

3-[(*E*)-(3-*tert*-Butyl-1-phenyl-1*H*-pyrazol-5-yl)iminomethyl]quinolin-2(1*H*)-one: chains built by π -stacking of hydrogen-bonded $R_2^2(8)$ dimers

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In the title compound, $C_{23}H_{22}N_4O$, there is evidence for some bond fixation in the aryl component of the quinolinone unit. Pairs of molecules related by inversion are linked into $R_2^2(8)$ dimers by almost linear $N-H\cdots O$ hydrogen bonds, and dimers related by inversion are linked into chains by a single aromatic π - π stacking interaction.

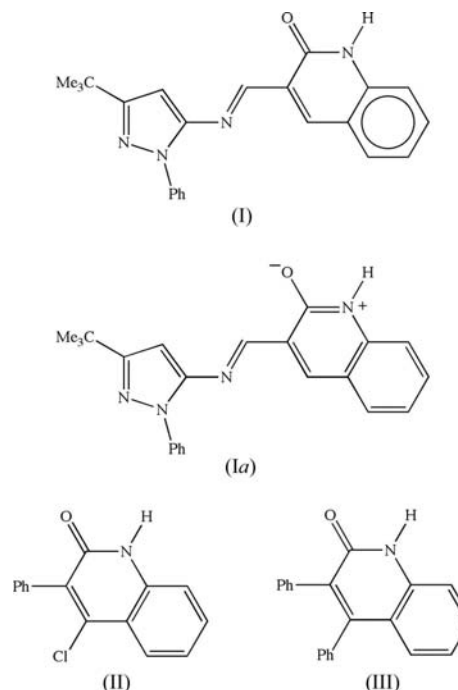
Comment

We report here the structure of the title compound, (I) (Fig. 1). It is related to a series of 5-benzylamino-3-*tert*-butyl-1-phenyl-1*H*-pyrazoles, the structures of which were reported recently (Castillo *et al.*, 2009), but differs from the earlier series in the nature of its arylidene moiety, the bicyclic heterocyclic 2-oxo-1,2-dihydro-3-quinolyl fragment, where the $N-H$ and $C=O$ groups play the leading role in the supramolecular aggregation.

Although the $C-C$ distances in the pendent aryl ring (C11–C16) span only a small range [1.380 (2)–1.392 (2) Å], the $C-C$ distances in the aryl component of the quinolinone unit show much wider variation (Table 1). In particular, the C65–C66 and C67–C68 distances (*cf.* Fig. 1) are significantly shorter than the other distances in this ring, suggesting some bond fixation analogous to that found in naphthalenes, so that the resonance forms (I) and (Ia) (see scheme) are probably both significant contributors to the overall electronic structure.

The *tert*-butyl substituent of (I) is oriented relative to the pyrazole ring such that one of the methyl C atoms, C32, is close to but displaced from the plane of the pyrazole ring, so that the *tert*-butylpyrazole fragment has only approximate local mirror symmetry. In effect (Table 1), the *tert*-butyl group is rotated by *ca* 6° about the C3–C31 bond away from the

mirror-symmetry conformation. On the other hand, the plane of the C11–C16 phenyl group makes a dihedral angle of 21.9 (2)° with that of the pyrazole ring. There is a short intramolecular $C-H\cdots N$ contact involving atom C12 (Table 2), but the dihedral angle makes it possible that this is actually a repulsive rather than an attractive contact. Apart from the *tert*-butyl and phenyl substituents, the rest of the molecular skeleton is nearly planar, as indicated by the leading torsion angles (Table 1).



The supramolecular aggregation of (I) is dominated by a fairly short and almost linear $N-H\cdots O$ hydrogen bond (Table 2). Pairs of these hydrogen bonds link molecules related by inversion into $R_2^2(8)$ (Bernstein *et al.*, 1995) dimers, with the reference dimer centred at $(0, \frac{1}{2}, \frac{1}{2})$. A single aromatic π - π stacking interaction links the hydrogen-bonded dimers into a chain. The C11–C16 phenyl rings in the molecules at (x, y, z) and $(2-x, 1-y, 2-z)$ are strictly parallel, with an

