

5-*tert*-Butyl-4-bromo-1,2-dihydro-1*H*-pyrazol-3(2*H*)-one monohydrateDaniel E. Lynch<sup>a\*</sup> and Ian McClenaghan<sup>b</sup><sup>a</sup>School of Science and the Environment, Coventry University, Coventry CV1 5FB, England, and <sup>b</sup>Key Organics Ltd, Highfield Industrial Estate, Camelford, Cornwall PL32 9QZ, EnglandCorrespondence e-mail:  
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## Key indicators

Single-crystal X-ray study  
 $T = 150$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.030  
 $wR$  factor = 0.069  
Data-to-parameter ratio = 15.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title compound,  $\text{C}_7\text{H}_{11}\text{BrN}_2\text{O}\cdot\text{H}_2\text{O}$ , exhibits an elaborate hydrogen-bonding network involving pyrazole  $\text{N}-\text{H}\cdots\text{O}$  dimers and two other hydrogen-bonding motifs, both including water molecules. One motif is a distorted hexagonal  $R_3^5(11)$  graph set, while the other is a distorted octagonal boat conformation  $R_6^4(14)$  graph set.

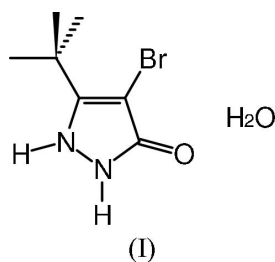
Received 21 April 2005

Accepted 22 April 2005

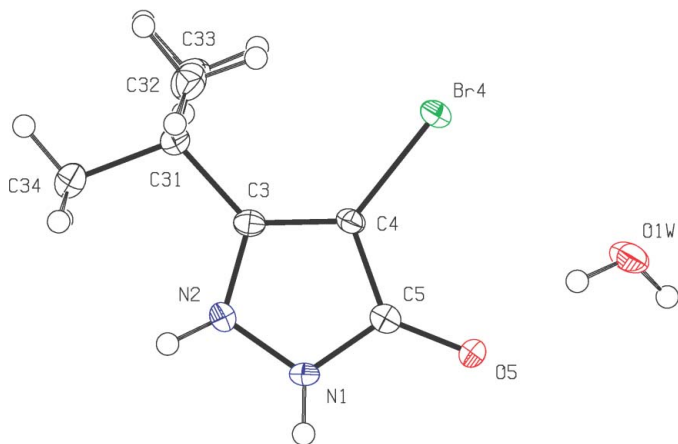
Online 6 July 2005

## Comment

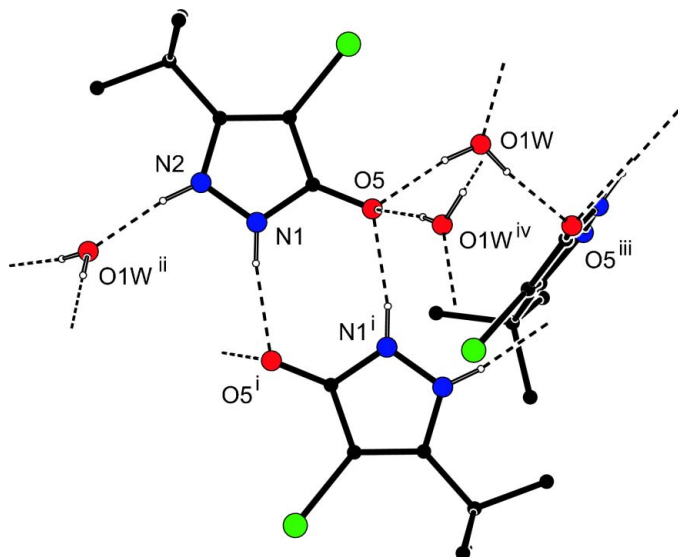
In a series of studies on the preparation and hydrogen-bonding properties of 3,4,5-tri-substituted pyrazoles, we recently characterized the structure of 5-*tert*-butyl-4-nitro-1*H*-pyrazol-3-ol (Lynch & McClenaghan, 2005). We report here the structure of the title compound, (I). Similar to 5-*tert*-butyl-4-nitro-1*H*-pyrazol-3-ol, compound (I) originated from 3,5-di-*tert*-butylpyrazole. Compound (I) was prepared by reacting 3,5-di-*tert*-butylpyrazole with bromine in chloroform solution at room temperature. In these reactions, 3,5-di-*t*-butylpyrazole is attacked by either nitric acid (as in the case of 5-*tert*-butyl-4-nitro-1*H*-pyrazol-3-ol) or bromine to form the onium species, which then displaces one *tert*-butyl group. The subsequent vacant position is then filled by an OH group that, in the case of (I), tautomerizes to form the pyrazolone.



