

A monoclinic polymorph of 3,7,7-trimethyl-1-phenyl-5,6,7,8-tetrahydro-1*H*-pyrazolo[3,4-*b*]quinolin-5-one

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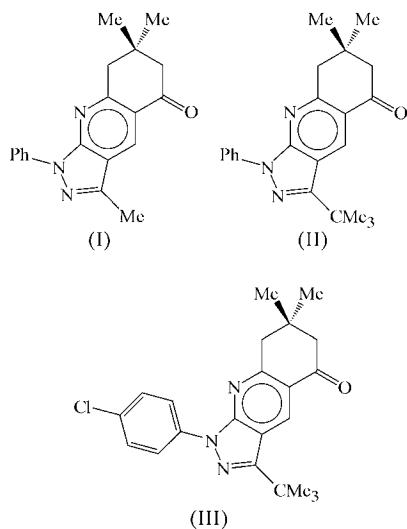
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A second, monoclinic, polymorph of the title compound, C₁₉H₁₉N₃O, is reported. In this polymorph, the molecules are linked into chains by paired C—H··· π hydrogen bonds and the chains are linked into sheets by π stacking interactions.

Comment

The structure of a triclinic form (space group $P\bar{1}$, $Z' = 2$) of the title compound, (I), has been reported recently (Low *et al.*, 2003); the crystals were grown from an ethanol solution. We now report the structure of a monoclinic polymorph of (I) (space group $P2_1/n$, $Z' = 1$; Fig. 1), for which the crystals were



grown from a dimethylformamide solution. In this polymorph, the supramolecular aggregation shows some interesting differences from both that of the triclinic form and that of

the analogous compound 3-*tert*-butyl-7,7-dimethyl-1-phenyl-5,6,7,8-tetrahydropyrazolo[3,4-*b*]quinolin-5-one, (II) (Low *et al.*, 2004). For convenience, we denote the monoclinic polymorph reported here as (Ia) and the previously reported triclinic polymorph as (Ib).

The bond lengths in monoclinic polymorph (Ia) are very similar to those in both the triclinic polymorph (Ib) and (II), and thus require no further discussion here. The ring-puckering parameters (Cremer & Pople, 1975) for the carbocyclic ring in monoclinic (Ia) are $\theta = 52.1(2)^\circ$ and $\varphi = 167.4(4)^\circ$ for the atom sequence C4a—C5—C6—C7—C8—C8a, with a total puckering amplitude $Q = 0.489(2) \text{ \AA}$; these parameters indicate an envelope conformation for this ring (Evans & Boeyens, 1989), with the ring folded across the vector

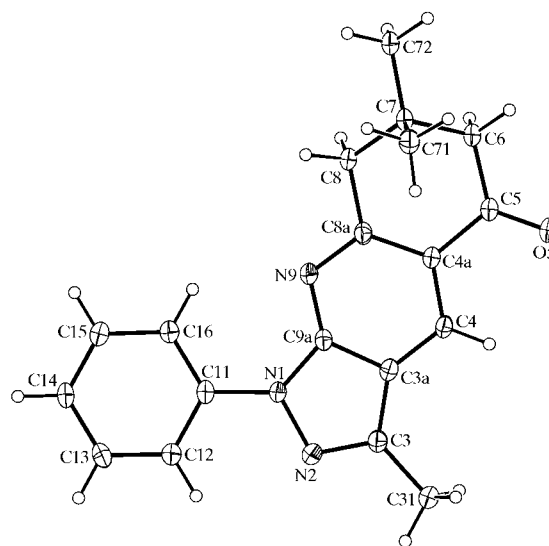


Figure 1

The molecule of compound (I) in the monoclinic polymorph (Ia), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

