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5-*tert*-Butyl-4-nitro-1*H*-pyrazol-3-ol

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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 = 13.4

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

The structure of the title compound, $C_7H_{11}N_3O_3$, 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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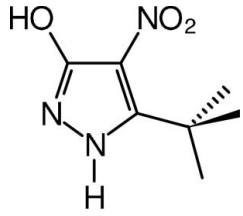
Comment

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.



(I)

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

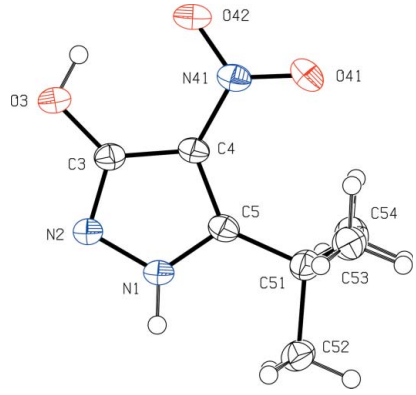


Figure 1
The molecular configuration and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.

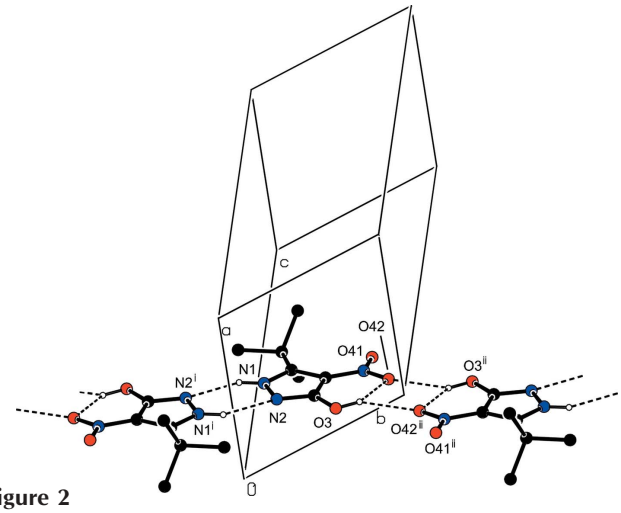


Figure 2
A partial packing diagram for (I), showing the hydrogen-bonded (dashed lines) ribbon motif. For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. [Symmetry codes: (i) $-x+1, -y, -z$ and (ii) $-x, -y+2, -z$.]

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

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

Data collection

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

Refinement

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

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···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 $1.25U_{eq}$ 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.* B**58**, 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., Meutermans, W., Elguero, J., Limbach, H.-H. & Aquilar-Parrilla, F. (1994). *Acta Cryst.* B**50**, 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.

supporting information

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$D_x = 1.399$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1899 reflections
$\theta = 2.9$–$27.5°$
$\mu = 0.11$ mm^{-1}
$T = 120$ K
Plate, colourless
0.30 × 0.05 × 0.01 mm

Data collection

Bruker Nonius 95 mm CCD camera on κ-goniostat diffractometer
Radiation source: Bruker Nonius FR591 rotating anode
10 cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.968$, $T_{max} = 0.999$
7496 measured reflections
1720 independent reflections
1494 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.4°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.153$
$S = 1.19$
1720 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.125P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.28 (3)

Special details

Experimental. The minimum and maximum absorption values stated above are those calculated in *SHELXL97* from the given crystal dimensions. The ratio of minimum to maximum apparent transmission was determined experimentally as 0.742732.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.3670 (3)	0.1639 (3)	0.10021 (14)	0.0270 (4)
H1	0.438 (4)	0.018 (4)	0.108 (2)	0.034*
N2	0.3749 (3)	0.2670 (3)	−0.01267 (14)	0.0275 (4)
C3	0.2598 (3)	0.4796 (3)	0.00586 (17)	0.0256 (5)
O3	0.2342 (2)	0.6286 (2)	−0.08679 (12)	0.0306 (4)
H3	0.166 (4)	0.761 (4)	−0.059 (2)	0.038*
C4	0.1789 (3)	0.5110 (3)	0.12948 (16)	0.0249 (5)
N41	0.0462 (3)	0.7199 (3)	0.17586 (15)	0.0296 (4)
O41	−0.0311 (2)	0.7382 (2)	0.28295 (13)	0.0371 (4)
O42	0.0128 (3)	0.8841 (2)	0.10277 (14)	0.0413 (5)
C5	0.2535 (3)	0.2983 (3)	0.18861 (17)	0.0250 (5)
C51	0.2309 (3)	0.2081 (3)	0.31659 (17)	0.0287 (5)
C52	0.3656 (4)	−0.0443 (3)	0.32335 (19)	0.0351 (5)
H51	0.3038	−0.1120	0.2780	0.044*
H52	0.3500	−0.1018	0.4067	0.044*
H53	0.5294	−0.0807	0.2897	0.044*
C53	−0.0255 (3)	0.2613 (4)	0.36904 (19)	0.0356 (5)
H54	−0.1153	0.4220	0.3616	0.044*
H55	−0.0415	0.2093	0.4533	0.044*
H56	−0.0832	0.1863	0.3257	0.044*
C54	0.3329 (4)	0.3093 (4)	0.38784 (19)	0.0397 (6)
H57	0.4971	0.2696	0.3540	0.050*
H58	0.3166	0.2514	0.4711	0.050*
H59	0.2500	0.4712	0.3839	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0287 (9)	0.0183 (8)	0.0280 (9)	−0.0040 (6)	−0.0050 (7)	−0.0006 (6)
N2	0.0303 (9)	0.0207 (9)	0.0261 (9)	−0.0059 (7)	−0.0040 (7)	−0.0005 (6)
C3	0.0232 (9)	0.0219 (9)	0.0290 (10)	−0.0063 (7)	−0.0064 (7)	0.0001 (7)
O3	0.0339 (8)	0.0206 (7)	0.0317 (8)	−0.0057 (6)	−0.0078 (6)	0.0018 (6)
C4	0.0218 (9)	0.0194 (10)	0.0295 (10)	−0.0038 (7)	−0.0052 (7)	−0.0026 (7)
N41	0.0261 (8)	0.0223 (9)	0.0356 (10)	−0.0043 (6)	−0.0064 (7)	−0.0035 (7)
O41	0.0372 (8)	0.0310 (8)	0.0352 (9)	−0.0069 (6)	0.0012 (6)	−0.0118 (6)
O42	0.0488 (10)	0.0195 (7)	0.0431 (10)	−0.0025 (6)	−0.0081 (7)	−0.0007 (6)
C5	0.0206 (9)	0.0225 (9)	0.0296 (10)	−0.0053 (7)	−0.0051 (7)	−0.0038 (7)
C51	0.0252 (10)	0.0283 (10)	0.0283 (10)	−0.0073 (8)	−0.0049 (8)	0.0003 (8)
C52	0.0335 (11)	0.0306 (11)	0.0333 (11)	−0.0077 (9)	−0.0062 (9)	0.0043 (8)
C53	0.0302 (11)	0.0339 (11)	0.0354 (11)	−0.0095 (9)	−0.0001 (8)	−0.0006 (9)

