

5-[N-(1*H*-Benzotriazol-1-ylmethyl)-amino]-3-*tert*-butyl-1-phenylpyrazole: sheets built from N—H···N, C—H···N and C—H··· π (pyrazole) interactions

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In the title compound, C₂₀H₂₂N₆, the molecules are linked into a chain of rings by N—H···N [H···N 2.16 Å, N···N 2.950 (3) Å and N—H···N 149°] and C—H···N [H···N 2.55 Å, C···N 3.481 (3) Å and C—H···N 165°] hydrogen bonds, and these chains are linked into sheets by means of C—H··· π (pyrazole) interactions.

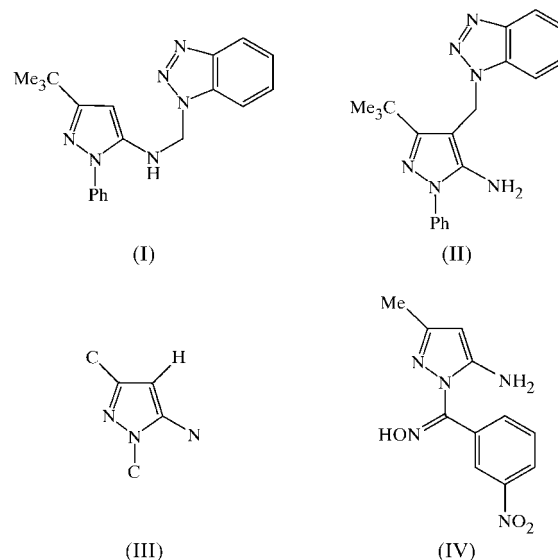
Comment

The title compound, (I) (Fig. 1), was prepared as a precursor for the synthesis of new hydrogenated pyrazolo-pyridines using the benzotriazole methodology (Katritzky *et al.*, 1995, 1998; Abonia *et al.*, 2001).

The C—C bond distances (Table 1) in the fused arene ring show some evidence for bond fixation, with bonds C3—C4 and C5—C6 being shorter than the neighbouring bonds; likewise, the N2—N3 bond is markedly shorter than both N1—N2 and N5—N6. The pattern of C—N distances is of interest; the C7—N1 and C7—N4 distances, which involve planar three-connected N and four-connected C atoms, are significantly different; likewise, the C1—N3 and C9—N6 distances, which involve two-connected N and planar three-connected C atoms, differ significantly, consistent with the occurrence of single and double bonds, respectively. On the other hand, the three distances C2—N1, C8—N4 and C8—N5, which involve two planar three-connected atoms, span only a small range.

The supramolecular structure of (I) is determined by a combination of N—H···N and C—H···N hydrogen bonds and C—H··· π (pyrazole) interactions (Table 2). The amino

atom N4 at (*x*, *y*, *z*) acts as hydrogen-bond donor to triazole N3 at (2 − *x*, −½ + *y*, ½ − *z*), while N4 at (2 − *x*, −½ + *y*, ½ − *z*), in turn, acts as donor to N3 at (*x*, −1 + *y*, *z*), so producing a C(6) chain generated by the 2₁ screw axis along (1, *y*, ¼). This is



augmented by a fairly weak C—H···N hydrogen bond; C3 at (*x*, *y*, *z*) acts as donor to triazole N2 at (2 − *x*, −½ + *y*, ½ − *z*), producing a C(5) chain generated by the same screw axis as before, so that the resulting chain of rings running parallel to the [010] direction (Fig. 2) has the descriptor C(5)C(6)[R₂²(9)] (Bernstein *et al.*, 1995). Two chains of this type run through each unit cell, in the domains 0.06 < *z* < 0.44 and 0.56 < *z* < 0.94, and within each domain, adjacent chains are linked into a (001) sheet by C—H··· π (pyrazole) interactions. Atom C19 in the molecule at (*x*, *y*, *z*), which lies in the hydrogen-bonded chain along (1, *y*, ¼), forms a short C—H··· π contact (Table 2) with the centroid, Cg2, of the pyrazole ring of the molecule at (1 − *x*, −½ + *y*, ½ − *z*), which itself lies in the hydrogen-bonded

