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8-*tert*-Butyl-7-(4-chlorophenyl)-10-phenyl-5,6-dihydro-10*H*-benzo[*h*]-pyrazolo[3,4-*b*]quinoline

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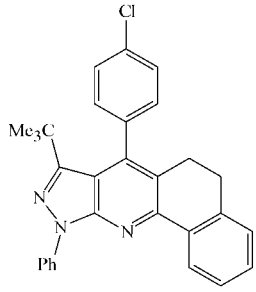
The title compound, $C_{30}H_{26}ClN_3$, crystallizes with $Z' = 3$ in the $P\overline{1}$ space group. The three independent molecules have very similar, although not identical, conformations, with almost perfect screw-boat forms adopted by the non-aromatic carbocyclic rings. Four independent C—H$\cdots\pi$(arene) hydrogen bonds link the molecules into centrosymmetric six-component aggregates.

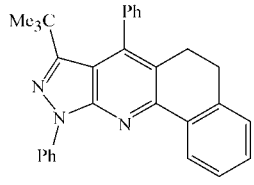
Comment

Pyrazolo[3,4-*b*]quinolines are of interest as possible antiviral and antimalarial agents, and because of their other biological properties, such as parasiticidic, bactericidal, vasodilator and enzyme-inhibitory activities (Quiroga *et al.*, 2001). We report here the structure of the title compound, (I), and we compare both its conformation and its supramolecular aggregation with those of the analogous compounds (II) (Low *et al.*, 2007), which differs from (I) in having no Cl substituent on the pendent aryl ring, and (III) (Portilla *et al.*, 2005), which differs from (II) in having a methyl substituent in place of the *tert*-butyl group (see scheme).

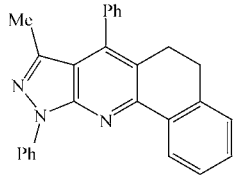
Compound (I) crystallizes with $Z' = 3$ in the $P\overline{1}$ space group. The molecules of (I) have no internal symmetry and hence they are chiral; the asymmetric unit was selected so that all three molecules are of the same hand as defined by the dihedral angles and the ring-puckering parameters (Figs. 1–3 and Table 2). The dihedral angles between the pyrazole and pyridine rings and their pendent aryl groups show only modest variations between the three independent molecules; the corresponding values for (II) and (III) show significantly wider variation than those between the independent molecules of (I). On the other hand, the ring-puckering parameters (Cremer & Pople, 1975) in (I), defined for the atom sequences C*x*1*A*—C*x*1*B*—C*x*14*A*—C*x*5—C*x*6—C*x*6*A*, where *x* takes the values 1, 2 and 3 for the three molecules, are remarkably similar to those defined by the comparable atom sequences in (II) and (III). In every case, the puckering angles are very close to the ideal values, *viz*. $\theta = 112.5^\circ$ and $\varphi = (60n + 30)^\circ$, where *n* represents zero or an integer, for a screw-boat conformation of the non-aromatic carbocylic ring.



(I)



(II)



(III)

In each of the independent molecules of (I), as in the molecules of (II) and (III), the bond distances are consistent with aromatic delocalization within the pyridine ring and strong bond fixation in the pyrazole ring.

Although intermolecular C—H$\cdots$N hydrogen bonds are absent from the structure of (I), the molecules are linked into

