Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2,5-Dimethyl-6,7-dihydrobenzo[*h*]-pyrazolo[1,5-*a*]quinazoline and 2-*tert*-butyl-5-methyl-6,7-dihydrobenzo[*h*]-pyrazolo[1,5-*a*]quinazoline

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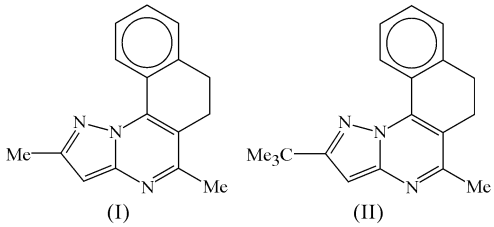
Received 4 June 2007
Accepted 13 June 2007
Online 14 July 2007

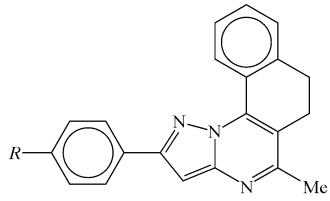
In both 2,5-dimethyl-6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]-quinazoline, $C_{16}H_{15}N_3$, (I), and 2-*tert*-butyl-5-methyl-6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]quinazoline, $C_{19}H_{21}N_3$, (II), which crystallizes with $Z' = 2$ in the space group $P\overline{1}$, the non-aromatic carbocyclic rings adopt screw-boat conformations. The molecules of (I) are linked into chains of rings by a combination of C—H···N and C—H···π(arene) hydrogen bonds, while in (II) there are no hydrogen bonds of any kind.

Comment

We report here the structures of two closely related 6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]quinazolines, (I) and (II) (Figs. 1 and 2), both prepared using solvent-free cyclo-condensation reactions between 2-acetyltetralone and the appropriate 3-alkyl-5-amino-1*H*-pyrazole. We compare the molecular and supramolecular structures of compounds (I) and (II) with those of the related aryl compounds (III) and (IV) (Portilla *et al.*, 2005) and with that of compound (V) (Low *et al.*, 2004) (see scheme).

In (I) and in each of the independent molecules of (II), the non-aromatic carbocyclic rings adopt a screw-boat conformation. The ring-puckering amplitudes (Cremer & Pople, 1975) are 0.506 (2) Å in (I), and 0.481 (2) and 0.482 (3) Å, respectively, for the molecules of types 1 and 2 (containing atoms N11 and N21, respectively, see Fig. 2) in (II). In (I), the corresponding ring-puckering angles are $\theta = 69.0\ (2)^\circ$ and $\varphi = 82.6\ (3)^\circ$ for the atom sequence C5*A*—C6—C7—C7*A*—C11*A*—C11*B*; in (II), for the atom sequences C*x*1*A*—C*x*1*B*—C*x*5*A*—C*x*6—C*x*7—C*x*7*A*, $\theta = 67.5\ (2)^\circ$ and $\varphi = 210.6\ (3)^\circ$ when $x = 1$ (molecule 1), and $\theta = 67.0\ (2)^\circ$ and $\varphi = 213.4\ (3)^\circ$ when $x = 2$ (molecule 2). For an idealized screw-boat conformation, the values are $\theta = 67.5^\circ$ and $\varphi = (60n + 30)^\circ$, where n represents zero or an integer (Evans & Boeyens, 1989). Similar conformations have been found for the corresponding rings in compounds (III)–(V) (Low *et al.*, 2004; Portilla *et al.*, 2005). Because of the puckering of the non-aromatic carbocyclic rings, the molecules exhibit no internal symmetry and hence they are chiral; however, the centrosymmetric space group in each case accommodates equal numbers of the two enantiomeric forms.