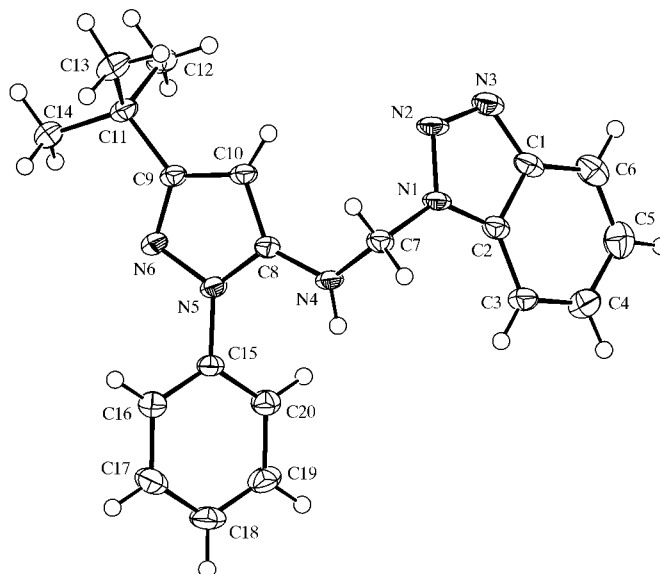


Figure 1

The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

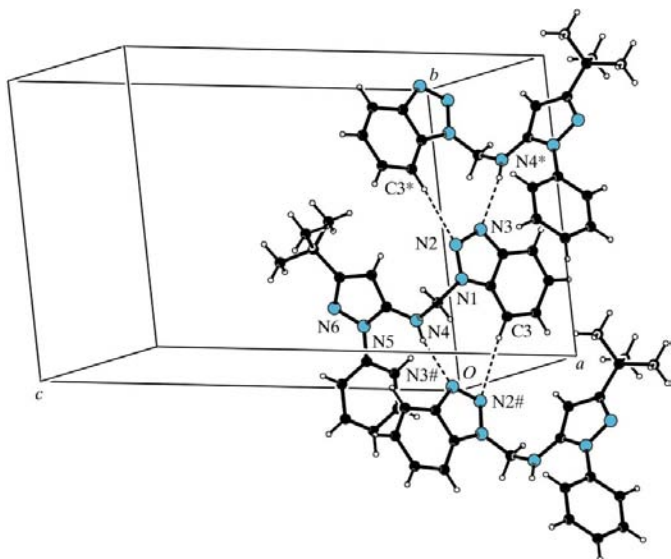


Figure 2

Part of the crystal structure of (I), showing the formation of a chain of rings along [010]. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

chain along $(\frac{1}{2}, y, \frac{1}{4})$ (Fig. 3). Propagation of this interaction thus links all of the [010] chains in a given domain of z into a single sheet. Two sheets run through each unit cell, but there are no direction-specific interactions between adjacent sheets.

The structure of the isomeric compound (II) (see *Scheme* above) has recently been reported in space group $P2_1/c$ (Low *et al.*, 2002). The supramolecular structure was described in terms of a single hydrogen bond, $N51 - H51 \cdots N43^i$ [symmetry

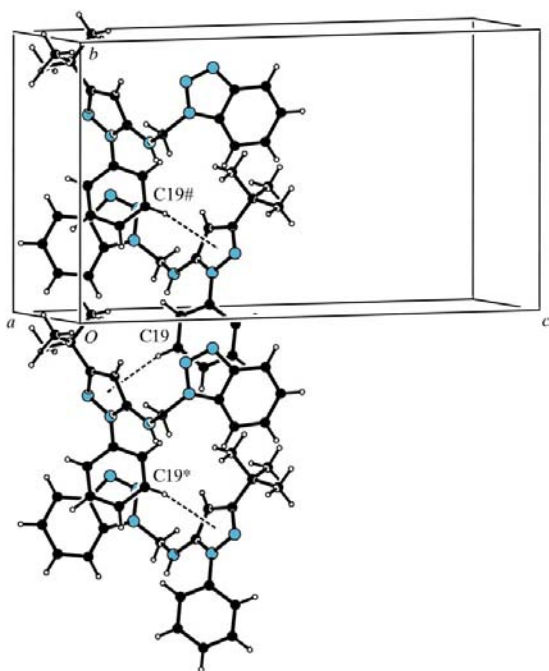


Figure 3

Part of the crystal structure of (I), showing the linking of the [010] chains by $C-H \cdots \pi$ (pyrazole) interactions. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

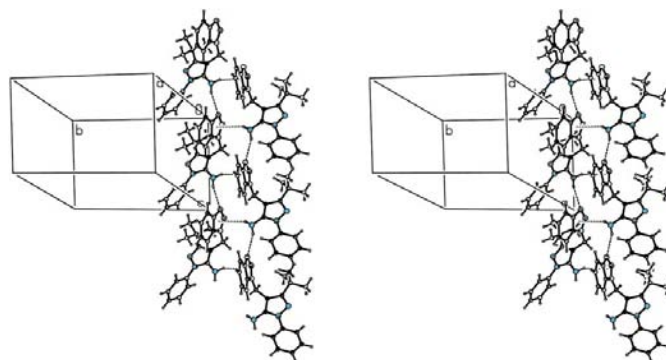


Figure 4

Stereoview of part of the crystal structure of (II), showing the formation of a molecular ladder built from $N-H \cdots N$ and $N-H \cdots \pi$ (triazole) interactions.

