

5-*tert*-Butyl-3-methyl-1*H*-pyrazole at 240 KConcepción Foces-Foces^{a*} and
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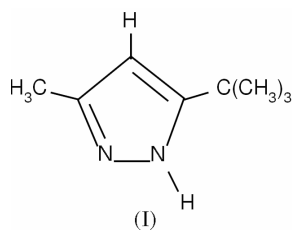
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Key indicators

Single-crystal X-ray study
T = 241 K
Mean $\sigma(\text{C}-\text{C})$ = 0.007 Å
R factor = 0.088
wR factor = 0.117
Data-to-parameter ratio = 11.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The title compound, C₈H₁₄N₂, exists in the solid state as a
tetramer with hydrogen bonding around the $\bar{4}$ axis.Received 10 October 2000
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Comment

One of our interests in crystalline pyrazoles involves elucidation of factors controlling the four intermolecular hydrogen-bonding modes (catemers, dimers, trimers and tetramers) that have been found in pyrazoles bearing only one conventional donor and/or including other acceptor groups apart from that of the pyrazole (Foces-Foces *et al.*, 2000). In the three 3,5-di-*tert*-butylpyrazole derivatives studied so far (with substituents at C4 = NO₂, H and NO; Llamas-Saiz *et al.*, 1994; Aguilar-Parrilla *et al.*, 1995; Fletcher *et al.*, 1997; CSD refcodes WILBAU, YULNUO and RIVBAZ, respectively), the dimeric association is the only hydrogen-bonding mode observed. The aim of this paper is to study the contribution of different types of substituents on the secondary structure (one methyl group at C3 instead of a *tert*-butyl group) which appear to govern the choice of a hydrogen-bonding mode.



It is noteworthy that the 5-*tert*-butyl-3-methyl-1*H*-pyrazole tautomer, (I), is present in the solid state (Fig. 1) in spite of the tendency of these compounds to present proton disorder. The bond distances and angles in the ring are unremarkable with respect to those of the unordered proton derivatives and the parent compound (*i.e.* N2–N1–C5 > N1–N2–C3; N2–C3–C4 > N1–C5–C4). The conformation of the *tert*-butyl group places the methyl C10 eclipsed with respect to the H4 atom whereas, in the previous reported derivatives with substituents at C4, one methyl group is eclipsed with respect to the N atoms to avoid steric repulsions (Table 1).

An intermolecular hydrogen bond between the N atoms of the pyrazole (Table 2) leads to the formation of tetramers, around the $\bar{4}$ axis (Figs. 2 and 3), in agreement with the proposed secondary structure model (Foces-Foces *et al.*, 2000) for methyl and butyl substituents at C3 and C5.

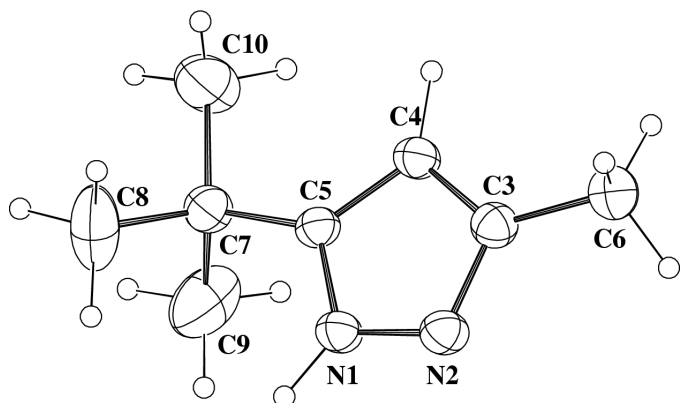


Figure 1
The molecular structure of (I) showing the numbering scheme. The displacement parameters are drawn at the 30% probability level.

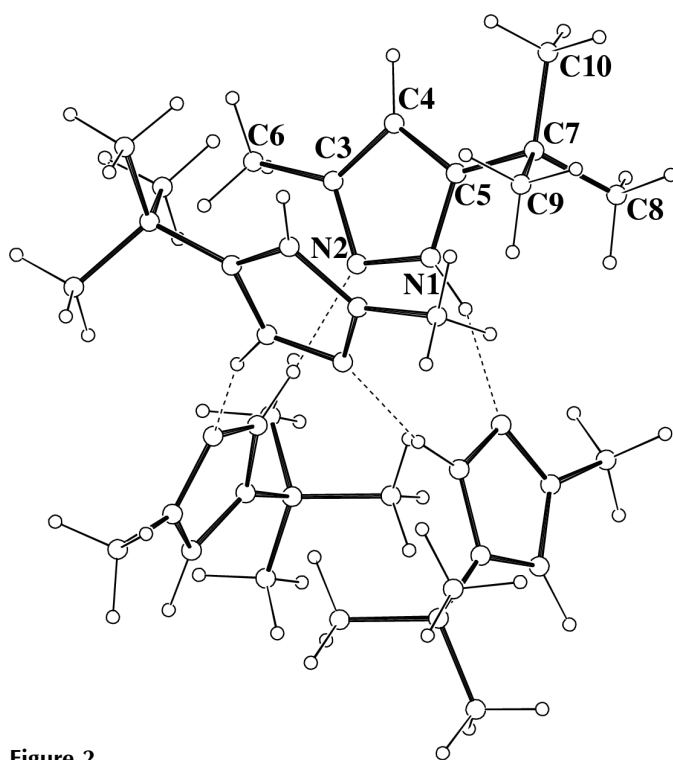


Figure 2
The tetrameric arrangement of molecules around the $\bar{4}$ axis. Dotted lines represent hydrogen-bond interactions.