(III) *R*=H
(IV) *R*=Me
(V) *R*=Cl

Within the heterobicyclic portions of the molecules, the patterns of the bond distances (Tables 1 and 3) are very similar for all three molecules. Hence, we discuss in detail only the distances in (I) as similar remarks apply to (II). In (I), the N1—C2 and C3*A*—N4 bonds, which are formally double and single bonds, respectively, are effectively of the same length; on the other hand, the C5—C5*A* bond, which is formally a single bond, is significantly longer than the C2—C3 and C5*A*—C11*B* bonds, which are formally double bonds. These observations are consistent with bond-fixation of the type characteristic of naphthalene rather than complete peripheral

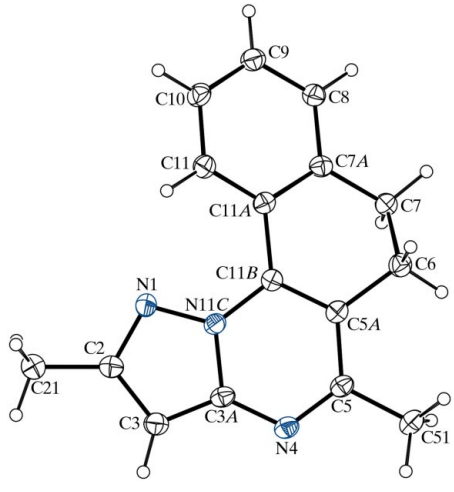


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

  DOI: 10.1107/S0108270107029010

delocalization of the ten π electrons. By contrast, the distances in the carbocylic ring (C7*A*/C8–C11/C11*A*) are indicative of typical aromatic delocalization.

The geometries and conformations of the two independent molecules in (II) are very similar. Although the ADDSYM routine in *PLATON* (Spek, 2003) indicated that no additional crystallographic symmetry is present in (II), examination of the atom coordinates showed that the two independent molecules are approximately related by a pseudo-*c*-glide plane at $x = 0.25$. Consistent with this approximate relationship, the reflections of type 0*kl* are, in general, very much weaker when *l* is odd than when *l* is even, although some exhibit significant intensity.

Two hydrogen bonds (Table 2) link the molecules of (I) into chains of rings. Atom C3 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the ring atom N4 in the molecule at ($1 - x$, $-y$, $2 - z$), so generating by inversion a cyclic centrosymmetric $R_2^2(8)$ (Bernstein *et al.*, 1995) dimer centred at ($\frac{1}{2}$, 0, 1). At the same time, atom C7 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* the axial atom H7*B*, to the C7*A*/C8–C11/C11*A* ring in the molecule at ($1 - x$, $1 - y$, $1 - z$), thus generating by inversion a second cyclic motif centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The propagation by inversion of these two hydrogen bonds therefore leads to the formation of a chain of centrosymmetric hydrogen-bonded rings running parallel to the [01$\bar{1}$] direction, with the rings formed by pairs of C—H$\cdots$N hydrogen bonds centred at ($\frac{1}{2}$, n, $1 - n$) (where n represents zero or an integer) alternating with the rings formed by pairs of C—H$\cdots\pi$(arene) hydrogen bonds centred at ($\frac{1}{2}$, $\frac{1}{2} + n$, $\frac{1}{2} - n$) (where n represents zero or an integer) (Fig. 3). There is a very weak π–π stacking interaction between pairs of pyrimidine rings. These rings in the molecules at (x, y, z) and ($1 - x$, $1 - y$, $2 - z$) are strictly parallel, with an interplanar spacing of 3.354 (2) Å; the ring-centroid separation is 3.840 (2) Å, corresponding to a ring-centroid offset of 1.870 (2) Å. If this interaction is regarded as significant, its action is to link the hydrogen-bonded chains into a sheet parallel to (100).

The supramolecular aggregation in (II), by contrast, is extremely simple. There are no hydrogen bonds of any kind in the structure, but the molecules of type 1 are linked into pairs by a single weak π–π stacking interaction between the benzene rings of the molecules at (x, y, z) and ($-x$, $-y$, $-z$). The interplanar spacing is 3.395 (2) Å and the ring-centroid separation is 3.974 (2) Å, which corresponds to a ring-centroid offset of 1.867 (2) Å. There are no direction-specific interactions of any kind involving the molecules of type 2.

