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Two isomeric 10-methyl-8-phenyl-11-pyridyl-6,8-dihydro-5*H*-benzo[*f*]-pyrazolo[3,4-*b*]quinolines: cyclic hydrogen-bonded tetramers *versus* isolated molecules

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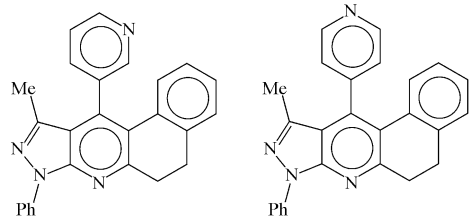
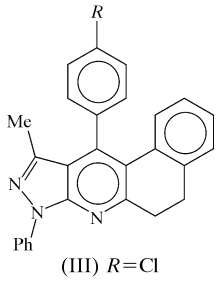
The molecules of 10-methyl-8-phenyl-11-(3-pyridyl)-6,8-dihydro-5*H*-benzo[*f*]pyrazolo[3,4-*b*]quinoline, $C_{26}H_{20}N_4$, (I), are linked by a single C—H···N hydrogen bond into cyclic $R_4^4(12)$ tetramers generated by a $\overline{4}$ axis. In isomeric 10-methyl-8-phenyl-11-(4-pyridyl)-6,8-dihydro-5*H*-benzo[*f*]pyrazolo[3,4-*b*]-quinoline, (II), which crystallizes with $Z' = 2$ in space group $P2_12_12$, the two independent molecules are nearly enantiomeric but there are no direction-specific interactions between them.

Comment

We report here the structures of two isomeric 11-pyridyl-10-methyl-8-phenyl-6,8-dihydro-5*H*-benzo[*f*]pyrazolo[3,4-*b*]quinolines, (I) and (II). Compound (I) is a pyridyl analogue of the isostructural pair 11-(4-chlorophenyl)-10-methyl-8-phenyl-6,8-dihydro-5*H*-benzo[*f*]pyrazolo[3,4-*b*]quinoline, (III) (Serrano *et al.*, 2005*a*), and 11-(4-bromophenyl)-10-methyl-8-phenyl-6,8-dihydro-5*H*-benzo[*f*]pyrazolo[3,4-*b*]quinoline, (IV) (Serrano *et al.*, 2005*b*), while compound (II) is a simple positional isomer of (I).

The non-aromatic carbocyclic rings in both compounds adopt screw-boat conformations, as shown by the ring-puckering parameters (Cremer & Pople, 1975; Evans & Boeyens, 1989). For (I), these are $\theta = 71.0\ (2)^\circ$ and $\varphi = 94.3\ (33)^\circ$ for the atom sequence C4a/C5/C6/C6a/C11a/C11b (Fig. 1), as compared with the idealized values, for an ring with equal bond distances throughout, of $\theta = 67.5^\circ$ and $\varphi = (60k + 30)^\circ$. In (II), for the atom sequences C11a—C11b—C14a—C15—C16—C16a in molecule 1 and C21a—C21b—C24a—C25—C26—C26a in molecule 2 (Fig. 2), the corresponding values are 69.9 (5) and 214.9 (5)°, respectively, in molecule 1, and 108.8 (4) and 33.1 (5)°, respectively, in molecule 2. In compounds (I) and (II), the molecules have no internal symmetry and they are chiral. For (I), the space group $P\overline{4}2_1c$ accommodates equal numbers of the two enantiomers, but for (II), in space group $P2_12_12$, each crystal will, in the absence of inversion twinning, contain just a single enantiomer. However, the ring-puckering parameters for compound (II) show that the two independent molecules are very close to being enantiomers (Fig. 2), although no possible additional symmetry was detected.





(III) R=Cl
(IV) R=Br

The overall conformations in (I) and (II) are very similar. For example, the dihedral angles between the pyrazole ring and its pendent aryl ring are 18.3 (2)° in (I), and 10.7 (2) and 16.7 (2)° in (II), the dihedral angles between the two pyridine rings are 66.6 (2)° in (I), and 75.4 (2) and 72.4 (2)° in (II), and the dihedral angles between the fused pyridine ring and the fused aryl ring are 27.3 (2)° in (I) and 24.4 (2) and 26.4 (2)° in (II). The difference in the orientation of the two pendent rings,