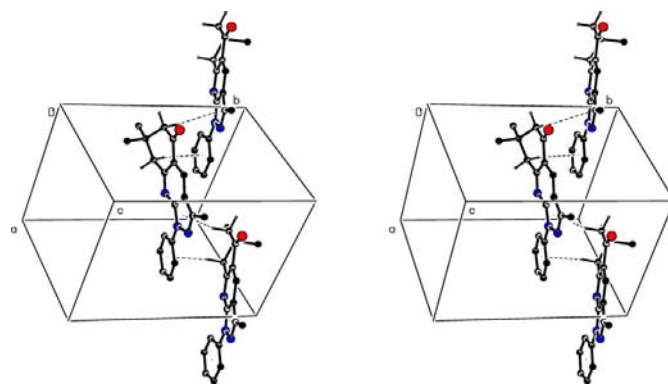


Figure 2

Stereoview of part of the crystal structure of polymorph (Ia), showing the formation of a hydrogen-bonded chain along [101]. For the sake of clarity, H atoms bonded to those C atoms not involved in the motifs shown have been omitted.

C6···C8. In this respect, (Ia) is very similar both to (Ib) and to (II). However, the patterns of supramolecular aggregation in (Ia), (Ib) and (II) are entirely different.

In monoclinic (Ia), the molecules are linked into chains by two independent C—H··· π hydrogen bonds acting in concert, and the resulting chains are linked into sheets by π stacking interactions; however, C—H···O and C—H···N hydrogen bonds are absent from the structure of (I). By contrast, the molecules in triclinic (Ib) are linked into ribbons by a combination of C—H···O, C—H···N and C—H··· π hydrogen bonds, while the molecules of (II) are linked into chains by a single C—H···N hydrogen bond; however, C—H··· π hydrogen bonds and π stacking interactions are both absent from the structure of (II).

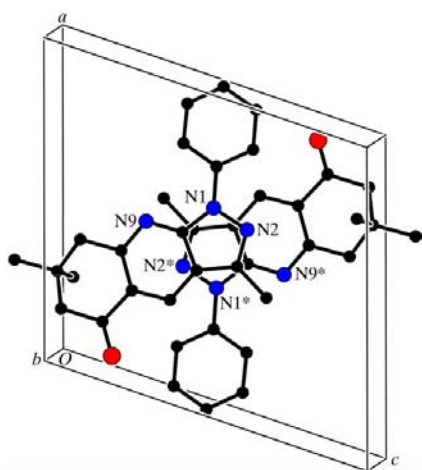


Figure 3
Part of the crystal structure of polymorph (Ia), showing a centrosymmetric π -stacked dimer. For the sake of clarity, H atoms have all been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

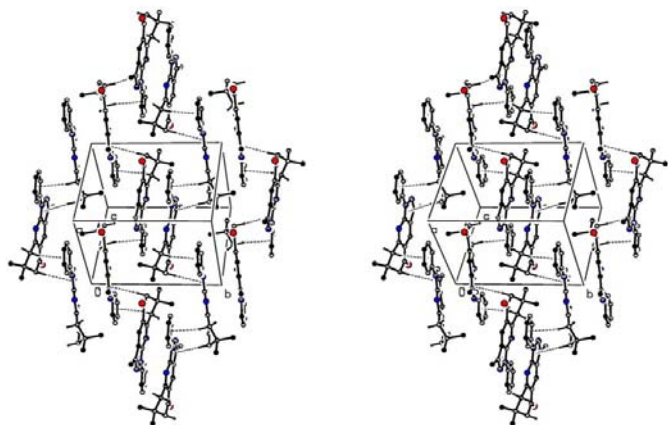


Figure 4
Stereoview of part of the crystal structure of polymorph (Ia), showing a $(10\bar{1})$ sheet of π stacked $[101]$ chains. For the sake of clarity, H atoms bonded to those C atoms not involved in the motifs shown have been omitted.