In the structure of (I) (Fig. 1), all strong hydrogen-bonding components are involved in the hydrogen-bonding network. The hydrogen-bonding geometry for this structure is listed in Table 1. The fourfold symmetry in (I) arises because of the unique hydrogen-bonded motif that is formed *via* contributions from eight pyrazole molecules and four water molecules. Each pyrazole molecule forms a centrosymmetric  $R_2^2(8)$  graph set (Etter, 1990) dimer *via*  $\text{N1}-\text{H}\cdots\text{O5}$  interactions, at  $(x, y, z)$  and  $(-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2})$ , centred at  $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ . The  $\text{N2}/\text{H}$  group associates with  $\text{O1W}$ , at  $(x, y, z)$  and  $(y + \frac{1}{4}, -x + \frac{5}{4}, z + \frac{1}{4})$ .  $\text{O1W}$ , at  $(x, y, z)$ , associates with two  $\text{O5}$  atoms, one at  $(x, y, z)$  and the other at  $(-y + \frac{5}{4}, x - \frac{3}{4}, -z + \frac{1}{4})$ . Thus, each  $\text{O5}$  atom is involved in a four-centre hydrogen-bonding association. For  $\text{O5}$ , at  $(x, y, z)$ , the three non-H-atom contacts are  $\text{O1W}$  at  $(x, y, z)$ ,  $\text{O1I}$  at  $(y + \frac{3}{4}, -x + \frac{5}{4}, -z + \frac{1}{4})$  and  $\text{N1}$  at  $(-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2})$  (Fig. 2). Three pyrazole molecules, at  $(x, y, z)$ ,  $(-x + \frac{3}{2},$

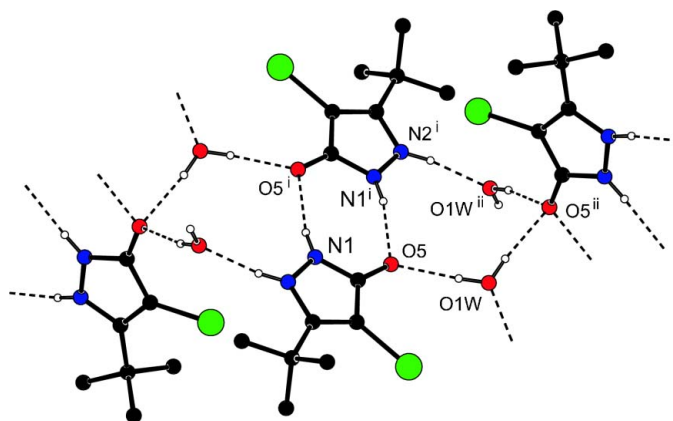


**Figure 1**  
Molecular configuration and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

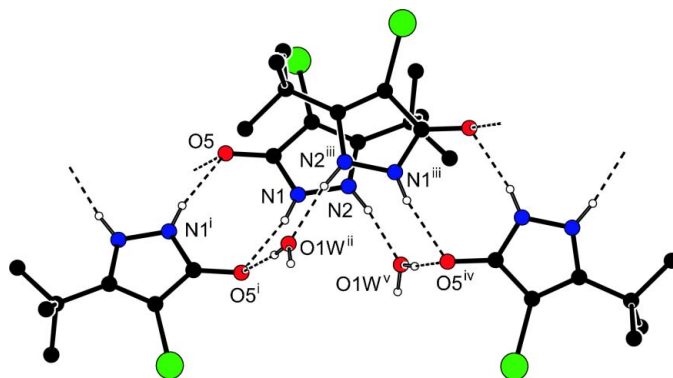


**Figure 2**  
Hydrogen-bonding environment for (I), at  $(x, y, z)$ , showing the centrosymmetric  $R_2^2(8)$   $N1-H \cdots O5$  dimer, the two hydrogen-bonding associations from  $O1W$ , and the four-centre hydrogen-bonding association involving  $O5$ . For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $y + \frac{1}{4}, -x + \frac{3}{4}, z + \frac{1}{4}$ ; (iii)  $-y + \frac{5}{4}, x - \frac{3}{4}, -z + \frac{1}{4}$ ; (iv)  $y + \frac{3}{4}, -x + \frac{5}{4}, -z + \frac{1}{4}$ ]

$-y + \frac{1}{2}, -z + \frac{1}{2}$ ) and  $(-y + \frac{5}{4}, x - \frac{3}{4}, -z + \frac{1}{4})$ , and two water molecules, at  $(x, y, z)$  and  $(-y + \frac{5}{4}, x - \frac{3}{4}, -z + \frac{1}{4})$ , form a distorted hexagonal hydrogen-bonding motif [graph set  $R_3^2(11)$ ], adjoining the  $N1-H \cdots O5$  dimer, fused *via* the same interaction (Fig. 3). The hexagonal motifs are also fused with each other *via* the  $O1W-H \cdots O5$  interaction at  $(x, y, z)$ . The resulting arrangement also creates a distorted octagonal boat conformation hydrogen-bonding motif [graph set  $R_6^4(14)$ ] involving four pyrazole groups, at  $(x, y, z)$ ,  $(-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2})$ ,  $(x - \frac{1}{2}, y, -z + \frac{1}{2})$  and  $(1 - x, -y + \frac{1}{2}, z)$ , and two water molecules, at  $(y + \frac{1}{4}, -x + \frac{5}{4}, z + \frac{1}{4})$  and  $(-y + \frac{3}{4}, x - \frac{3}{4}, z + \frac{1}{4})$