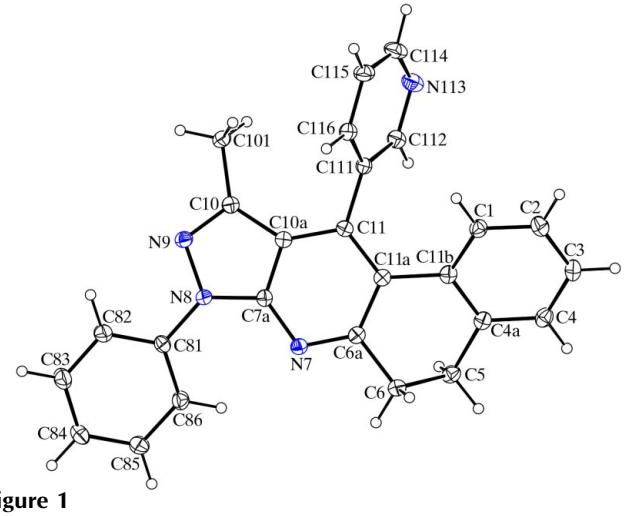


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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viz. one aryl and one pyridyl, is striking. The near coplanarity of the pyrazole and pendent aryl rings may be associated with the short intramolecular C—H···N contacts involving these rings (Tables 1 and 2). The modest differences between the corresponding values for the two molecules in compound (II)

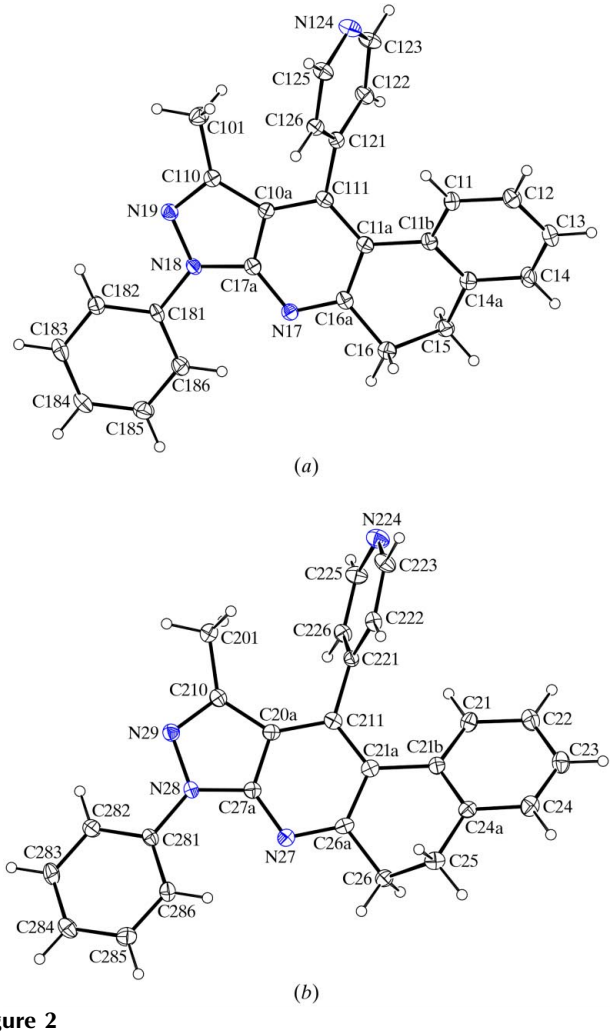

Figure 2
The two independent molecules of (II), showing the atom-labelling schemes for (*a*) molecule 1 and (*b*) molecule 2. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

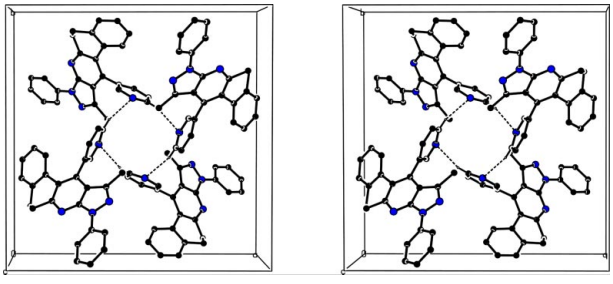

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a cyclic hydrogen-bonded $R_4^4(12)$ tetramer generated by a $\overline{4}$ axis. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

are sufficient to preclude the possibility of additional symmetry. The bond distances and angles show no unusual values.

The molecules in compound (I) are linked by a single C—H···N hydrogen bond (Table 1). Aryl atom C114 in the molecule at (x, y, z) acts as hydrogen-bond donor to the pyridyl atom N113 in the molecule at (y, $1-x$, $2-z$), while atom C114 at (y, $1-x$, $2-z$) in turn acts as donor to atom N113 at ($1-x$, $1-y$, z). Propagation of this hydrogen bond thus produces a puckered $R_4^4(12)$ tetramer generated by the $\overline{4}$ axis along ($\frac{1}{2}$, $\frac{1}{2}$, z) (Fig. 3). A second such tetramer, related to the first by the action of the *c*-glide planes, is generated by the $\overline{4}$ axis along (0, 0, z), but there are no direction-specific interactions between adjacent tetramers. By contrast, there are no direction-specific interactions of any kind between molecules of compound (II). In particular, the pyridyl N atoms N114 and N224 have no potential hydrogen-bond donors with N···H distances less than 2.65 Å.

