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3-*tert*-Butyl-7,7-dimethyl-1-phenyl-5,6,7,8-tetrahydroimidazo[3,4-*b*]quinolin-5-one and 2,8,8-trimethyl-5-phenyl-6,7,8,9-tetrahydroimidazo[2,3-*a*]quinolin-6-one: chains generated by C—H···N hydrogen bonds

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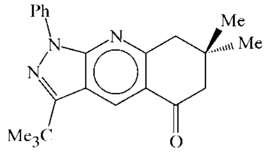
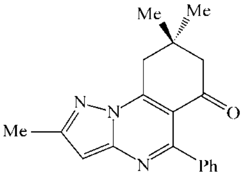
In both 3-*tert*-butyl-7,7-dimethyl-1-phenyl-5,6,7,8-tetrahydroimidazo[3,4-*b*]quinolin-5-one, $C_{22}H_{25}N_3O$, (I), and 2,8,8-trimethyl-5-phenyl-6,7,8,9-tetrahydroimidazo[2,3-*a*]quinolin-6-one, $C_{19}H_{19}N_3O$, (II), the heterobicyclic portions of the molecules are planar, with naphthalene-type delocalization in (II), while the carbocyclic ring in each compound adopts an envelope conformation. In both (I) and (II), the molecules are linked weakly into chains by a single C—H···N hydrogen bond.

Comment

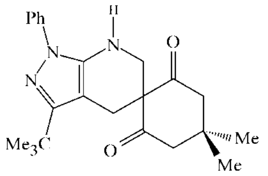
As part of a program for the synthesis of fused pyrazole derivatives (Quiroga *et al.*, 1998, 2001; Cannon *et al.*, 2001*a*,*b*; Low *et al.*, 2001), we have been investigating three-component cyclocondensation reactions induced by microwave irradiation. We report here the molecular and supramolecular structures of two compounds, (I) and (II), obtained from condensation reactions between a substituted aminopyrazole, 5,5-dimethylcyclohexane-1,3-dione (dimedone) and a simple carbonyl compound or its equivalent. Thus, from the reaction involving 5-amino-3-*tert*-butyl-1-phenylpyrazole and formaldehyde, we have now obtained 3-*tert*-butyl-7,7-dimethyl-1-phenyl-5,6,7,8-tetrahydroimidazo[3,4-*b*]quinolin-5-one, (I), in which a single formaldehyde unit has been utilized in the construction of the fused ring system. When two such units are incorporated, spiro compound (III) results (Low *et al.*, 2004). When 5-amino-3-methyl-1*H*-pyrazole is used in combination with orthobenzoic acid trimethyl ester, the product is (II), analogous to the compound, (IV), formed from this pyrazole in the presence of formaldehyde (Low *et al.*, 2004).



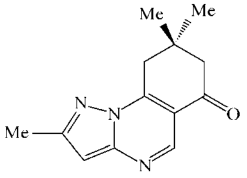
(I)



(II)



(III)



(IV)

In both (I) (Fig. 1) and (II) (Fig. 2), the heterobicyclic portions of the fused ring systems are planar, but the carbocyclic rings are puckered. The ring-puckering parameters (Cremer & Pople, 1975) for (I) [θ = 127.4 (3)° and φ = 353.8 (3)° for the atom sequence C4a—C5—C6—C7—C8—C8a] and (II) [θ = 65.2 (2)° and φ = 174.3 (3)° for the atom

