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5-Amino-3-*tert*-butyl-1-(4-nitrophenyl)-1*H*-pyrazole forms hydrogen-bonded sheets of alternating $R_2^2(20)$ and $R_6^6(32)$ rings

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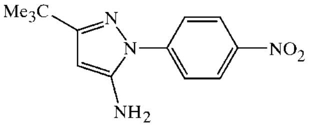
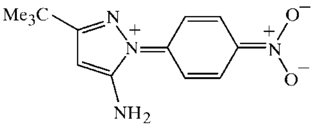
Molecules of the title compound, $C_{13}H_{16}N_4O_2$, are linked by one N—H···O hydrogen bond [H···O = 2.47 Å, N···O = 3.326 (2) Å and N—H···O = 166°] and one N—H···N hydrogen bond [H···N = 2.19 Å, N···N = 3.063 (2) Å and N—H···N = 173°] into sheets containing alternating $R_2^2(20)$ and $R_6^6(32)$ rings, both types of which are centrosymmetric.

Comment

The title compound, (I), is a frequently used intermediate for the synthesis of interesting fused pyrazolo[3,4-*b*]pyridine or similar derivatives. In the molecules of the title compound (Fig. 1), the dihedral angle between the aryl and heterocyclic rings is 33.7 (2)°, possibly as a result, in part, of the tendency of atom H12 and the amine group bonded to atom C5 to avoid one another. On the other hand, the nitro group is almost coplanar with the adjacent aryl ring, with a dihedral angle between the aryl plane and the C—NO_2 plane of only 2.2 (2)°. As well as the dihedral angle between the rings, the bond lengths provide no evidence for any delocalization of the lone pair at atom N1 into the nitro group to form the polarized structure (I*a*). In particular, the C—N distances exocyclic to the aryl ring (Table 1) are typical of their type (Allen *et al.*, 1987), while the C—C bond distances in the aryl ring span the small range 1.378 (3)–1.396 (3) Å, with no sign of quinonoid-type bond fixation. However, there is marked bond fixation within the heterocyclic ring (Table 1), where the C3—C4 and C4—C5 distances differ significantly, as do the N2—C3 and N1—C5 distances. Consistent with the pyramidal nature of atom N5, the C5—N5 bond is long for its type. The dihedral angle between the two rings and the conformation adopted by the *tert*-butyl group render the molecules chiral; however, the space group accommodates equal numbers of the two enantiomeric forms.



(I)



(I*a*)

The molecules of (I) are linked into sheets by one N—H···O hydrogen bond and one N—H···N hydrogen bond (Table 2), and the sheet formation is readily analysed by considering the action of each of these hydrogen bonds in turn.

Amine atom N5 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H5*B*, to nitro atom O142 in the molecule at ($1-x$, $1-y$, $1-z$), thereby generating a centrosymmetric $R_2^2(20)$ (Bernstein *et al.*, 1995) dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The action of the N—H···N hydrogen bond is to link each of these dimers to four adjacent dimers, thereby forming a continuous sheet. Amine atoms N5 at (x, y, z) and ($1-x$, $1-y$, $1-z$) both lie in the dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), and these atoms act as hydrogen-bond donors, this time *via* atom H5*A*, to atoms N52 in the molecules at (x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) and ($1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$), respectively, which themselves lie in the dimers centred at ($\frac{1}{2}$, 0, 0) and ($\frac{1}{2}$, 1, 1), respectively. Likewise, atoms N52 at (x, y, z) and ($1-x$, $1-y$, $1-z$) accept hydrogen bonds from atoms N5 in the molecules at (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$) and ($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$), which themselves lie in the dimers centred at ($\frac{1}{2}$, 0, 1) and ($\frac{1}{2}$, 1, 0). Propagation by the space group of these two hydrogen bonds then generates a (100) sheet built from alternating $R_2^2(20)$ and $R_6^6(32)$ rings, where both ring types are centrosymmetric (Fig. 2). If the $R_2^2(20)$ dimers are regarded as the nodes of the resulting net then this is of (4,4)-type (Batten & Robson, 1998).

