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3-*tert*-Butyl-1-(4-chlorophenyl)-7,7-dimethyl-5,6,7,8-tetrahydropyrazolo[3,4-*b*]quinolin-5-one: centrosymmetric dimers generated by C—H···π(arene) hydrogen bonds

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.053
wR factor = 0.122
Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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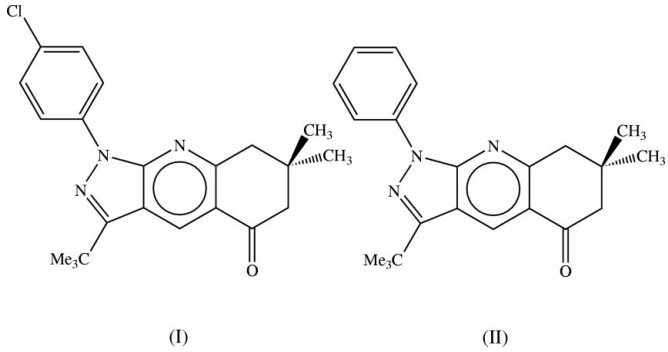
Molecules of the title compound, $C_{22}H_{24}ClN_3O$, are linked by two pairs of C—H···π(arene) hydrogen bonds into centrosymmetric dimers.

Comment

We report here the structure of the title compound, (I) (Fig. 1), whose supramolecular aggregation shows some interesting differences from that in the unsubstituted analogue (II) (Low *et al.*, 2004).



The bond lengths in (I) are very similar to those in (II) and require no further discussion here. The ring-puckering parameters (Cremer & Pople, 1975) for the carbocyclic rings in (I) and (II) are quite similar [for the atom sequence C4*A*—C5—

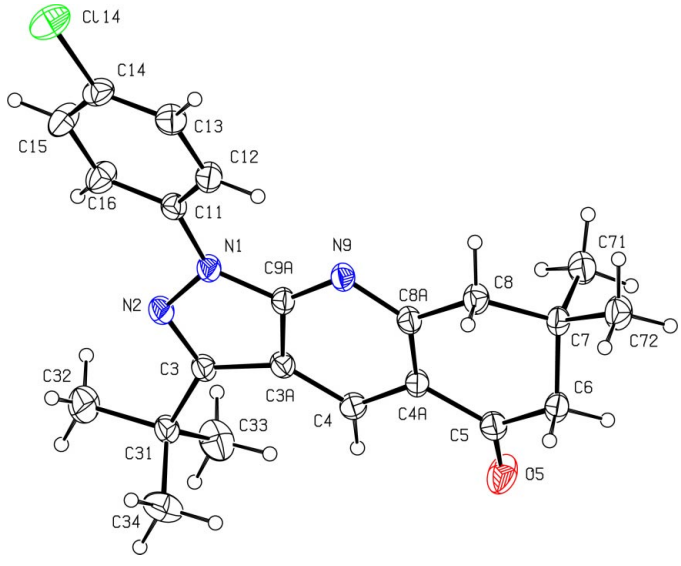


Figure 1
The molecule of compound (I), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

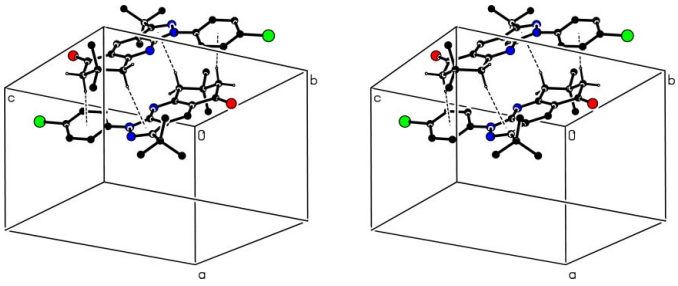


Figure 2
Stereoview of part of the crystal structure of compound (I), showing the formation of a centrosymmetric hydrogen-bonded dimer. For clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted. C—H···π hydrogen bonds are shown as dashed lines.