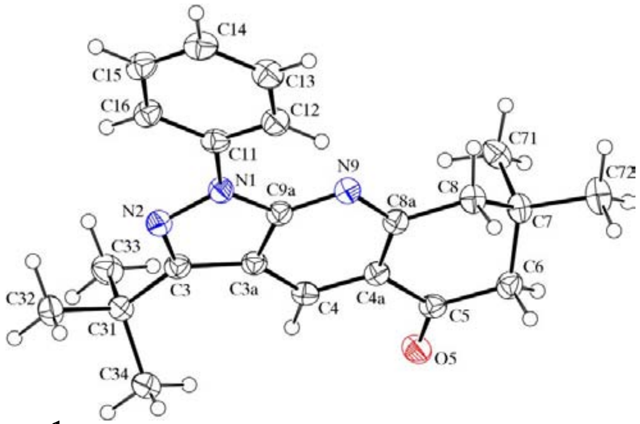


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

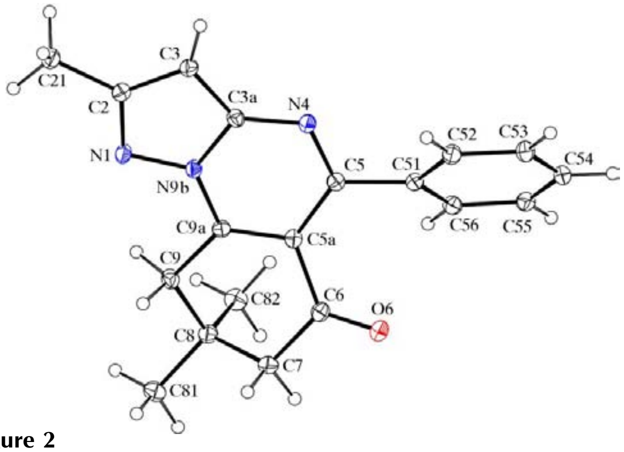


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

sequence C5a—C6—C7—C8—C9—C9a] indicate envelope conformations for both these rings (Evans & Boeyens, 1989), consistent with the enforced coplanarity of atoms C5, C4a, C8a and C8 in (I), and of atoms C6, C5a, C9a and C9 in (II).

In (I), the C3a—C4 and C4—C4a bonds are of very similar length (Table 1), as are the C8a—N9 and N9—C9a bonds, consistent with aromatic delocalization within the central ring of (I). The formally single C3a—N4 and C9a—N9b bonds in (II) (Table 3) are only slightly longer than the formal double bond N1═C2, although each is significantly longer than the cross-ring C3a—N9b bond, also formally a single bond. The lengths of the C2—C3 and C3═C3a bonds, formally single and double, respectively, differ by less than 0.03 Å. These observations suggest that this heterocyclic system exhibits a degree of naphthalene-type delocalization, involving a peripheral system of ten π electrons but with only modest participation by the cross-ring bond (Glidewell & Lloyd, 1984).

In each of (I) and (II), the molecules are linked weakly into chains by means of a single C—H$\cdots$N hydrogen bond (Tables 2 and 4); the structure of neither compound exhibits any C—H$\cdots\pi$(arene) hydrogen bonds or aromatic π–π stacking interactions. In (I), atom C6 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H6*B*, to pyridine ring atom N9 in the molecule at ($1 + x$, y, z), so generating by translation a *C*(6) chain (Bernstein *et al.*, 1995) running parallel to the [100] direction (Fig. 3). In (II), aryl atom C54 in the molecule at (x, y, z) acts as a hydrogen-bond donor to pyrazole-ring atom N1 in the molecule at ($1 + x, \frac{3}{2} - y, -\frac{1}{2} + z$), so producing a zigzag *C*(10) chain running parallel to the [20$\overline{1}$] direction and generated by the *c*-glide plane at $y = \frac{3}{4}$ (Fig. 4).

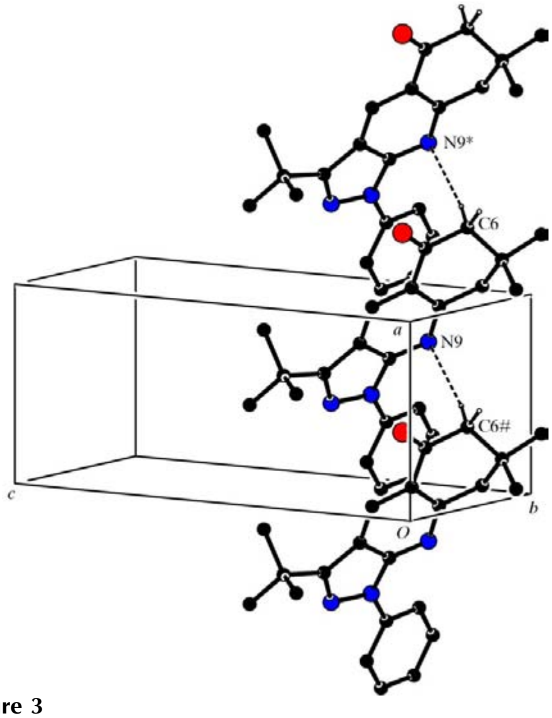


Figure 3
Part of the crystal structure of (I), showing the formation of a *C*(6) chain along [100]. For clarity, H atoms bonded to C atoms not participating in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($1 + x$, y, z) and ($-1 + x$, y, z), respectively.