The stacking interaction in (II) closely resembles that in the 4-methylphenyl analogue (IV) (Portilla *et al.*, 2005), where pairs of molecules are again linked into isolated dimers. In the unsubstituted phenyl compound (III), the molecules are linked into chains by a combination of a C—H$\cdots\pi$(arene) hydrogen bond and a π–π stacking interaction. The

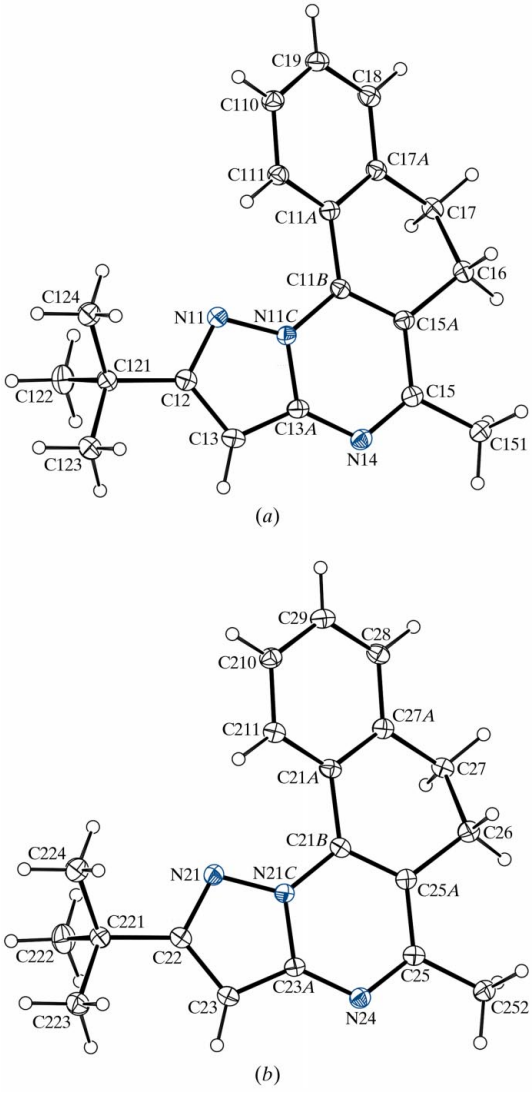


Figure 2
The two independent molecules of compound (II), showing the atom-labelling scheme for (*a*) a molecule of type 1 containing atom N11 and (*b*) a molecule of type 2 containing atom N21. Displacement ellipsoids are drawn at the 30% probability level.

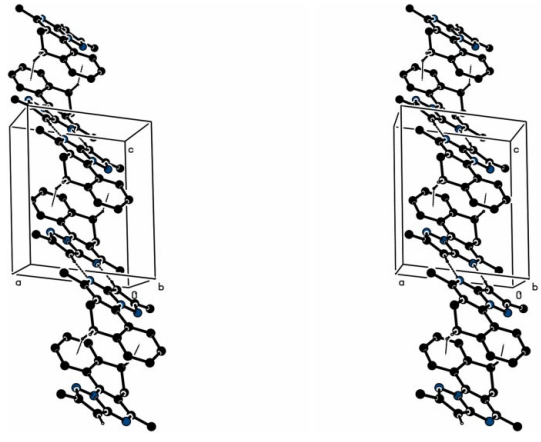


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain of rings along [01$\bar{1}$]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

4-chlorophenyl derivative (V) crystallizes with $Z' = 2$ (Low *et al.*, 2004), and the molecules are linked by two independent π–π stacking interactions into chains in which the two types of molecules alternate.