C6—C7—C8—C8*A*, $\theta = 132.1\ (4)^\circ$ and $\varphi = 351.0\ (5)$ in (I), and $\theta = 127.4\ (3)^\circ$ and $\varphi = 353.8\ (3)$ in (II)] and indicate an envelope conformation in each compound (Evans & Boeyens, 1989).

The principal difference between (I) and (II) arises from the intermolecular aggregation. In (I), the molecules are linked into centrosymmetric dimers by two pairs of C—H···π(arene) interactions (Table 1). Atoms C6 and C8 in the molecule at (x, y, z) act as donors, *via* the axial H atoms H6*A* and H8*A*, to the aryl and pyrazole rings, respectively, in the molecule at ($-x$, $1-y$, $1-z$) (Fig. 2). There are no other types of intermolecular hydrogen bond in the structure of (I) and there are no direction-specific interactions between the dimers. By contrast, in (II), the molecules are linked into chains by means of a C—H···N hydrogen bond, and C—H···π(arene) hydrogen bonds are absent from the structure of (II). It is striking that the presence of a single remote Cl substituent in (I) is associated with such a change in the hydrogen bonding.

Experimental

A mixture of 5-amino-3-*tert*-butyl-1-(4-chlorophenyl)pyrazole (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (1 mmol) and formaldehyde (3 mmol) was placed in an open Pyrex-glass vessel and irradiated in a domestic microwave oven for 3 min (at 600 watts). After reaction, the mixture was extracted with ethanol; the extract was filtered and the product, (I), was purified by column chromatography on silica gel, with dichloromethane/hexane (7:3, *v*/*v*) as eluant. Yield 39%, m.p. 428 K. MS (EI 70 eV) *m*/*z* (%): 383/381 (15/49), 382 (12), 368/366 (37/100), 149 (16), 57 (11). Crystals suitable for single-crystal X-ray diffraction were grown from ethanol.

Crystal data

$C_{22}H_{24}ClN_3O$
$M_r = 381.89$
Triclinic, $P\overline{1}$
$a = 8.6851\ (11)$ Å
$b = 10.6167\ (9)$ Å
$c = 12.4330\ (12)$ Å
$\alpha = 106.724\ (8)^\circ$
$\beta = 101.049\ (10)^\circ$
$\gamma = 107.406\ (8)^\circ$
$V = 998.1\ (2)$ Å^3
$Z = 2$
$D_x = 1.271$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4289 reflections
$\theta = 5.0$–27.5°
$\mu = 0.21$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.40 × 0.20 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*EVALCCD*; Duisenberg *et al.*, 2003)
$T_{min} = 0.925$, $T_{max} = 0.980$
13 573 measured reflections
4289 independent reflections
1940 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$
$\theta_{max} = 27.5^\circ$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.122$
$S = 0.93$
4289 reflections
250 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.3921P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

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

	D—H	H···A	D···A	D—H···A
C6—H6*A*···*Cg*1^{i}	0.97	2.77	3.649 (3)	151
C8—H8*A*···*Cg*2^{i}	0.97	2.82	3.768 (3)	165

Symmetry code: (i) $-x, -y+1, -z+1$. Notes: *Cg*1 and *Cg*2 are the centroids of rings C11–C16 and N1/N2/C3/C3*A*/C9*A*, respectively.

All H atoms were located in difference maps and then treated as riding atoms, with C—H distances 0.93 Å (aromatic), 0.96 Å (CH_3) or 0.97 Å (CH_2), and with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for the methyl groups. This structure was determined at room temperature and both the data completeness and the ratio of observed-to-unique reflections are rather low. Since this structure is, in all respects, similar to its non-chlorinated analogue (II), a second data-collection, at low temperature, was not justified.

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: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *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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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Evans, D. G. & Boeyens, J. C. A. (1989). *Acta Cryst.* B**45**, 581–590.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Low, J. N., Cobo, J., Mera, J., Quiroga, J. & Glidewell, C. (2004). *Acta Cryst.* C**60**, o479–o482.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.