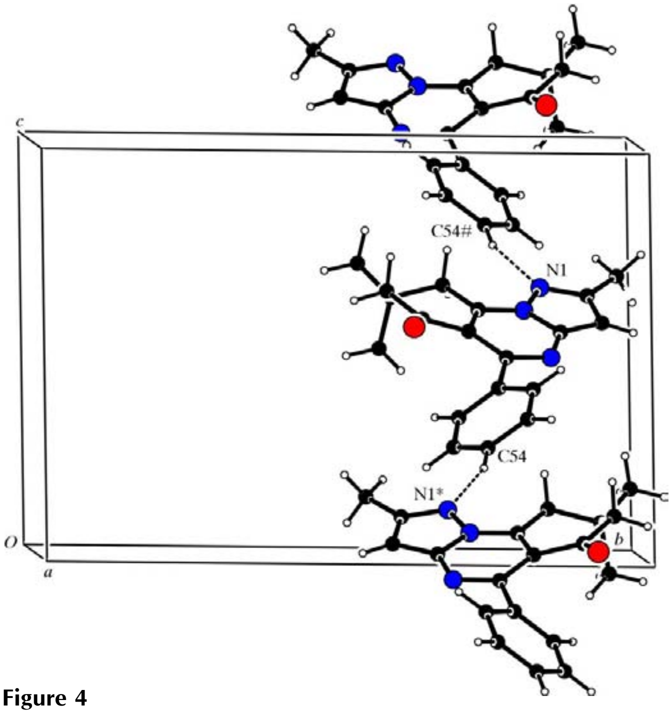


Figure 4
Part of the crystal structure of (II), showing the formation of a *C*(10) chain along [20$\overline{1}$]. For clarity, H atoms bonded to C atoms not participating in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($1 + x, \frac{3}{2} - y, -\frac{1}{2} + z$) and ($-1 + x, \frac{3}{2} - y, \frac{1}{2} + z$), respectively.

The constitutions of (II) and (IV) differ only by the presence of the phenyl substituent in (II); however, this difference profoundly influences the differences in the supramolecular structures of these compounds. In (IV), the C—H bond that is replaced by the C–phenyl bond in (II) acts as the sole hydrogen-bond donor, forming, by means of paired C—H$\cdots$N hydrogen bonds, a centrosymmetric $R_2^2(6)$ dimer. Dimers of this type are then linked into chains by a single π–π stacking interaction (Low *et al.*, 2004).

Experimental

For the synthesis of (I), a mixture of 5-amino-3-*tert*-butyl-1-phenylpyrazole (1 mmol), dimedone (1 mmol) and formaldehyde (3 mmol) was placed in Pyrex-glass open vessels and irradiated in a domestic microwave oven for 4 min (at 600 W). The reaction mixture was extracted with ethanol and the product, (I), was isolated by column chromatography on silica gel, using $CHCl_3$ as eluant, and crystallized from ethanol, yielding crystals suitable for single-crystal X-ray diffraction (m.p. 413 K; yield 41%). Analysis found: C 75.5, H 7.3, N 12.1%; $C_{22}H_{25}N_3O$ requires: C 76.0, H 7.3, N 12.1%. For the synthesis of (II), an equimolar mixture of 5-amino-3-methyl-1*H*-pyrazole, dimedone and orthobenzoic acid trimethyl ester (1 mmol of each) was placed in Pyrex-glass open vessels and irradiated in a domestic microwave oven for 2 min (at 600 W). The reaction mixture was extracted with ethanol and the product, (II), was crystallized from ethanol, producing crystals suitable for single-crystal X-ray diffraction (m.p. 533 K; yield 55%). MS EI (70 eV) m/z (%): 306 (23), 305 (100, M^+), 304 (60), 291 (13), 290 (54), 250 (14), 249 (73), 248 (14), 220

(13), 153 (11), 127 (16), 126 (10), 77 (29), 66 (10), 55 (10), 53 (16), 52 (13), 351 (17), 42 (20), 41 (34), 39 (35).

Compound (I)

Crystal data

$C_{22}H_{25}N_3O$
$M_r = 347.45$
Triclinic, $P\overline{1}$
$a = 6.1514$ (2) Å
$b = 10.3171$ (5) Å
$c = 15.7351$ (8) Å
$\alpha = 71.722$ (2)°
$\beta = 85.780$ (3)°
$\gamma = 85.306$ (3)°
$V = 943.84$ (7) Å^3
$Z = 2$
$D_x = 1.223$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4348 reflections
$\theta = 3.3$–27.6°
$\mu = 0.08$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.18 × 0.08 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.964$, $T_{\max} = 0.994$
21 211 measured reflections
4348 independent reflections
2666 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.105$
$\theta_{\max} = 27.6°$
$h = -7 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.160$
$S = 1.02$
4348 reflections
240 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.3463P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I).