code: (i) $x, y, 1 + z$], forming $C(8)$ chains by translation. However, re-examination of the structure of (II) in the light of the above analysis for (I), shows that there is also a short $N-H \cdots \pi$ (triazole) interaction, involving the $N51 - H52$ bond, which does not participate in conventional hydrogen bonding, and the centroid ($Cg2$) of the triazole ring; $H52 \cdots Cg2^{ii}$ 2.72 Å, $N51 \cdots Cg2^{ii}$ 3.477 (2) Å and $N51 - H52 \cdots Cg2^{ii}$ 146° [symmetry code: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. This interaction produces a zigzag chain parallel to [001], generated by the c -glide plane at $y = -\frac{1}{4}$. The combination of $N-H \cdots N$ and $N-H \cdots \pi$ interactions thus generates a double chain, or molecular ladder (Fig. 4).

Since $C-H \cdots \pi$ interactions most frequently involve benzenoid rings as acceptors (Desiraju & Steiner, 1999; Suezawa *et al.*, 2001), with rather few examples involving

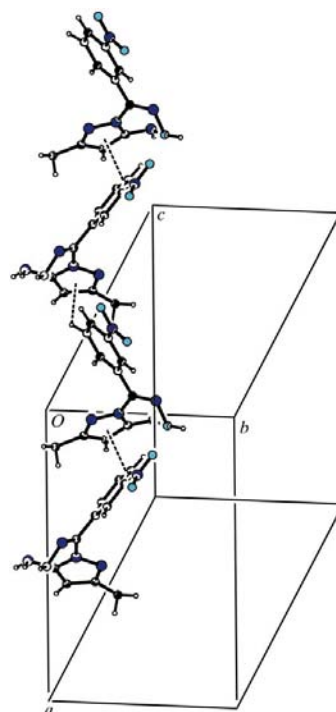


Figure 5

Part of the crystal structure of (IV), showing the formation of a $C-H \cdots \pi$ (pyrazole) chain consisting of type 1 molecules only.

heterocycles, we have briefly investigated the occurrence of C—H... π (pyrazole) interactions by examining the structures of pyrazoles in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) containing the fragment (III), namely a pyrazole ring carrying the same substituent atoms as found in (I). Nine examples were retrieved; the structures of three of these contained only C—H... π (arene) interactions, those of five others contained no C—H... π interactions at all, but the structure of the ninth [CSD refcode TIXPEV, (IV); Ramm *et al.*, 1996], which crystallizes in space group $P2_1/a$ with $Z' = 2$, displays quite short C—H... π (pyrazole) interactions, such that the two independent molecules each form simple chains. For the type 1 molecules, the chain is generated by the a -glide plane at $y = -\frac{1}{4}$ [H...Cg1ⁱⁱⁱ 2.84 Å, C...Cg1ⁱⁱⁱ 3.645 (2) Å and C—H...Cg1ⁱⁱⁱ 127°; symmetry code: (iii) $-\frac{1}{2} + x, -\frac{1}{2} - y, z$] (Fig. 5), while for the type 2 molecules, the chain is generated by the a -glide plane at $y = \frac{1}{4}$ [H...Cg2^{iv} 2.69 Å, C...Cg2^{iv} 3.537(2) Å and C—H...Cg2^{iv} 145°; symmetry code: (iv) $\frac{1}{2} + x,$

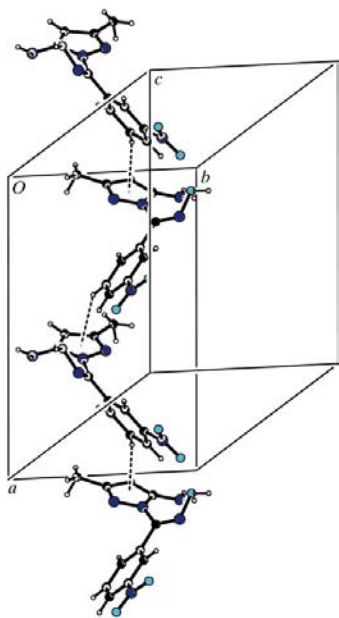


Figure 6
Part of the crystal structure of (IV), showing the formation of a C—H... π (pyrazole) chain consisting of type 2 molecules only.

$\frac{1}{2} - y, z$] (Fig. 6), where Cg1 and Cg2 represent the ring centroids of the pyrazole rings in the molecules of types 1 and 2, respectively.