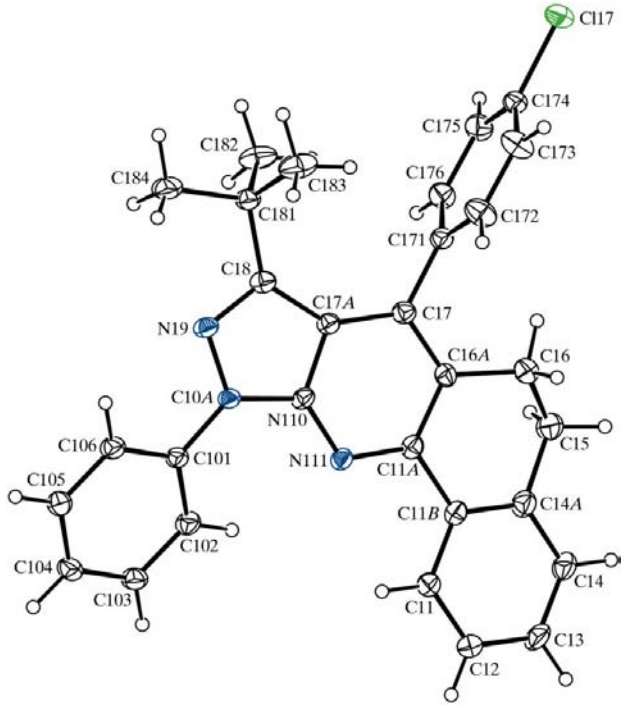


Figure 1
The type 1 molecule in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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finite multi-component aggregates by means of four independent C—H···π(arene) hydrogen bonds (Table 1). Atom C175 in the type 1 molecule (Fig. 1) at (x, y, z) acts as a hydrogen-bond donor to the pendent aryl ring (C101–C106) in the molecule at ($1-x, 1-y, -z$), so generating by inversion a centrosymmetric dimer unit, centred at ($\frac{1}{2}$, $\frac{1}{2}$, 0). In addition, atoms C173 in the type 1 molecule at ($1-x$, $1-y$, $-z$) and C375 in the type 3 molecule at ($1+x$, y, z) act as hydrogen-bond donors, respectively, to the C21/C21*B*/C24*A*/C24/C23/C22 and C201–C206 rings, both in the type 2 molecule at ($1+x$, y, z). This last pair of hydrogen bonds may be weakly reinforced by the final such interaction, involving atom C273 and the C301–C306 ring. Propagation of all these interactions by inversion then generates a centrosymmetric six-component aggregate containing two molecules of each type (Fig. 4).

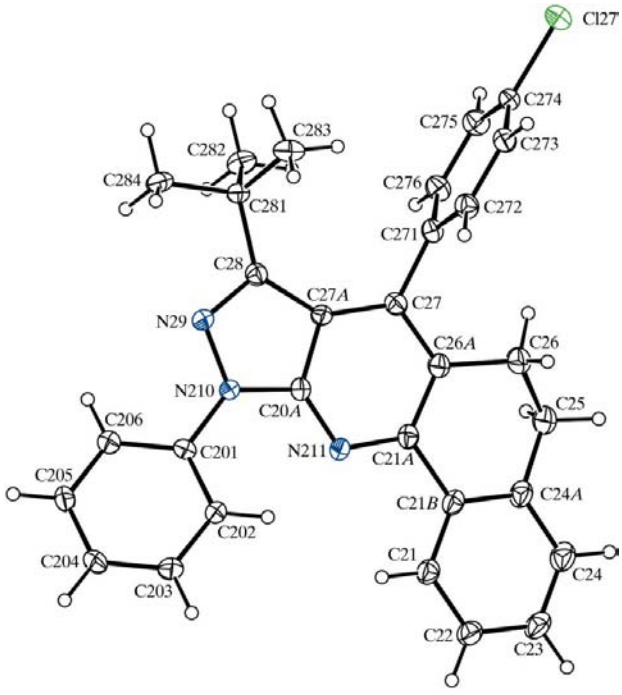

Figure 2
The type 2 molecule in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

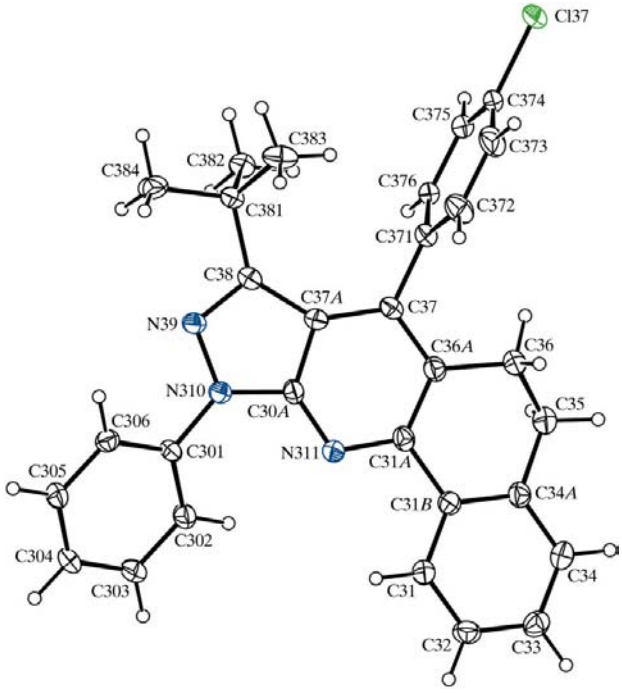

Figure 3
The type 3 molecule in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

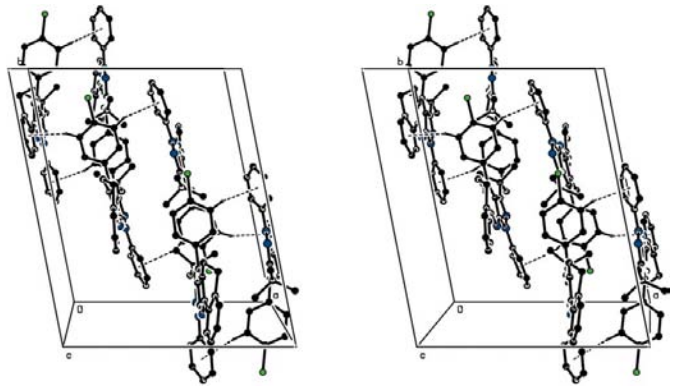

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a centrosymmetric six-component aggregate containing four independent C—H···π(arene) hydrogen bonds.