N1—N2	1.384 (2)	C7—C8	1.529 (3)
N2—C3	1.320 (3)	C8—C8a	1.500 (3)
C3—C3a	1.438 (3)	C8a—N9	1.338 (3)
C3a—C4	1.386 (3)	N9—C9a	1.340 (3)
C4—C4a	1.386 (3)	C9a—N1	1.368 (3)
C4a—C5	1.482 (3)	C3a—C9a	1.408 (3)
C5—C6	1.500 (3)	C4a—C8a	1.416 (3)
C6—C7	1.532 (3)		

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

D—H···a	D—H	H···A	D···A	D—H···A
C6—H6B···N9$^{\rm i}$	0.99	2.56	3.512 (3)	161

Symmetry code: (i) $1 + x, y, z$.

Compound (II)

Crystal data

$C_{19}H_{19}N_3O$
$M_r = 305.37$
Monoclinic, $P2_1/c$
$a = 7.7988$ (3) Å
$b = 17.0950$ (6) Å
$c = 12.0231$ (3) Å
$\beta = 108.8000$ (18)°
$V = 1517.41$ (9) Å^3
$Z = 4$
$D_x = 1.337$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3477 reflections
$\theta = 3.0$–27.6°
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
0.40 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.974$, $T_{\max} = 0.993$
21 719 measured reflections
3477 independent reflections
2503 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.060$
$\theta_{\max} = 27.6°$
$h = -9 \rightarrow 10$
$k = -21 \rightarrow 22$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.134$
$S = 1.03$
3477 reflections
212 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.3887P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.027 (3)

Table 3
Selected interatomic distances (Å) for (II).

N1—C2	1.340 (2)	C8—C9	1.535 (2)
C2—C3	1.407 (2)	C9—C9a	1.493 (2)
C3—C3a	1.383 (2)	C9a—N9b	1.355 (2)
C3a—N4	1.358 (2)	N9b—N1	1.3625 (18)
N4—C5	1.325 (2)	C3a—N9b	1.393 (2)
C5—C5a	1.446 (2)	C5a—C9a	1.379 (2)
C5a—C6	1.495 (2)	C7—C8	1.523 (2)
C6—C7	1.513 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C54—H54···N1$^{\rm ii}$	0.95	2.58	3.492 (2)	162

Symmetry code: (ii) $1 + x, \frac{3}{2} - y, z - \frac{1}{2}$.

Crystals of (I) are triclinic; space group $P\overline{1}$ was selected and confirmed by the successful structure analysis. For (II), space group $P2_1/c$ was uniquely determined from the systematic absences. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2), and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C) [$1.5U_{\rm eq}$(C) for the methyl groups].

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXS*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: GG1220). Services for accessing these data are described at the back of the journal.

References

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.

Cannon, D., Quesada, A., Quiroga, J., Mejía, D., Insuasty, B., Abonia, R., Cobo, J., Nogueras, M., Sánchez, A. & Low, J. N. (2001*a*). *Acta Cryst.* E**57**, o151–o153.

Cannon, D., Quesada, A., Quiroga, J., Mejía, D., Insuasty, B., Abonia, R., Cobo, J., Nogueras, M., Sánchez, A. & Low, J. N. (2001*b*). *Acta Cryst.* E**57**, o157–o159.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Evans, D. G. & Boeyens, J. C. A. (1989). *Acta Cryst.* B**45**, 581–590.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Glidewell, C. & Lloyd, D. M. G. (1984). *Tetrahedron*, **40**, 4455–4472.

Low, J. N., Cobo, J., Mera, J., Quiroga, J. & Glidewell, C. (2004). *Acta Cryst.* C**60**, o265–o269.

Low, J. N., Cobo, J., Nogueras, M., Sánchez, A., Quiroga, J. & Mejía, D. (2001). *Acta Cryst.* C**57**, 1356–1358.

McArdle, P. (2003). *OSCAIL for Windows. Program for Structure Solution.* 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.

Quiroga, J., Hormaza, A., Insuasty, B., Saitz, C. & Jullian, C. (1998). *J. Heterocycl. Chem.* **35**, 575–578.

Quiroga, J., Mejía, D., Insuasty, B., Abonia, R., Nogueras, M., Sánchez, A., Cobo, J. & Low, J. N. (2001). *Tetrahedron*, **57**, 6947–6953.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.