Experimental

Equimolar quantities (2.6 mmol of each component) of 2-acetyltetralone and either 5-amino-3-methyl-1*H*-pyrazole [for (I)] or 5-amino-3-*tert*-butyl-1*H*-pyrazole [for (II)] were thoroughly mixed at room temperature. The solvent-free mixtures were then heated in an oil bath at 393 K for 1.5–2 min. The resulting melts were stirred briefly and then allowed to cool to ambient temperature to solidify. The resulting solids were extracted with ethanol and, after removal of the solvent under reduced pressure, the products (I) and (II) were recrystallized from dimethylformamide to give crystals suitable for single-crystal X-ray diffraction. (I): pale orange crystals, yield 86%, m.p. 385–387 K; MS (70 eV) *m*/*z* (%): 249 (100, M^+), 234 (8), 221 (9), 127 (16), 39 (22). (II): pale yellow crystals, yield 84%, m.p. 439–441 K; MS (70 eV) *m*/*z* (%): 291 (96, M^+), 276 (92), 246 (100), 128 (25), 57 (25), 41 (57), 39 (56).

Compound (I)

Crystal data

$C_{16}H_{15}N_3$
$M_r = 249.31$
Triclinic, $P\overline{1}$
$a = 7.9430$ (19) Å
$b = 7.9660$ (11) Å
$c = 9.943$ (3) Å
$\alpha = 87.637$ (13)°
$\beta = 82.632$ (18)°
$\gamma = 89.941$ (17)°
$V = 623.4$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 120$ (2) K
0.49 × 0.44 × 0.07 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.971$, $T_{max} = 0.994$
15496 measured reflections
2867 independent reflections
1600 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.220$
$S = 1.04$
2867 reflections
174 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

N1—C2	1.350 (3)	C5—C5*A*	1.423 (3)
C2—C3	1.385 (4)	C5*A*—C11*B*	1.379 (3)
C3—C3*A*	1.370 (3)	C11*B*—N11*C*	1.372 (3)
C3*A*—N4	1.351 (3)	N11*C*—N1	1.360 (3)
N4—C5	1.320 (3)	C3*A*—N11*C*	1.402 (3)

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

Cg is the centroid of the C7*A*/C8–C11/C11*A* ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···N4^{i}	0.95	2.55	3.495 (3)	175
C7—H7*B*···*Cg*^{ii}	0.99	2.97	3.789 (3)	141

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $-x+1, -y+1, -z+1$.

Compound (II)

Crystal data

$C_{19}H_{21}N_3$
$M_r = 291.39$
Triclinic, $P\overline{1}$
$a = 11.2632$ (5) Å
$b = 11.4574$ (7) Å
$c = 12.1317$ (6) Å
$\alpha = 93.449$ (5)°
$\beta = 90.313$ (4)°
$\gamma = 102.791$ (6)°
$V = 1523.66$ (14) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 120$ (2) K
0.52 × 0.35 × 0.15 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.972$, $T_{max} = 0.989$
37817 measured reflections
6991 independent reflections
4144 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.213$
$S = 1.06$
6991 reflections
405 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

N11—C12	1.347 (3)	N21—C22	1.345 (3)
C12—C13	1.404 (3)	C22—C23	1.399 (3)
C13—C13*A*	1.383 (3)	C23—C23*A*	1.379 (3)
C13*A*—N14	1.353 (3)	C23*A*—N24	1.355 (3)
N14—C15	1.324 (3)	N24—C25	1.323 (3)
C15—C15*A*	1.424 (3)	C25—C25*A*	1.430 (3)
C15*A*—C11*B*	1.377 (3)	C25*A*—C21*B*	1.375 (3)
C11*B*—N11*C*	1.381 (3)	C21*B*—N21*C*	1.373 (3)
N11*C*—N11	1.364 (3)	N21*C*—N21	1.365 (3)
C13*A*—N11*C*	1.389 (3)	C23*A*—N21*C*	1.393 (3)

Crystals of both (I) and (II) are triclinic, and for each the space group $P\overline{1}$ was selected and confirmed by the structure analysis. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2), and with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups and $k = 1.2$ for all other H atoms. A search for possible additional symmetry in (II) revealed none.

For both compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The authors thank 'Servicios Técnicos de Investigación of Universidad de Jaén' and the staff for data collection. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JP and JQ thank COLCIENCIAS and UNIVALLE (Universidad del Valle, Colombia) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3137). Services for accessing these data are described at the back of the journal.

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