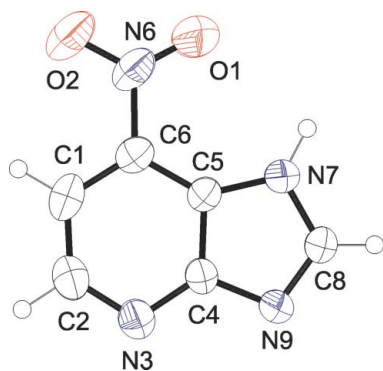


Figure 1
View of the title compound, showing displacement ellipsoids at the 50% probability level.

above-mentioned nine N7–H tautomers are coincidentally identical to the values observed in the title structure (103.7 and 106.4°). For comparison, the respective average angles in the N9–H tautomers are 106.3 and 103.3°. In addition, the C8–N7 and C8–N9 bond lengths of 1.352 (3) and 1.303 (3) Å agree well with the sequence of single and double bonds as given in the chemical scheme. A theoretical calculation with the *ADF* program (te Velde *et al.*, 2001; Fonseca Guerra *et al.*, 1998; *ADF2005.01*, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com/>) further supports these findings by showing that, in the gas phase, the N7–H tautomer is more stable by 14.1 kJ mol⁻¹ than the N9–H form. The p*K*_a value of the N7–H proton as determined by pD-dependent ¹H NMR spectroscopy is 1.4 (1).

Experimental

The title compound was synthesized according to published protocols (Cristalli *et al.*, 1987) and recrystallized from water. It gave a satisfactory elemental analysis: calculated for C₆H₄N₄O₂: C 43.9, H 2.5, N 34.1%; found: C 43.6, H 2.4, N 34.8%. Theoretical calculations with the *ADF* program were carried out as described in the literature (Fonseca Guerra *et al.*, 2000). The determination of the p*K*_a value was performed as described in the literature (Müller, Böhme *et al.*, 2005).

Crystal data

C ₆ H ₄ N ₄ O ₂	<i>D</i> _x = 1.512 Mg m ⁻³
<i>M</i> _r = 164.13	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 6291 reflections
<i>a</i> = 11.684 (2) Å	<i>θ</i> = 3–27.5°
<i>b</i> = 9.5750 (19) Å	<i>μ</i> = 0.12 mm ⁻¹
<i>c</i> = 7.2052 (14) Å	<i>T</i> = 298 (2) K
<i>β</i> = 116.53 (3)°	Block, yellow
<i>V</i> = 721.2 (3) Å ³	0.2 × 0.05 × 0.05 mm
<i>Z</i> = 4	

Data collection

Bruker–Nonius KappaCCD diffractometer	728 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>ω</i> scans	<i>R</i> _{int} = 0.082
Absorption correction: none	<i>θ</i> _{max} = 26.5°
6047 measured reflections	<i>h</i> = -14 → 14
1483 independent reflections	<i>k</i> = -12 → 10
	<i>l</i> = -9 → 6

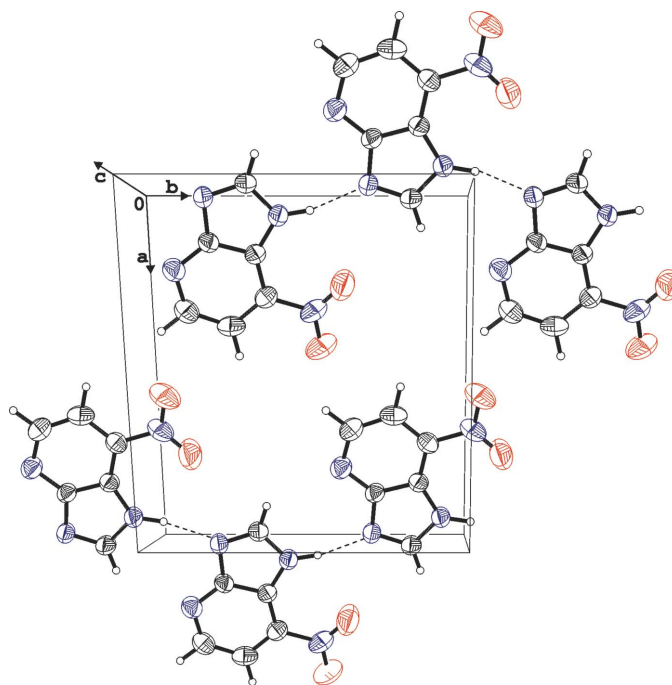


Figure 2
Hydrogen-bonded chain structure formed by the title compound. Displacement ellipsoids are drawn at the 50% probability level and dashed lines indicate hydrogen bonds.

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.099$
S = 1.01
 1483 reflections
 125 parameters
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.1392P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N3–C2	1.335 (3)	N9–C4	1.381 (3)
N3–C4	1.337 (3)	C1–C6	1.379 (3)
N6–C6	1.465 (3)	C1–C2	1.387 (4)
N7–C8	1.352 (3)	C4–C5	1.403 (3)
N7–C5	1.365 (3)	C5–C6	1.374 (3)
N9–C8	1.303 (3)		
C2–N3–C4	114.3 (2)	N7–C5–C6	137.3 (2)
C8–N7–C5	106.4 (2)	N7–C5–C4	105.1 (2)
C8–N9–C4	103.7 (2)	C6–C5–C4	117.7 (2)
C6–C1–C2	119.2 (3)	C5–C6–C1	118.3 (2)
N3–C2–C1	124.8 (3)	C5–C6–N6	120.4 (2)
N3–C4–N9	124.1 (2)	C1–C6–N6	121.3 (2)
N3–C4–C5	125.7 (2)	N9–C8–N7	114.6 (2)
N9–C4–C5	110.2 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N7–H7...N9 ⁱ	0.94 (3)	1.88 (3)	2.797 (3)	166 (3)
C2–H2...O2 ⁱⁱ	0.99 (3)	2.51 (3)	3.224 (4)	129 (2)

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

All H atoms were found in a difference Fourier map and refined isotropically [C–H = 0.92 (2)–0.99 (3) Å].

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Deutsche Forschungsgemeinschaft (Emmy Noether Programme), the Department of Chemistry at the University of Dortmund and the Fonds der Chemischen Industrie. We thank Tushar van der Wijst for performing the DFT calculations. JM thanks Professor Dr Bernhard Lippert for his continuous support.

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