The finite aggregation in (I), based on multiple C—H···π(arene) hydrogen bonds, may be briefly compared with the aggregation in (II) and (III), which crystallize, respectively, in space group $P\overline{1}$ with $Z'=1$ (Low *et al.*, 2007) and $P2_1/c$ with $Z'=1$ (Portilla *et al.*, 2005). In (II), pairs of molecules are linked into centrosymmetric dimers by paired C—H···π(pyridyl) hydrogen bonds, while in (III) a combination of C—H···π(arene) and C—H···π(pyridyl) hydrogen bonds links the molecules into sheets, generated by a combination of glide plane and inversion. Hence, just as the change in the hydrocarbyl substituent between compounds (I) and (II) leads to a major change in the pattern of supramolecular aggregation, so too the notional introduction of a single chloro substituent into one of the pendent aryl rings leads to significant differences between compounds (I) and (II), both in respect of the crystallization characteristics as manifested by the Z'' values and in the nature of the supramolecular aggregation.

Experimental

Equimolar quantities (1 mmol of each component) of 5-amino-3-*tert*-butyl-1-phenylpyrazole and 2-(4-chlorobenzylidene)-1-tetralone were thoroughly mixed at room temperature. The mixture was heated in an oil bath at 423 K for 3.5 min, stirred briefly and allowed to cool to ambient temperature, at which point it solidified. The solid was extracted with ethanol and, after removal of the solvent from the extract, the product (I) was recrystallized from ethanol–dimethylformamide (1:1 *v*/*v*) to give yellow crystals suitable for single-crystal X-ray diffraction (yield 72%, m.p. 468–470 K).

Crystal data

$C_{30}H_{26}ClN_3$
M_r = 463.99
Triclinic, $P\overline{1}$
a = 13.1170 (18) Å
b = 15.948 (3) Å
c = 17.717 (2) Å
α = 93.750 (11)°
β = 91.803 (9)°
γ = 101.155 (13)°
V = 3624.7 (10) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 0.18 mm^{-1}
T = 120 (2) K
0.57 × 0.32 × 0.19 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.904, T_{max} = 0.966
87246 measured reflections
16583 independent reflections
8207 reflections with $I > 2\sigma(I)$
R_{int} = 0.074

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.211
S = 1.05
16583 reflections
928 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C101–C106 ring, *Cg*2 is the centroid of the C21/C21*B*/C24*A*/C24/C23/C22 ring, *Cg*3 is the centroid of the C201–C206 ring and *Cg*4 is the centroid of the C301–C306 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C173—H173···*Cg*2^{i}	0.95	2.62	3.532 (4)	162
C175—H175···*Cg*1^{ii}	0.95	2.64	3.513 (4)	153
C273—H273···*Cg*4^{iii}	0.95	2.85	3.687 (3)	147
C375—H375···*Cg*3^{iv}	0.95	2.69	3.698 (4)	161

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

Table 2
Ring-puckering parameters and selected torsion angles (°) for (I)–(III).

Parameter	(I), x = 1	(I), x = 2	(I), x = 3	(II)	(III)
θ	116.6 (4)	116.1 (4)	115.1 (5)	116.6 (5)	115.4 (2)
φ	31.1 (6)	32.3 (5)	30.7 (6)	29.7 (5)	34.1 (2)
(Pyrazole)/(C*x*01–C*x*06)	22.0 (2)	28.3 (2)	26.9 (2)	8.3 (2)	33.16 (8)
(Pyridine)/(C*x*71–C*x*76)	89.0 (2)	89.9 (2)	84.7 (2)	85.9 (2)	63.45 (7)

Note: the data for (II) are taken from Low *et al.* (2007) and the data for (III) are taken from Portilla *et al.* (2005); for both (II) and (III), x is nul for the C*x*71–C*x*76 ring and 1 for the C*x*01–C*x*06 ring.

Crystals of compound (I) are triclinic; 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 1.2 for all other H atoms. Examination of the refined structure using the ADDSYM option in *PLATON* (Spek, 2003) revealed no additional symmetry.

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) and *WinGX* (Farrugia, 1999); 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3154). Services for accessing these data are described at the back of the journal.

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