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3-*tert*-Butyl-4-(4-nitrophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.057
wR factor = 0.137
Data-to-parameter ratio = 16.9

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

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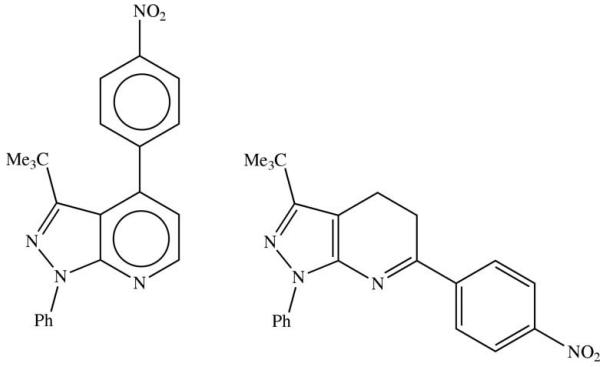
Molecules of the title compound, $C_{22}H_{20}N_4O_2$, are linked by paired C—H···O hydrogen bonds into centrosymmetric $R_2^2(18)$ dimers and these dimers are linked into chains by paired C—H···π(arene) hydrogen bonds.

Comment

We have recently described the preparation of pyrazolo[3,4-*b*]pyridines from 5-aminopyrazoles in solution with different reactants (Low *et al.*, 2002, and references therein), and we have reported the crystal structure of the fully aromatized 3-methyl-1,4-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridine (Low *et al.*, 2002). We report here an analogous structure, that of 3-*tert*-butyl-4-(4-nitrophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine, (I), obtained from the solvent-free reaction of the corresponding 5-aminopyrazole and the Mannich adduct β-dimethylamino-4-nitropropiophenone hydrochloride, under microwave irradiation. The title compound, (I), was obtained along with the reduced 6-(4-nitrophenyl) analogue, (II); however, in pyridine solution under reflux, a similar reaction yielded regioselectively the isomeric 6-arylpyrazolo[3,4-*b*]pyridine (Quiroga *et al.*, 1998).



(I) (II)

Neither of the aryl rings in compound (I) (Fig. 1) is coplanar with the pyrazolopyridine system; unsubstituted phenyl ring C11–C16 makes a dihedral angle of 25.3 (2)° with the adjacent pyrazole ring, while substituted ring C41–C46 is nearly orthogonal to the pyridine ring, with a dihedral angle between these ring planes of 85.1 (2)°; in addition, the nitro group makes a dihedral angle of 11.6 (2)° with the adjacent aryl ring. The bond distances within the fused heterocyclic ring system (Table 1) are consistent with electronic delocalization in the pyridine ring and strong bond fixation in the pyrazole ring.

The molecules of compound (I) are linked into chains of fused rings by a combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond (Table 2). Pyridine

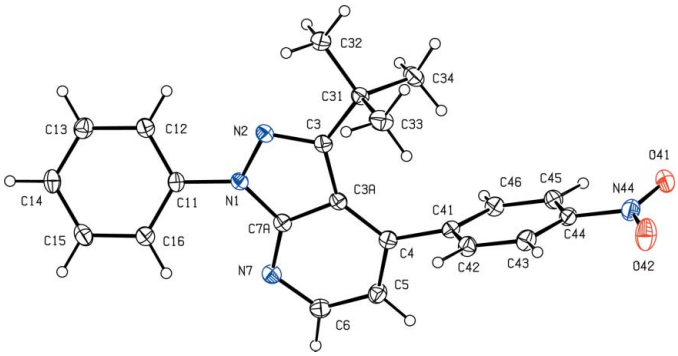


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

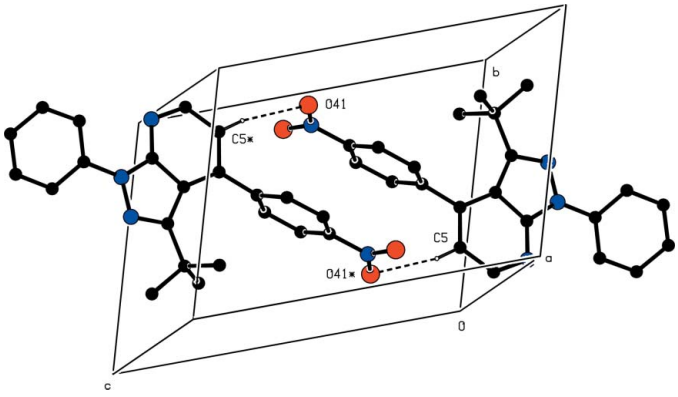


Figure 2
Part of the crystal structure of (I), showing the formation of a centrosymmetric $R_2^2(18)$ dimer. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$. Dashed lines indicate hydrogen bonds.