Experimental

The title compound was prepared according to López *et al.* (1993) and crystals were obtained by recrystallization from cyclohexane. The melting point (440 K) was determined by DSC with a Seiko 220 C instrument with a scanning rate of 2° min^{-1} .

Crystal data

$\text{C}_8\text{H}_{14}\text{N}_2$
 $M_r = 138.21$
Tetragonal, $I4_1/a$
 $a = 18.2451 (16) \text{ \AA}$
 $c = 10.6667 (8) \text{ \AA}$
 $V = 3550.8 (7) \text{ \AA}^3$
 $Z = 16$
 $D_x = 1.034 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
Cell parameters from 56 reflections
 $\theta = 2-45^\circ$
 $\mu = 0.48 \text{ mm}^{-1}$
 $T = 240 \text{ K}$
Prism, colourless
 $0.50 \times 0.10 \times 0.10 \text{ mm}$

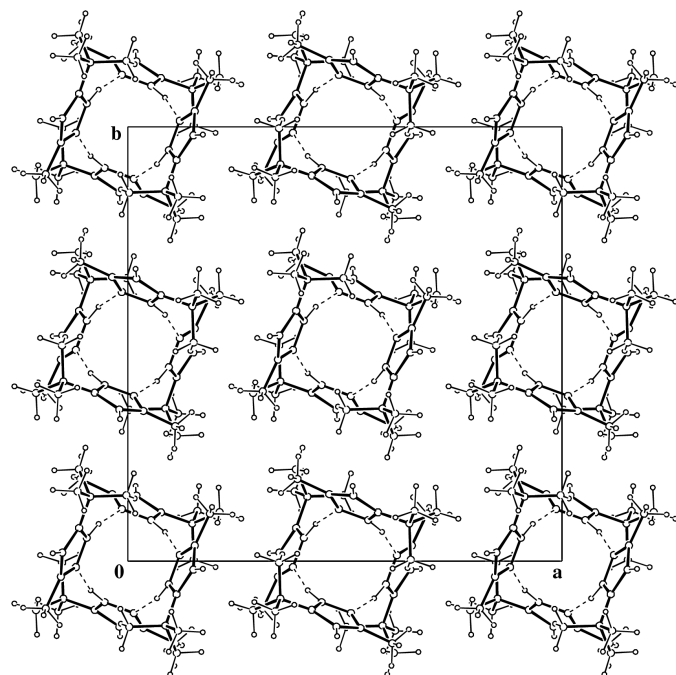


Figure 3
The crystal packing viewed along the c axis.

Data collection

Philips PW100 diffractometer
 $\omega/2\theta$ scans
1509 measured reflections
1509 independent reflections
1100 reflections with $I > 2\sigma(I)$
 $\theta_{\text{max}} = 65^\circ$

$h = 0 \rightarrow 21$
 $k = 0 \rightarrow 21$
 $l = 0 \rightarrow 12$
2 standard reflections
frequency: 90 min
intensity decay: 3%

Refinement

Refinement on F
 $R = 0.088$
 $wR = 0.117$
 $S = 0.989$
1100 reflections
95 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = k/[(A+BF_o)^2(C+D(\sin\theta)/\lambda)]$
 $(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|-------------|-----------|--------------|-----------|
| N2—N1—C5 | 112.8 (3) | N2—C3—C4 | 109.2 (3) |
| N1—N2—C3 | 105.5 (3) | N1—C5—C4 | 105.1 (3) |
| N1—C5—C7—C8 | 58.2 (6) | N1—C5—C7—C10 | 179.2 (5) |
| N1—C5—C7—C9 | −59.4 (6) | | |

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------------------|----------|--------------|--------------|----------------|
| $\text{N1—H1} \cdots \text{N2}^i$ | 0.93 (5) | 1.99 (6) | 2.896 (5) | 165 (5) |

Symmetry code: (i) $y, -x, -z$.

Considering the possibility of disorder of the *tert*-butyl group the data were collected at 240 K using an Oxford Cryosystems Cryo-

stream device (Cosier & Glazer, 1986) and the stated temperature was measured continuously during data collection. Due to the disposition of the low-temperature device, the maximum θ angle available is 65° . Rotational disorder of the *tert*-butyl group around the C5–C7 bond was apparent from their large displacement parameters; however, attempts to establish a disordered model failed. The highest peaks of $0.39 \text{ e } \text{\AA}^{-3}$ in the final difference synthesis are close to the *tert*-butyl group. All H atoms were obtained from difference Fourier synthesis although only H1 was refined freely; others were constrained. The weighting schemes were established in an empirical way as to give no trends in $\langle w\Delta^2F \rangle$ versus $\langle F_o \rangle$ or $\langle \sin\theta/\lambda \rangle$, using different parameters in the weighting formula for different ranges of these variables (PESOS; Martínez-Ripoll & Cano, 1975). There are four voids in the structure located at $(0,0,\frac{1}{2})$ and equivalent positions, spherical in shape and of 3.5 \AA diameter approximately (Cano & Martínez-Ripoll, 1992). According to the ^1H and ^{13}C NMR experiments no solvent molecules were detected. The calculated density for the title compound is in the range found for the analogous derivatives (WILBAU, YULNUO and RIVBAZ).

Data collection: Philips PW1100 software (Hornstra & Vossers, 1973); cell refinement: LSUCRE (Appleman, 1984); data reduction: Xtal3.6 ADDREF DIFDAT SORTRF (Hall *et al.*, 1999); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1997); program(s) used to refine structure: Xtal3.6 CRYLSQ; molecular graphics: Xtal3.6; software used to prepare material for publication: Xtal3.6 BONDLA CIFIO.

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