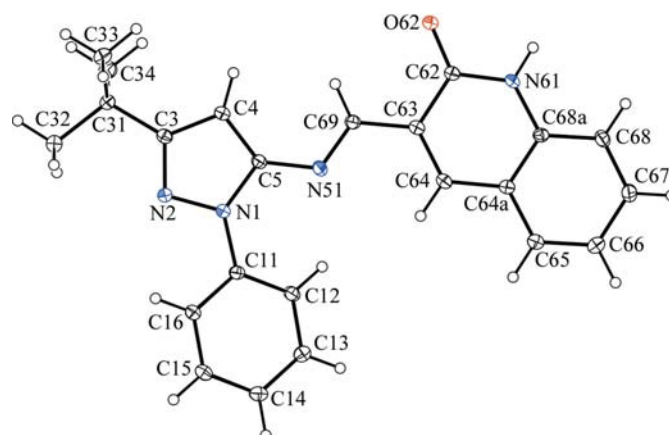


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

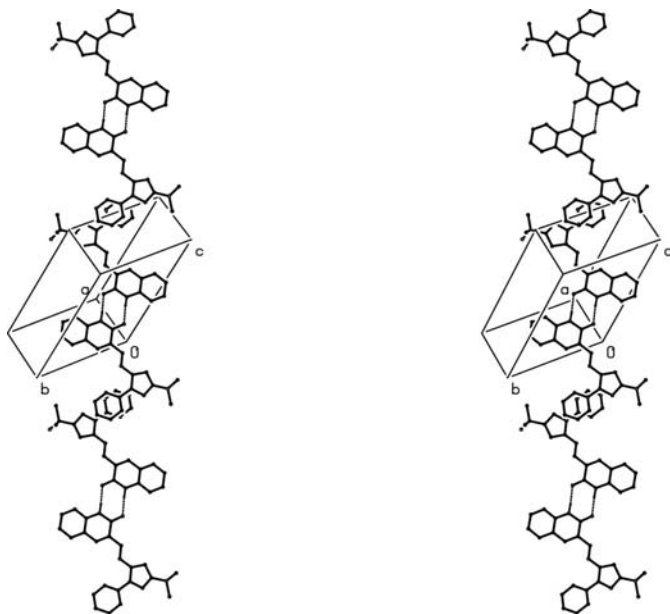


Figure 2

A stereoview of part of the crystal structure of (I), showing the formation of a chain parallel to [201] consisting of π -stacked hydrogen-bonded dimers. For the sake of clarity, H atoms bonded to C atoms have all been omitted.

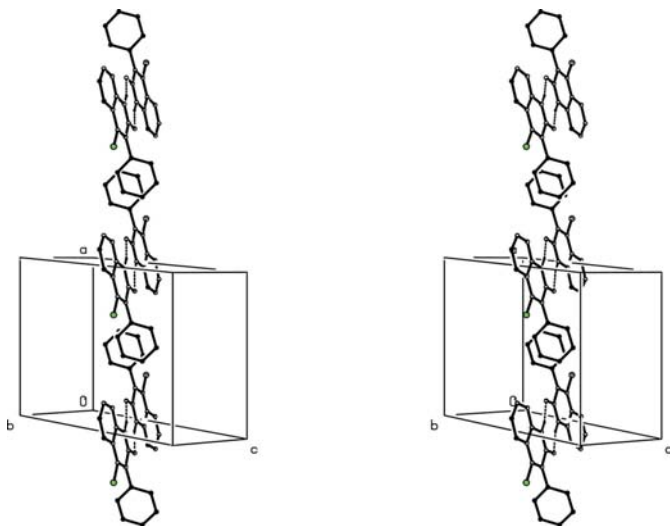


Figure 3

A stereoview of part of the crystal structure of (II), showing the formation of a chain parallel to [100] consisting of π -stacked hydrogen-bonded dimers. The original atom coordinates (Li *et al.*, 2004) were used and, for the sake of clarity, H atoms bonded to C atoms have all been omitted.

interplanar spacing of 3.484 (2) Å, a ring-centroid separation of 3.871 (2) Å and a ring-centroid offset of 1.687 (2) Å. The two molecules involved form parts of hydrogen-bonded dimers centred at $(0, \frac{1}{2}, \frac{1}{2})$ and $(2, \frac{1}{2}, \frac{3}{2})$, respectively, and propagation by inversion of the hydrogen bond and the π - π stacking interaction generates a chain of π -stacked hydrogen-bonded dimers running parallel to the [201] direction (Fig. 2). Within this chain, $R_2^2(8)$ rings centred at $(2n, \frac{1}{2}, n + \frac{1}{2})$, where n represents an integer, alternate with π - π stacking interactions across $(2n + 1, \frac{1}{2}, n + 1)$, where n again represents an integer

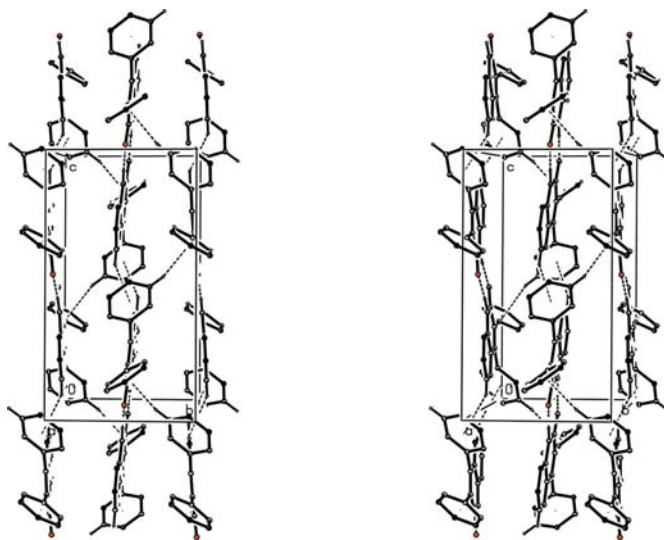


Figure 4

A stereoview of part of the crystal structure of (III), showing the formation of a sheet lying parallel to (100) and built from $N-H \cdots O$ and $C-H \cdots \pi(\text{arene})$ hydrogen bonds. The original atom coordinates (Vicente *et al.*, 2005) were used and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

(Fig. 2). There are no direction-specific interactions between the chains. In particular, $C-H \cdots \pi(\text{arene})$ hydrogen bonds are absent.