C54	0.0398 (12)	0.0468 (13)	0.0339 (12)	−0.0156 (10)	−0.0116 (9)	−0.0039 (9)

Geometric parameters (Å, º)

N1—C5	1.328 (3)	C51—C52	1.531 (3)
N1—N2	1.379 (2)	C51—C54	1.538 (3)
N1—H1	0.88 (3)	C51—C53	1.538 (3)
N2—C3	1.316 (2)	C52—H51	0.98
C3—O3	1.333 (2)	C52—H52	0.98
C3—C4	1.420 (3)	C52—H53	0.98
O3—H3	0.87 (3)	C53—H54	0.98
C4—N41	1.402 (2)	C53—H55	0.98
C4—C5	1.409 (3)	C53—H56	0.98
N41—O41	1.228 (2)	C54—H57	0.98
N41—O42	1.248 (2)	C54—H58	0.98
C5—C51	1.508 (3)	C54—H59	0.98
C5—N1—N2	115.54 (16)	C52—C51—C53	108.58 (16)
C5—N1—H1	126.1 (15)	C54—C51—C53	111.13 (17)
N2—N1—H1	118.4 (15)	C51—C52—H51	109.5
C3—N2—N1	103.85 (15)	C51—C52—H52	109.5
N2—C3—O3	119.47 (17)	H51—C52—H52	109.5
N2—C3—C4	110.65 (17)	C51—C52—H53	109.5
O3—C3—C4	129.88 (17)	H51—C52—H53	109.5
C3—O3—H3	107.6 (16)	H52—C52—H53	109.5
N41—C4—C5	129.88 (17)	C51—C53—H54	109.5
N41—C4—C3	123.47 (17)	C51—C53—H55	109.5
C5—C4—C3	106.64 (16)	H54—C53—H55	109.5
O41—N41—O42	122.35 (16)	C51—C53—H56	109.5
O41—N41—C4	121.21 (16)	H54—C53—H56	109.5
O42—N41—C4	116.44 (16)	H55—C53—H56	109.5
N1—C5—C4	103.32 (16)	C51—C54—H57	109.5
N1—C5—C51	121.22 (17)	C51—C54—H58	109.5
C4—C5—C51	135.46 (17)	H57—C54—H58	109.5
C5—C51—C52	109.91 (16)	C51—C54—H59	109.5
C5—C51—C54	109.69 (16)	H57—C54—H59	109.5
C52—C51—C54	108.19 (16)	H58—C54—H59	109.5
C5—C51—C53	109.32 (15)		
C5—N1—N2—C3	0.2 (2)	N2—N1—C5—C51	179.91 (15)
N1—N2—C3—O3	−179.93 (15)	N41—C4—C5—N1	178.52 (17)
N1—N2—C3—C4	−0.2 (2)	C3—C4—C5—N1	−0.03 (19)
N2—C3—C4—N41	−178.50 (16)	N41—C4—C5—C51	−1.5 (3)
O3—C3—C4—N41	1.2 (3)	C3—C4—C5—C51	179.94 (19)
N2—C3—C4—C5	0.2 (2)	N1—C5—C51—C52	3.3 (2)
O3—C3—C4—C5	179.83 (18)	C4—C5—C51—C52	−176.7 (2)
C5—C4—N41—O41	−2.5 (3)	N1—C5—C51—C54	122.10 (19)
C3—C4—N41—O41	175.83 (17)	C4—C5—C51—C54	−57.9 (3)

C5—C4—N41—O42	177.17 (18)	N1—C5—C51—C53	−115.81 (19)
C3—C4—N41—O42	−4.5 (3)	C4—C5—C51—C53	64.2 (3)
N2—N1—C5—C4	−0.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*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*.