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High-temperature phase of 5-*tert*-butylpyrazole

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Key indicators

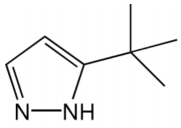
Single-crystal X-ray study
T = 195 K
Mean σ(C–C) = 0.003 Å
R factor = 0.060
wR factor = 0.151
Data-to-parameter ratio = 22.7

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

The title compound, $C_7H_{12}N_2$, has two independent molecules in the asymmetric unit. The structure contains N—H···N hydrogen-bonded tetramers. The *tert*-butyl groups show large amplitudes of internal rotational motion.

Comment

Polypyrazolylborate ligands have attracted a great deal of attention in inorganic, bioinorganic and organometallic chemistry (Trofimenko, 1999). Recently, we have reported several novel bitopic bis- and tris(1-pyrazolyl)borate ligands (Bieller *et al.*, 2004). Our research is currently focused on the synthesis of bitopic bis(3-*tert*-butylpyrazol-1-yl)borate ligands. We report here the structure of the starting material 5-*tert*-butylpyrazole, (I), at 195 (2) K.



(I)

Compound (I) shows a phase transition at 170 (1) K. The crystals are destroyed upon cooling through the phase transition. Thus, only the crystal structure of the high-temperature phase can be determined, while the low-temperature structure is not accessible.

The asymmetric unit of (I) contains two independent molecules (Fig. 1). The two molecules have very similar dimensions. Both five-membered rings are essentially planar. The *tert*-butyl groups have conformations with one methyl group almost coplanar with the pyrazole ring: C5 deviates by 0.26 Å from the plane of the pyrazole group N1/N2/C1/C2/C3 and

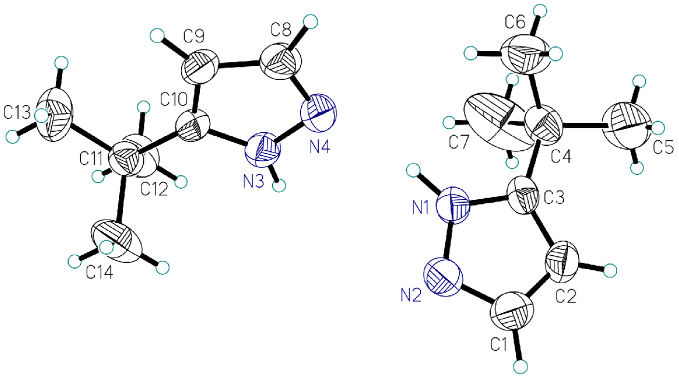


Figure 1
The two independent molecules of (I), shown with 50% probability displacement ellipsoids. The H atoms are drawn as small spheres of arbitrary radius.

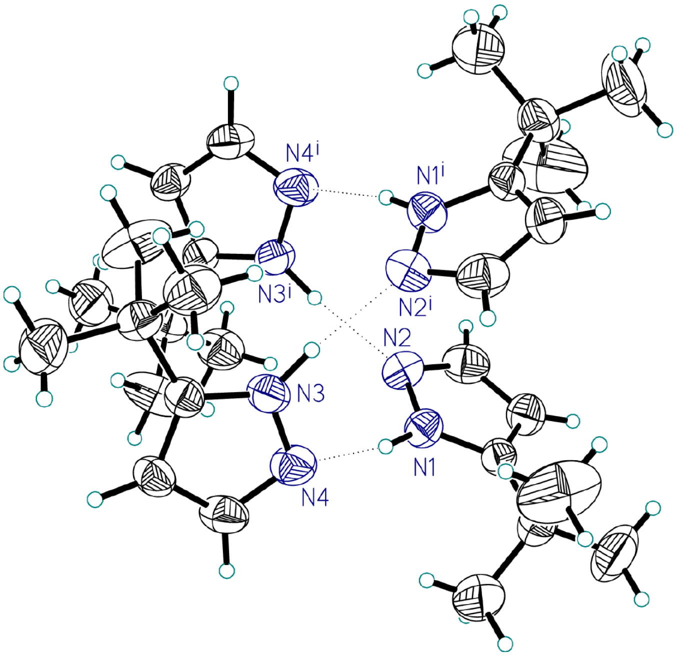


Figure 2
A hydrogen-bonded (dashed lines) tetramer of (I), shown with 50% probability displacement ellipsoids. [Symmetry code (i): $-x, y, \frac{1}{2} - z$.]