atom C5 in the molecule at (x, y, z) acts as hydrogen-bond donor to nitro atom O41 in the molecule at $(1-x, 1-y, 1-z)$, generating a centrosymmetric $R_2^2(18)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). In addition, aryl atoms C43 in the molecules at (x, y, z) and $(1-x, 1-y, 1-z)$, which are both components of the $R_2^2(18)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as donors respectively to aryl rings C11–C16 in the molecules at $(-x, 1-y, -z)$ and $(1+x, y, 1+z)$, which themselves are components of the $R_2^2(18)$ dimers centred at $(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ and $(\frac{3}{2}, \frac{1}{2}, \frac{3}{2})$. Propagation by inversion of these two interactions thus generates a chain of edge-fused rings running parallel to the [101] direction, rings built from paired C—H···O hydrogen bonds centred at $(n+\frac{1}{2}, \frac{1}{2}, n+\frac{1}{2})$ (n = zero or integer) and rings built from paired C—H···π(arene) hydrogen bonds centred at $(n, \frac{1}{2}, n)$ (n = zero or integer) (Fig. 3).

Experimental

Equimolar quantities (0.465 mmol) of 5-amino-3-*tert*-butyl-1-phenyl-1*H*-pyrazole and β-dimethylamino-4-nitropropiophenone hydrochloride were placed in open Pyrex-glass vessels and irradiated in a domestic microwave oven for 15 s (at 600 W). The reaction mixture was extracted with ethyl acetate and the product was purified by column chromatography on silica gel, using hexane/ethyl acetate (15:1 (*v*/*v*) as eluent. Evaporation of the eluate yielded colourless crystals of compound (I) (yield 45%; m.p. 448–450 K) suitable for single-crystal X-ray diffraction, accompanied by a small quantity of the reduced 6-(4-nitrophenyl) derivative, (II). MS (EI 30 eV), *m*/*z* (%): 372 (M^+, 10), 357, (17), 149 (58), 57 (100).

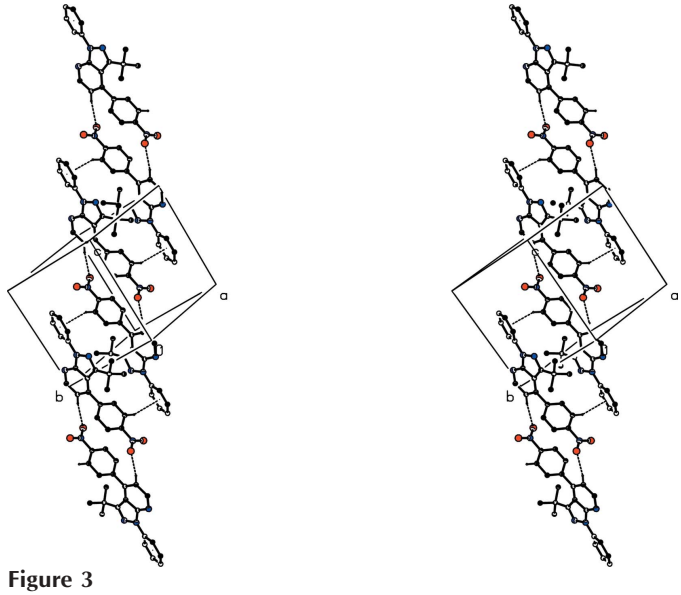


Figure 3
Stereoview of part of the crystal structure of (I), showing the formation of a [101] chain of edge-fused rings. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted. Dashed lines indicate hydrogen bonds.

Crystal data

$C_{22}H_{20}N_4O_2$	$Z = 2$
$M_r = 372.42$	$D_x = 1.311$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 9.5877$ (5) Å	Cell parameters from 4338 reflections
$b = 9.8541$ (5) Å	$\theta = 3.2$–$27.7°$
$c = 11.7050$ (4) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 105.982$ (2)°	$T = 120$ (2) K
$\beta = 103.570$ (2)°	Plate, colourless
$\gamma = 108.433$ (2)°	0.19 × 0.08 × 0.05 mm
$V = 943.75$ (8) Å^3	

Data collection

Bruker–Nonius KappaCCD diffractometer	4338 independent reflections
φ and ω scans	2724 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$R_{int} = 0.070$
$T_{min} = 0.980$, $T_{max} = 0.996$	$\theta_{max} = 27.7°$
23240 measured reflections	$h = -12 \rightarrow 12$
	$k = -12 \rightarrow 12$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 0.1475P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.137$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.34$ e Å^{-3}
4338 reflections	
256 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

N1—N2	1.371 (2)	C5—C6	1.394 (3)
N2—C3	1.327 (2)	C6—N7	1.332 (2)
C3—C3*A*	1.447 (3)	N7—C7*A*	1.340 (2)
C3*A*—C4	1.415 (3)	C7*A*—N1	1.363 (2)
C4—C5	1.386 (3)	C3*A*—C7*A*	1.419 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O41^{i}	0.95	2.46	3.399 (2)	169
C43—H43···*Cg*^{ii}	0.95	2.65	3.501 (2)	149

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z$.

All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.98 Å (methyl), and with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for the methyl groups.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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