There are no direction-specific interactions between adjacent sheets; in particular, there are neither C—H···$\pi_{\rm arene}$ hydrogen bonds nor aromatic π–π stacking interactions

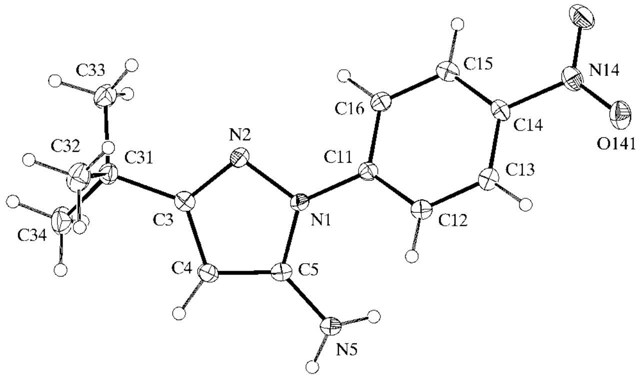


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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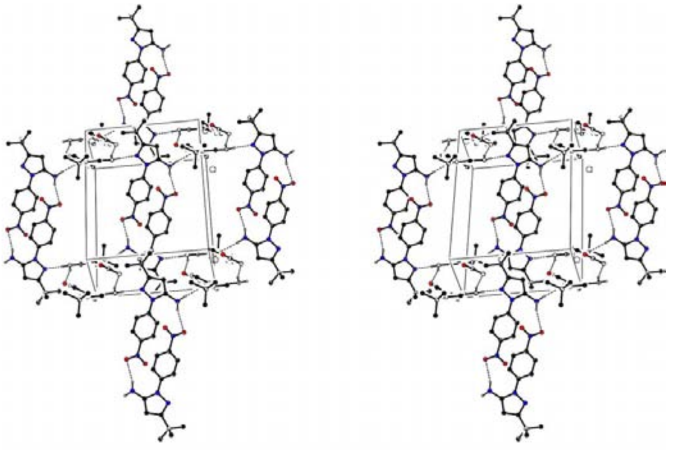

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a (100) sheet built from alternating $R_2^2(20)$ and $R_6^6(32)$ rings.

present in the structure. The $R_6^6(32)$ rings are largely occupied by a pair of *tert*-butyl groups, one pendent from each of the adjacent (100) sheets, and there are no solvent-accessible voids in the structure.

Experimental

A suspension of equimolar amounts (16 mmol) of 4-nitrophenylhydrazine and 4,4-dimethyl-3-oxopentanenitrile in concentrated HCl (10 ml) and water (20 ml) was stirred at room temperature for 10 min. The volume was then reduced to half the original, concentrated HCl (20 ml) was added, and the resulting mixture was heated with stirring for 15 min. The mixture was then cooled and neutralized with aqueous ammonia. The solid product, (I), was collected and recrystallized from water (yield 90%, m.p. 445 K).

Crystal data

$C_{13}H_{16}N_4O_2$
$M_r = 260.30$
Monoclinic, $P2_1/c$
$a = 5.9581$ (2) Å
$b = 18.3064$ (11) Å
$c = 12.0776$ (7) Å
$\beta = 93.4150$ (12)°
$V = 1314.98$ (12) Å^3
$Z = 4$
$D_x = 1.315$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3001 reflections
$\theta = 3.4$–27.5°
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
Lath, yellow
0.20 × 0.10 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.977$, $T_{\max} = 0.996$
14 938 measured reflections
3001 independent reflections
1700 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$
$\theta_{\max} = 27.5°$
$h = -7 \rightarrow 7$
$k = -23 \rightarrow 21$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.124$
$S = 0.96$
3001 reflections
175 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.393 (2)	N1—C11	1.415 (2)
N2—C3	1.327 (2)	C5—N5	1.366 (2)
C3—C4	1.411 (3)	C14—N14	1.466 (2)
C4—C5	1.373 (3)	N14—O141	1.226 (2)
C5—N1	1.370 (2)	N14—O142	1.229 (2)
N2—N1—C11—C12	147.35 (17)	C13—C14—N14—O141	2.8 (3)
C5—N1—C11—C12	−36.0 (3)	C13—C14—N14—O142	−178.3 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···N2$^{\rm i}$	0.88	2.19	3.063 (2)	173
N5—H5B···O142$^{\rm ii}$	0.88	2.47	3.326 (2)	166

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

Space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps, which showed clearly the pyramidal nature of the amine group based on atom N5, and all H atoms were then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.98 Å (methyl), and N—H distances of 0.88 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement and data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); 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: SK1695). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.