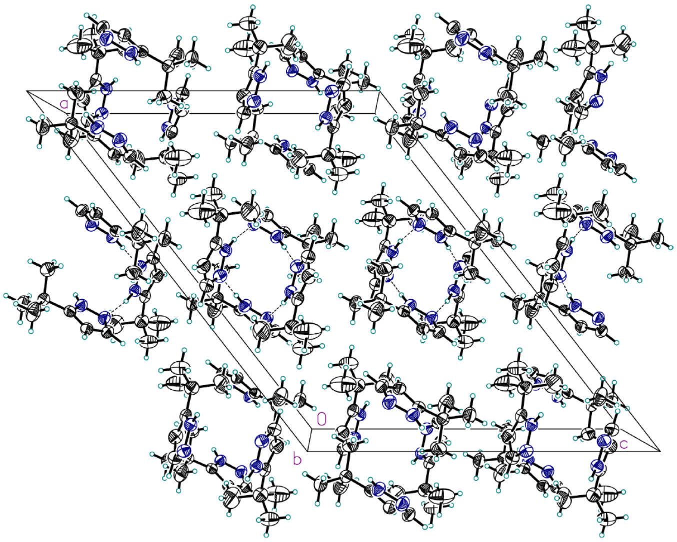


Figure 3
The crystal packing of (I), viewed down *b*, shown with 50% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

C13 deviates by 0.14 Å from the plane of the pyrazole group N3/N4/C8/C9/C10. Both molecules show a large amplitude of rotational motion. The major part of this motion is due to internal rotation of the *tert*-butyl group about the C3—C4 or C10—C11 bond. A thermal motion analysis using program *THMA*14*c* (Schomaker & Trueblood, 1998) calculated the internal rotations about the C3—C4 and C10—C11 bonds to be 104 (10) and 52 (7)$^{\circ 2}$, the librations to be 52 (7) and 34 (6)$^{\circ 2}$, and the overall motions of the *tert*-butyl groups about these axes to be 156 (12) and 87 (9)$^{\circ 2}$, respectively. Thus, the observed C—C$_{\rm methyl}$ bond lengths may be significantly too short.

The molecules are connected by N—H$\cdots$N hydrogen bonds (Table 1) into tetramers (Figs. 2 and 3). The tetramers have twofold symmetry. Crystal structures of substituted pyrazoles are known to contain either hydrogen-bonded cyclic structures or polymeric chains. Trimers have been observed in the crystal structure of 4-methylpyrazole (Goddard *et al.*, 1999), tetramers in the crystal structure of 3(5)-phenylpyrazole (Haghiri *et al.*, 2003), hexamers in the crystal structure of 3-phenylpyrazole (Haghiri *et al.*, 2002) and polymeric chains were reported for the crystal structures of 5-phenylpyrazole (García *et al.*, 2002) and 4-phenylpyrazole (Reger *et al.*, 2003). Neighboring tetramers of (I) are connected by weak intermolecular C(methy)—H$\cdots\pi$(pyrazole) interactions with H$\cdots$*Cg* distances of 3.01, 3.03 and 3.07 Å (Table 1).

Experimental

The title compound was prepared as described by Trofimenko *et al.* (1987). Colorless rods were obtained by recrystallization from hexane at room temperature.

Crystal data

$C_7H_{12}N_2$
$M_r = 124.19$
Monoclinic, $C2/c$
$a = 22.105$ (3) Å
$b = 10.7547$ (13) Å
$c = 17.074$ (2) Å
$\beta = 127.879$ (4)°
$V = 3203.8$ (7) Å^3
$Z = 16$

$D_x = 1.030$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 185 reflections
$\theta = 3$–26°
$\mu = 0.06$ mm^{-1}
$T = 195$ (2) K
Rod, colorless
0.44 × 0.12 × 0.12 mm

Data collection

Siemens SMART 1K CCD diffractometer
ω scans
Absorption correction: none
24776 measured reflections
4268 independent reflections

1858 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.088$
$\theta_{\rm max} = 29.5°$
$h = -30 \rightarrow 30$
$k = -14 \rightarrow 14$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.151$
$S = 1.06$
4268 reflections
188 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0035 (6)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$N4	0.93 (2)	1.94 (2)	2.858 (2)	169 (2)
N3—H3N$\cdots$N2$^{\rm i}$	0.96 (2)	1.94 (2)	2.889 (3)	174 (2)
C7—H7$B\cdots Cg2^{\rm ii}$	0.98	3.01	3.935	158
C12—H12$B\cdots Cg1^{\rm iii}$	0.98	3.03	3.972	161
C14—H14$B\cdots Cg2^{\rm i}$	0.98	3.07	3.663	120

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $x, -y, \frac{1}{2} + z$. *Cg*1 and *Cg*2 represent the centroids of pyrazole rings N1/N2/C1/C2/C3 and N3/N4/C8/C9/C10, respectively

The H atoms attached to the five-membered rings were located in a difference Fourier synthesis and were refined with individual isotropic displacement parameters. H atoms on the methyl groups were geometrically positioned using a fixed distance: $C_{methyl}-H = 0.98$ Å and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$. The thermal motion analysis was performed with the *WinGX* program package (Farrugia, 1999).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL*97.

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