**Figure 3**  
Part of the structure of (I), at  $(x, y, z)$ , showing the distorted  $R_3^2(11)$  hexagonal motif, and its position with respect to the  $N1-H \cdots O5$  dimer. For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-y + \frac{5}{4}, x - \frac{3}{4}, z - \frac{1}{4}$ ]



**Figure 4**  
Part of the structure of (I), at  $(x, y, z)$ , showing the distorted  $R_6^4(14)$  octagonal boat motif and its position with respect to the  $N1-H \cdots O5$  dimer. For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-y + \frac{3}{4}, x - \frac{3}{4}, z + \frac{1}{4}$ ; (iii)  $1 - x, -y + \frac{1}{2}, z$ ; (iv)  $x - \frac{1}{2}, y, -z + \frac{1}{2}$ ; (v)  $y + \frac{1}{4}, -x + \frac{5}{4}, z + \frac{1}{4}$ ]

(Fig. 4). A stereoview of the unit cell contents of (I) is shown in Fig. 5. The Br atom does not contribute to the hydrogen-bonding network; atom Br4 is 3.469 (3) Å from  $O1W$ , and 3.412 (3) Å from  $N2(-y + \frac{5}{4}, x - \frac{3}{4}, z - \frac{1}{4})$ .

## Experimental

The title compound was obtained from Key Organics Ltd, and crystals were grown from an ethanol solution.

### Crystal data

$C_7H_{11}BrN_2O \cdot H_2O$   
 $M_r = 237.10$   
Tetragonal,  $I4_1/a$   
 $a = 13.6840(4)$  Å  
 $c = 21.4734(8)$  Å  
 $V = 4020.9(2)$  Å<sup>3</sup>  
 $Z = 16$   
 $D_x = 1.567$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 2331 reflections  
 $\theta = 2.9-27.5^\circ$   
 $\mu = 4.06$  mm<sup>-1</sup>  
 $T = 150(2)$  K  
Prism, colourless  
 $0.36 \times 0.27 \times 0.20$  mm

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.288$ ,  $T_{\max} = 0.444$   
 12 489 measured reflections  
 1977 independent reflections

1633 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.069$   
 $\theta_{\text{max}} = 26.0^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -15 \rightarrow 14$   
 $l = -19 \rightarrow 26$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.069$   
 $S = 1.02$   
 1977 reflections  
 124 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 7.0406P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.64 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O5^i$	0.82 (3)	1.97 (3)	2.773 (3)	168 (3)
$N2-H2\cdots O1W^{ii}$	0.85 (3)	1.80 (3)	2.646 (3)	171 (3)
$O1W-H1W\cdots O5$	0.83 (2)	1.91 (2)	2.733 (3)	169 (3)
$O1W-H2W\cdots O5^{iii}$	0.83 (2)	1.91 (2)	2.739 (3)	173 (3)

Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $y + \frac{1}{4}, -x + \frac{5}{4}, z + \frac{1}{4}$ ; (iii)  $-y + \frac{5}{4}, x - \frac{3}{4}, -z + \frac{1}{4}$ .

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  $\text{\AA}$ . All NH H atoms involved in the hydrogen-bonding associations (Table 1) were located in Fourier syntheses and positional parameters were refined. The water H atoms were located and were refined with O—H distance restraints of 0.83 (2)  $\text{\AA}$  and H $\cdots$ H restraints of 1.40 (2)  $\text{\AA}$ . 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 reduc-

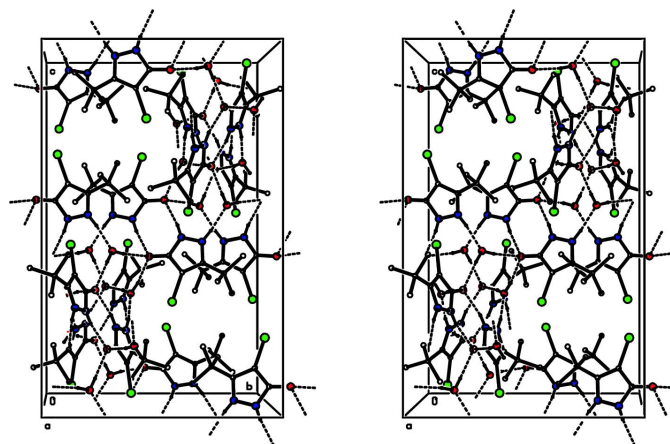


Figure 5  
 Stereoview of the unit cell contents of (I).

tion: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON97* (Spek, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank the EPSRC National Crystallography Service (Southampton, England).

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