Experimental

A solution of 5-amino-3-*tert*-butyl-1-phenylpyrazole (Grandberg *et al.*, 1961; Abonia *et al.*, 2002) (1.00 g, 4.65 mmol) and 1-hydroxymethylbenzotriazole (Burckhalter *et al.*, 1952) (0.70 g, 4.69 mmol) in ethanol (5 ml) was heated under reflux for 3 min. After cooling, the precipitate which formed was filtered off and washed with ethanol, giving (I) as a white solid (84% yield; m.p. 453 K; analysis, found: C 69.3, H 6.4, N 24.2%; C₂₀H₂₂N₆ requires: C 69.3, H 6.4, N 24.3%). Crystals suitable for single-crystal X-ray diffraction were grown from a solution in ethanol.

Crystal data

C₂₀H₂₂N₆
 $M_r = 346.44$
 Orthorhombic, $P2_12_12_1$
 $a = 7.2380$ (5) Å
 $b = 11.9743$ (9) Å
 $c = 21.2062$ (16) Å
 $V = 1837.9$ (2) Å³
 $Z = 4$
 $D_x = 1.252$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 2418 reflections
 $\theta = 1.9$ – 27.4°
 $\mu = 0.08$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 0.30 × 0.20 × 0.07 mm

Data collection

Bruker SMART1000 CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\min} = 0.979, T_{\max} = 0.995$
 12 704 measured reflections
 2418 independent reflections

2200 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 27.4^\circ$
 $h = -7 \rightarrow 9$
 $k = -15 \rightarrow 15$
 $l = -27 \rightarrow 27$
 Intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.108$
 $S = 1.07$
 2418 reflections
 238 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 + 0.2514P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Selected interatomic distances (Å).

C1—C2	1.397 (3)	N2—N3	1.305 (3)
C2—C3	1.408 (3)	N1—C7	1.468 (3)
C3—C4	1.371 (3)	C7—N4	1.422 (3)
C4—C5	1.415 (4)	N4—C8	1.372 (3)
C5—C6	1.373 (4)	C8—N5	1.359 (3)
C6—C1	1.397 (3)	N5—N6	1.383 (2)
C1—N3	1.376 (3)	N6—C9	1.327 (3)
C2—N1	1.361 (3)	C9—C10	1.412 (3)
N1—N2	1.361 (2)	C10—C8	1.388 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

Cg2 is the centroid of the N5/N6/C8—C10 pyrazole ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4A...N3 ⁱ	0.88	2.16	2.950 (3)	149
C3—H3...N2 ⁱ	0.95	2.55	3.481 (3)	165
C19—H19...Cg2 ⁱⁱ	0.95	2.85	3.779 (3)	167

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

Compound (I) crystallized in the orthorhombic system; space group $P2_12_12_1$ was assigned uniquely from the systematic absences. H atoms were treated as riding, with C—H distances in the range 0.95–0.99 Å and an N—H distance of 0.88 Å. The Friedel equivalent reflections were merged prior to the final refinements, as the absolute structure could not be assigned.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

PLATON (Spek, 2002); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England. The authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1550). Services for accessing these data are described at the back of the journal.

References

- Abonia, R., Albornoz, A., Insuasty, B., Quiroga, J., Meier, H., Hormaza, A., Nogueras, M., Sánchez, A., Cobo, J. & Low, J. N. (2001). *Tetrahedron*, **57**, 4933–4938.
- Abonia, R., Albornoz, A., Larrahondo, H., Quiroga, J., Insuasty, B., Insuasty, H., Hormaza, A., Sánchez, A. & Nogueras, M. (2002). *J. Chem. Soc. Perkin Trans. 1*. In the press.
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (1997). *SADABS*, *SMART* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burckhalter, J. H., Stephens, V. C. & Hall, L. A. (1952). *J. Am. Chem. Soc.* **74**, 3868–3870.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 122–193. Oxford University Press.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Grandberg, I. I., Ting, W.-P. & Kost, A. N. (1961). *Zh. Obshch. Khim.* **31**, 2311–2315; *Chem. Abstr.* (1962), **56**, 4746h.
- Katritzky, A. R., Abonia, R., Yang, B., Qi, M. & Insuasty, B. (1998). *Synthesis*, pp. 1487–1490.
- Katritzky, A. R., Rachwal, B. & Rachwal, S. (1995). *J. Org. Chem.* **60**, 3993–4001.
- Low, J. N., Cobo, J., Nogueras, M., Sánchez, A., Rengifo, E. & Abonia, R. (2002). *Acta Cryst.* **E58**, o53–o54.
- Ramm, M., Luger, P., Kirschke, K. & Wolff, E. (1996). *Z. Kristallogr.* **211**, 539–543.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Spek, A. L. (2002). *PLATON*. Version of March 2002. University of Utrecht, The Netherlands.
- Suezawa, H., Yoshida, T., Hirota, M., Takahashi, H., Umezawa, Y., Honda, K., Tsuboyama, S. & Nishio, M. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 2053–2058.