Almost all of the quinolin-2-ones with the same substituent pattern as in (I) for which structures are recorded in the Cambridge Structural Database (CSD, Version 5.30, March 2009 release; Allen, 2002) carry other substituents with potential hydrogen-bonding capacity, particularly hydroxy, amino and carbonyl groups. However, two compounds of this type, namely (II) (CSD refcode ABABEL; Li *et al.*, 2004) and (III) (CSD refcode XAWHEJ; Vicente *et al.*, 2005), carry no further conventional hydrogen-bonding groups. Since both of these structures were reported on a proof-of-constitution basis, with no description or discussion of the intermolecular interactions, it is of interest briefly to compare the crystal structures of (II) and (III) with that of (I).

In each of (II) and (III), pairs of molecules related by inversion are linked, as in (I), into centrosymmetric $R_2^2(8)$ dimers by $N-H \cdots O$ hydrogen bonds which, as in (I), are fairly short and almost linear. In (II), a weak π - π stacking interaction involving the pendent phenyl rings in molecules related by inversion leads to a chain of π -stacked dimers running parallel to the [100] direction (Fig. 3), but otherwise rather similar to the chain in (I). There are no aromatic π - π stacking interactions in the structure of (III), despite the rich availability of aryl rings, but instead the hydrogen-bonded dimers are linked by two independent $C-H \cdots \pi(\text{arene})$ hydrogen bonds to form sheets lying parallel to (100) (Fig. 4).

Experimental

A mixture of 3-*tert*-butyl-1-phenyl-1*H*-pyrazol-5-amine (100 mg, 1.0 mmol) and 2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1.0 mmol) in ethanol (4 ml) was heated under reflux with stirring for 2–3 h.

Table 1

Selected geometric parameters (Å, °).

N61—C62	1.3719 (19)	C66—C67	1.402 (2)
C62—C63	1.462 (2)	C67—C68	1.370 (2)
C63—C64	1.360 (2)	C68—C68a	1.396 (2)
C64—C64a	1.424 (2)	C68a—N61	1.378 (2)
C64a—C65	1.398 (2)	C64a—C68a	1.405 (2)
C65—C66	1.372 (2)		
N2—N1—C11—C12	155.89 (14)	N1—C5—N51—C69	177.94 (14)
N2—C3—C31—C32	5.9 (2)	C5—N51—C69—C63	−178.71 (14)
N2—C3—C31—C33	127.02 (16)	N51—C69—C63—C62	178.88 (14)
N2—C3—C31—C34	−113.92 (16)		

After complete disappearance of the starting materials, as monitored by thin-layer chromatography, the mixture was cooled to ambient temperature. The resulting solid product was collected by filtration and then washed with cold ethanol (2 × 0.5 ml) to give the title compound, (I), as a yellow solid [yield 86%, m.p. 553 K (decomposition)]. MS (70 eV) *m/z* (%): 370 (68) [*M*⁺], 313 (42), 287 (100), 262 (47), 226 (46), 128 (21), 77 (64). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation from a solution in ethanol.

Crystal data

C ₂₃ H ₂₂ N ₄ O	$\gamma = 98.539 (2)^\circ$
<i>M_r</i> = 370.45	<i>V</i> = 938.99 (6) Å ³
Triclinic, <i>P</i> $\bar{1}$	<i>Z</i> = 2
<i>a</i> = 6.3601 (2) Å	Mo <i>K</i> α radiation
<i>b</i> = 11.2750 (5) Å	$\mu = 0.08 \text{ mm}^{-1}$
<i>c</i> = 13.8028 (5) Å	<i>T</i> = 120 K
$\alpha = 105.972 (2)^\circ$	0.25 × 0.18 × 0.15 mm
$\beta = 91.253 (3)^\circ$	

Data collection

Bruker–Nonius APEXII CCD camera on κ goniostat	19114 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	4310 independent reflections
<i>T</i> _{min} = 0.976, <i>T</i> _{max} = 0.988	2929 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.064

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.053	256 parameters
<i>wR</i> (<i>F</i> ²) = 0.151	H-atom parameters constrained
<i>S</i> = 1.04	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
4310 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

All H atoms were located in difference maps and then treated as riding, with C—H = 0.95 (aromatic and heteroaromatic) or 0.98 Å (methyl) and N—H = 0.90 Å, and with *U*_{iso}(H) = *kU*_{eq}(carrier), where *k* = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N61—H61···O62 ⁱ	0.90	1.92	2.8110 (17)	176
C12—H12···N51	0.95	2.37	2.951 (2)	119

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

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000) and *DENZO* (Otwinowski & Minor, 1997); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3342). Services for accessing these data are described at the back of the journal.

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