The very different space groups and patterns of supramolecular aggregation manifested by isomers (I) and (II) may be contrasted with their 4-haloaryl analogues (III) and (IV), which are strictly isomorphous and isostructural in space group $P\overline{1}$, and where the molecules are linked by C—H···π(arene) hydrogen bonds, although C—H···N hydrogen bonds, as found here for (I), are absent from both (III) and (IV).

Experimental

Equimolar amounts of 5-amino-3-methyl-1-phenylpyrazole (173 mg, 1.0 mmol), 2-tetralone (146 mg, 1.0 mmol) and the appropriate pyridinecarbaldehyde [pyridine-3-carbaldehyde for (I) and pyridine-4-carbaldehyde for (II)] (107.0 mg, 1.0 mmol) were placed in open Pyrex glass vessels and irradiated in a domestic microwave oven for 4.5 min at 600 W. The reaction mixtures were then extracted with ethanol and, after removal of the solvent, the products were recrystallized from ethanol–dimethylformamide (1:1 *v*/*v*) to give crystals suitable for single-crystal X-ray diffraction. Compound (I), yellow crystals, 55% yield, m.p. 445–446 K; MS (30 eV) *m*/*z* (%): 389 (30), 388 (100, M^+), 387 (58), 373 (4). Compound (II), yellow crystals, 40% yield, m.p. 493 K; MS (30 eV) *m*/*z* (%): 388 (100, M^+), 373 (5).

Compound (I)

Crystal data

$C_{26}H_{20}N_4$
M_r = 388.46
Tetragonal, $P\overline{4}2_1c$
a = 19.2181 (6) Å
c = 10.8347 (2) Å
V = 4001.64 (19) Å^3
Z = 8
D_x = 1.290 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2537 reflections
θ = 3.7–27.5°
μ = 0.08 mm^{-1}
T = 120 (2) K
Lath, yellow
0.44 × 0.35 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.955, T_{max} = 0.992
28744 measured reflections
2537 independent reflections
2004 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 27.5°
h = −21 → 24
k = −24 → 20
l = −11 → 13

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.2954P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.089$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
2537 reflections	
272 parameters	
H-atom parameters constrained	

Table 1
Geometry of hydrogen bonds and short intramolecular contacts (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C86—H86···N7	0.95	2.39	3.007 (3)	123
C114—H114···N113^{i}	0.95	2.49	3.417 (3)	165

Symmetry code: (i) $y, 1-x, 2-z$.

Compound (II)

Crystal data

$C_{26}H_{20}N_4$	Mo $K\alpha$ radiation
$M_r = 388.46$	Cell parameters from 4952 reflections
Orthorhombic, $P2_12_12$	$\theta = 3.6$–$27.5°$
$a = 18.6288$ (8) Å	$\mu = 0.08$ mm^{-1}
$b = 19.1956$ (8) Å	$T = 120$ (2) K
$c = 10.8885$ (3) Å	Lath, yellow
$V = 3893.6$ (3) Å^3	0.42 × 0.18 × 0.10 mm
$Z = 8$	
$D_x = 1.325$ Mg m^{-3}	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	4952 independent reflections
	3590 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.075$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 27.5°$
	$h = -24 \rightarrow 23$
$T_{min} = 0.976$, $T_{max} = 0.992$	$k = -18 \rightarrow 24$
25232 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 3.0251P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.065$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.152$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
4952 reflections	
543 parameters	
H-atom parameters constrained	

Table 2
Geometry of short intramolecular contacts (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C182—H182···N19	0.95	2.45	2.786 (6)	101
C186—H186···N17	0.95	2.34	2.980 (5)	125
C282—H282···N29	0.95	2.49	2.808 (5)	100
C286—H286···N27	0.95	2.35	2.976 (5)	123

Space group $P\bar{4}2_1c$ for (I) and $P2_12_12$ for (II) were both assigned uniquely 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_{iso}(H) = $1.2U_{eq}$(C), or $1.5U_{eq}$(C) for the methyl groups. In the absence of significant anomalous scattering, the Flack (1983) parameter was indeterminate for both compounds (Flack & Bernardinelli, 2000). Hence, Friedel-equivalent reflections were merged prior to the final refinements. Accordingly, it was not possible to establish the absolute axis assignment in (I) or the absolute configurations of the molecules in the crystal of (II) selected for data collection (Jones, 1986).

For both compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); publication software: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1280). Services for accessing these data are described at the back of the journal.

References

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.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Jones, P. G. (1986). *Acta Cryst.* A**42**, 57.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
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.
Serrano, H., Quiroga, J., Cobo, J., Low, J. N. & Glidewell, C. (2005*a*). *Acta Cryst.* E**61**, o1058–o1060.
Serrano, H., Quiroga, J., Cobo, J., Low, J. N. & Glidewell, C. (2005*b*). *Acta Cryst.* E**61**, o1702–o1703.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.