organic compounds

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

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In the title compound, $C_{20}H_{22}N_6$, 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 threeconnected 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 $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, while N4 at $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, in turn, acts as donor to N3 at (x, -1 + y, z), so producing a C(6) chain generated by the 2_1 screw axis along $(1, y, \frac{1}{4})$. This is



augmented by a fairly weak $C-H\cdots N$ hydrogen bond; C3 at (x, y, z) acts as donor to triazole N2 at $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, 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 $C(5)C(6)[R_2^2(9)]$ (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 $C-H\cdots \pi$ (pyrazole) interactions. Atom C19 in the molecule at (x, y, z), which lies in the hydrogen-bonded chain along $(1, y, \frac{1}{4})$, forms a short $C-H\cdots \pi$ contact (Table 2) with the centroid, Cg2, of the pyrazole ring of the molecule at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, 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.





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...N43ⁱ [symmetry



Figure 3

Part of the crystal structure of (I), showing the linking of the [010] chains by C-H·· π (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...Cg2ⁱⁱ 2.72 Å, N51...Cg2ⁱⁱ 3.477 (2) Å and N51-H52...Cg2ⁱⁱ 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···N and N-H··· π 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- $H \cdot \cdot \cdot \pi$ (pyrazole) chain consisting of type 1 molecules only.

heterocycles, we have briefly investigated the occurrence of $C-H\cdots\pi$ (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 $C-H \cdots \pi$ (arene) interactions, those of five others contained no $C-H \cdots \pi$ 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 $y = -\frac{1}{4} [H \cdots Cg1^{iii} 2.84 \text{ Å}, C \cdots Cg1^{iii} 3.645 (2) \text{ Å and}$ $C - H \cdots Cg1^{iii} 127^{\circ}$; 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 $y = \frac{1}{4} [H \cdots Cg2^{iv} 2.69 \text{ Å}, C \cdots Cg2^{iv}]$ 3.537(2) Å and C-H···Cg2^{iv} 145°; symmetry code: (iv) $\frac{1}{2} + x$,





Part of the crystal structure of (IV), showing the formation of a C– $H \cdot \cdot \pi$ (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.

$C_{20}H_{22}N_6$
$M_r = 346.44$
Orthorhombic, $P2_12_12_1$
a = 7.2380(5) Å
b = 11.9743 (9) Å
c = 21.2062 (16) Å
$V = 1837.9 (2) \text{ Å}^3$
Z = 4
$D_x = 1.252 \text{ Mg m}^{-3}$

Data collection

Bruker SMART1000 CCD22diffractometer R_{ii} φ and ω scans θ_m Absorption correction: multi-scanh =(SADABS; Bruker, 1997)k = $T_{min} = 0.979, T_{max} = 0.995$ l =12 704 measured reflectionsIn2418 independent reflectionsIn

Refinement

Refinement on F^2 $w = 1/[R[F^2 > 2\sigma(F^2)] = 0.044$ $R[F^2 > 2\sigma(F^2)] = 0.044$ + C $wR(F^2) = 0.108$ whereS = 1.07 $(\Delta/\sigma)_m$ 2418 reflections $\Delta\rho_{max}$ 238 parameters $\Delta\rho_{min} =$ H-atom parameters constrained

Mo K α radiation Cell parameters from 2418 reflections $\theta = 1.9-27.4^{\circ}$ $\mu = 0.08 \text{ mm}^{-1}$ T = 120 (2) K Plate, colourless $0.30 \times 0.20 \times 0.07 \text{ mm}$

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

$$\begin{split} &w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 \\ &+ 0.2514P] \\ &where \ P = (F_o^2 + 2F_c^2)/3 \\ (\Delta/\sigma)_{\max} < 0.001 \\ \Delta\rho_{\max} = 0.32 \ e \ {\rm \AA}^{-3} \\ \Delta\rho_{\min} = -0.25 \ e \ {\rm \AA}^{-3} \end{split}$$

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, $^{\circ}$).

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

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$N4-H4A\cdots N3^{i}$	0.88	2.16	2.950 (3)	149
$C3-H3\cdots N2^{i}$	0.95	2.55	3.481 (3)	165
$C19-H19\cdots Cg2^{ii}$	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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

PLATON (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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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.

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