

5-*tert*-Butyl-4-nitro-1*H*-pyrazol-3-olDaniel E. Lynch^a and
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Key indicators

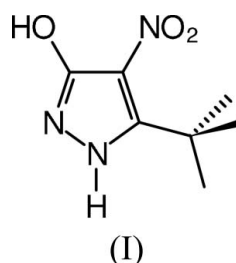
Single-crystal X-ray study
T = 120 K
Mean σ (C–C) = 0.003 Å
R factor = 0.059
wR factor = 0.153
Data-to-parameter ratio = 13.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The structure of the title compound, C₇H₁₁N₃O₃, consists of molecules that pack in a linear hydrogen-bonded ribbon motif. This hydrogen-bonding arrangement is constructed through two dimer formations, one that is atypical of pyrazoles (N–H···N) and the other *via* an interaction from the hydroxy OH group to one of the nitro O atoms.

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Comment

Pyrazoles and related compounds are common molecules used in coordination or organometallic chemistry as bridging ligands, utilizing the ring positions of the two N atoms. There are 1388 structures in the Cambridge Structural Database (CSD; Version 5.26, November 2004; Allen, 2002) that contain a pyrazole ring with the extra search constraints ‘no extra cyclic routes’ and ‘require 3D coordinates’. This number reduces to 23 for 4-nitropyrazoles, 80 for 5-*tert*-butylpyrazoles, and 15 for 3-hydroxypyrazoles. Interestingly, there is only one structure (CSD refcode: WILBAU), that of 3,5-di-*tert*-butyl-4-nitropyrazole (Llamas-Saiz *et al.*, 1994), which contains two of the three mentioned substituents.



In a series of studies on the preparation and hydrogen-bonding properties of 3,4,5-trisubstituted pyrazoles, we now

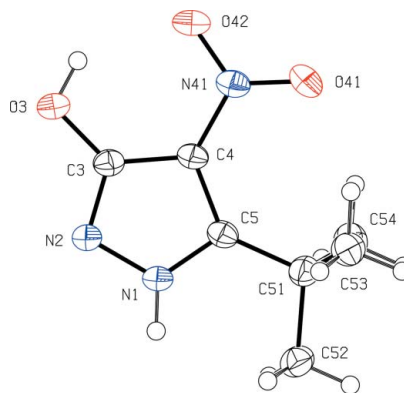
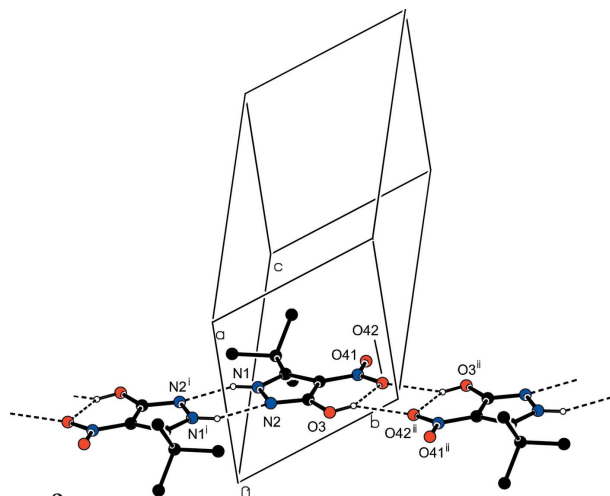


Figure 1
The molecular configuration and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.


Figure 2

A partial packing diagram for (I), showing the hydrogen-bonded (dashed lines) ribbon motif. For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. [Symmetry codes: (i) $-x + 1, -y, -z$ and (ii) $-x, -y + 2, -z$.]

report 5-*tert*-butyl-4-nitro-1*H*-pyrazol-3-ol, (I). The structure of (I) (Fig. 1) consists of molecules that pack to form a linear hydrogen-bonded ribbon motif (Fig. 2). The hydrogen-bonding arrangement can be described by two centrosymmetric dimer formations (Table 1). The first of these dimer formations is atypical of pyrazoles and involves an N1—H...N2 interaction, centred at $(\frac{1}{2}, 0, 0)$ described by an $R_2^2(6)$ graph set (Etter, 1990), while the second dimer formation, centred at $(0, 1, 0)$, involves one intramolecular hydrogen-bonding association from O3—H to O42, forming an $S(6)$ graph-set motif, and an $R_2^2(4)$ graph-set motif arising from the three-centre association involving H3 and two O42 atoms. The other O atom (O41) of the nitro group is not involved in the hydrogen-bond network. The ribbon motifs are stacked in the *a*-axis direction, the perpendicular distances between ribbon planes being 3.263 (2) and 3.195 (2) Å (calculated with *PLATON*; Spek, 2003).

Experimental

Synthetically, (I) originated from 3,5-di-*tert*-butylpyrazole, being produced by gently warming this compound in concentrated nitric acid. In this reaction, 3,5-di-*tert*-butylpyrazole is attacked by nitric acid to form the onium species, which then displaces one *tert*-butyl group. The subsequent vacant position is then filled by an OH group that does not tautomerize to form the pyrazolone. The title compound was obtained from Key Organics Ltd and crystals were grown from ethanol solution.

Crystal data

$C_7H_{11}N_3O_3$	$Z = 2$
$M_r = 185.19$	$D_x = 1.399 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.4870$ (5) Å	Cell parameters from 1899 reflections
$b = 6.6560$ (4) Å	$\theta = 2.9\text{--}27.5^\circ$
$c = 11.5588$ (8) Å	$\mu = 0.11 \text{ mm}^{-1}$
$\alpha = 81.227$ (4)°	$T = 120$ (2) K
$\beta = 76.733$ (3)°	Plate, colourless
$\gamma = 65.037$ (5)°	$0.30 \times 0.05 \times 0.01 \text{ mm}$
$V = 439.50$ (6) Å ³	

Data collection

Bruker Nonius KappaCCD diffractometer	1720 independent reflections
φ and ω scans	1494 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	$R_{\text{int}} = 0.054$
$T_{\text{min}} = 0.968, T_{\text{max}} = 0.999$	$\theta_{\text{max}} = 26.0^\circ$
7496 measured reflections	$h = -7 \rightarrow 7$
	$k = -7 \rightarrow 8$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.125P]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.153$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.19$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
1720 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
128 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.28 (3)

Table 1

Hydrogen-bond geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1—H1...N2 ⁱ	0.88 (3)	2.09 (3)	2.847 (2)	144 (2)
O3—H3...O42	0.87 (3)	2.02 (3)	2.718 (2)	136 (2)
O3—H3...O42 ⁱⁱ	0.87 (3)	2.19 (3)	2.948 (2)	145 (2)

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

All *tert*-butyl H atoms were included in the refinement at calculated positions, in the riding-model approximation, with C—H distances of 0.98 Å. All H atoms involved in the hydrogen-bonding associations were located in Fourier syntheses and positional parameters were refined. The isotropic displacement parameters for all H atoms were set equal to $1.25U_{\text{eq}}$ of the carrier atom.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
 Fletcher, D. A., McMeeking, R. F. & Parkin, D. J. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
 Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
 Llamas-Saiz, A. L., Foces-Foces, C., Cano, F. H., Jimenez, P., Laynez, J., Meuterms, W., Elguero, J., Limbach, H.-H. & Aquilar-Parrilla, F. (1994). *Acta Cryst.* **B50**, 746–762.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*. Vol. 276, Macromolecular Crystallography, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sheldrick, G. M. (2003). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.