Atoms C6 and C8 in the molecule of (Ia) at (x, y, z) act as hydrogen-bond donors, *via* the axial atoms H6A and H8A, respectively, to the pyrazole and aryl rings of the molecule at $(-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, thereby forming a $[101]$ chain generated by the n -glide plane at $y = 0.75$ (Fig. 2). We may note here that the exactly corresponding pair of C—H bonds act as donors to aryl and pyrazole rings in the analogous chloro-substituted compound 3-*tert*-butyl-1-(4-chlorophenyl)-7,7-dimethyl-5,6,7,8-tetrahydropyrazolo[3,4-*b*]quinolin-5-one, (III), but such that H6A is donor to the aryl ring and H8A is donor to the pyrazole ring in a cyclic centrosymmetric dimer (Low *et al.*, 2005).

The hydrogen-bonded chains in polymorph (Ia) are linked into sheets by π stacking interactions. The pyrazole rings in the molecules at (x, y, z) and $(1-x, 1-y, 1-z)$ are strictly parallel, with an interplanar spacing of 3.311 (2) Å, a ring centroid separation of 3.416 (2) Å and a centroid offset of 0.841 (2) Å; at the same time, the pyrazole ring at (x, y, z) and the pyridine ring containing N9 at $(1-x, 1-y, 1-z)$ make an interplanar angle of only 1.1 (2)°; the interplanar spacing is *ca* 3.30 Å, the corresponding ring centroid separation is 3.547 (2) Å and the centroid offset is 1.300 (2) Å (Fig. 3). The molecules at (x, y, z) and $(1-x, 1-y, 1-z)$ form parts of the hydrogen-bonded chains generated by the n -glide planes at $y = 0.75$ and $y = 0.25$, respectively; hence, propagation by the space group of these π stacking interactions links all of the $[101]$ chains into a $(10\bar{1})$ sheet (Fig. 4); however, there are no direction-specific interactions between adjacent sheets.

Experimental

The title compound was prepared as described previously (Low *et al.*, 2003). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a dimethylformamide solution.

Crystal data

| | |
|---------------------------------|---|
| $C_{19}H_{19}N_3O$ | $D_x = 1.324 \text{ Mg m}^{-3}$ |
| $M_r = 305.37$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 3503 reflections |
| $a = 11.1485$ (12) Å | $\theta = 3.8\text{--}27.6^\circ$ |
| $b = 12.3739$ (15) Å | $\mu = 0.08 \text{ mm}^{-1}$ |
| $c = 11.7412$ (12) Å | $T = 120$ (2) K |
| $\beta = 108.894$ (6)° | Block, colourless |
| $V = 1532.4$ (3) Å ³ | $0.34 \times 0.23 \times 0.13 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Bruker–Nonius 95mm CCD camera on a κ -goniostat diffractometer | 3503 independent reflections |
| φ and ω scans | 2030 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2003) | $R_{\text{int}} = 0.090$ |
| $T_{\text{min}} = 0.967$, $T_{\text{max}} = 0.989$ | $\theta_{\text{max}} = 27.6^\circ$ |
| 17074 measured reflections | $h = -14 \rightarrow 14$ |
| | $k = -15 \rightarrow 16$ |
| | $l = -15 \rightarrow 15$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0933P)^2 + 0.13P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.179$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 1.03$ | $\Delta\rho_{\text{max}} = 0.28 \text{ e } \text{Å}^{-3}$ |
| 3503 reflections | $\Delta\rho_{\text{min}} = -0.30 \text{ e } \text{Å}^{-3}$ |
| 211 parameters | |
| H-atom parameters constrained | |

Table 1

Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of rings N1/N2/C3/C3a/C9a and C11–C16, respectively.

| <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> |
|------------------------------------|-------------|---------------|-----------------------|-------------------------|
| C6–H6A... <i>Cg</i> 1 ⁱ | 0.99 | 2.97 | 3.716 (3) | 133 |
| C8–H8A... <i>Cg</i> 2 ⁱ | 0.99 | 2.80 | 3.708 (3) | 153 |

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

The space group $P2_1/n$ was uniquely assigned 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 (methyl) or 0.99 Å (CH₂), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl groups.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England, using a Nonius KappaCCD diffractometer. JC thanks the Consejería

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1847). Services for accessing these data are described at the back of the journal.

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