organic compounds

C—H···π and π–π interactions in the supramolecular structure of 3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine

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The supramolecular structure of the title compound, $C_{19}H_{15}N_3$, is defined by π–π-stacking and C—H···π interactions. There are no conventional hydrogen bonds in the structure.

Comment

Previously, we have reported different syntheses of biologically active compounds with a pyrazolo[3,4-b]pyridine skeleton. 5-Aminopyrazoles were used as starting materials with α,β-unsaturated ketones, as shown in the *Scheme* (Quiroga, Insuasty, Cruz *et al.*, 1998; Quiroga, Cruz *et al.*, 2001), with benzaldehydes and Meldrum's acid (Quiroga, Hormaza *et al.*, 1998; Quiroga, Insuasty, Hormaza *et al.*, 1998) or with dimedone (Quiroga, Mejía *et al.*, 2001) as reactants. We now report the crystal structure of fully aromatized 3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine, (I), which was prepared to test the synthetic application of 5-(3-aryl-2-propenylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones [the structures of some examples have been reported recently; see, for example, Low *et al.* (2002)]. Reaction of the phenyl derivative with 5-amino-3-methyl-1-phenylpyrazole yielded (I). In this reaction, the Meldrum's acid fragment was completely eliminated, resulting in a fully aromatized product.

The pyrazole and pyridine rings in (I) are planar within experimental error and have a dihedral angle between them of 5.13 (10)°. The only other compound with a similar pyrazolo–pyridine structure reported in the Cambridge Structural Database (CSD; Version 5.22 of October 2001; Allen & Kennard, 1993) is 6-amino-5-cyano-3-methyl-1,4-diphenyl-pyrazolo[3,4-b]pyridine (Quiroga *et al.*, 1999), (II), which crystallizes in space group $P2_1/n$. In (II), the dihedral angle between the pyrazole and pyridine rings is 3.6 (3)°. N.B. The

atomic numbering differs for (I) and (II); all values are quoted with respect to the numbering of (I).
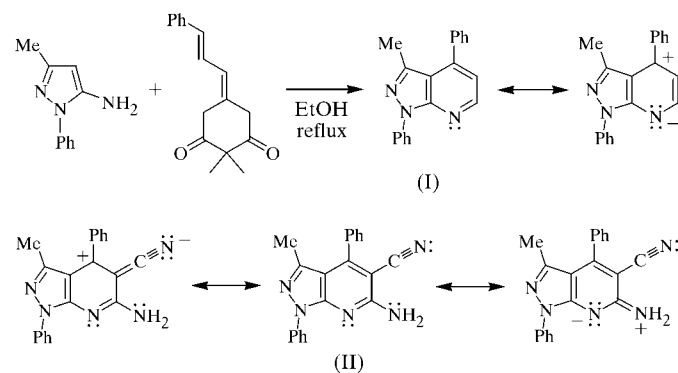
The torsion angles for the phenyl groups in (I) are given in Table 1. As can be seen from the examples given below, the conformations of the phenyl rings in compounds (I) and (II) are very similar, for example, in the case of ring 4 (atoms C41–C46) [values for (II) are given in parenthesis], C5—C4—C41—C42 = 112.8 (2)° [118.2 (5)°], but differ by nearly 23° in the case of phenyl ring 3 (atoms C11–C16), where C7a—N1—C11—C12 = 135.2 (2)° [158.0 (5)°].

In (I), the π–π stacking involves the pyridine ring of the pyrazolo–pyridine group. The ring in the molecule at (x, y, z) stacks above the ring at (−x, 2 − y, 1 − z) across the centre of inversion at $(0,1,\frac{1}{2})$, with a distance of 3.563 (2) Å between the ring centroids, a perpendicular distance between the rings of 3.443 (2) Å and a centroid offset of 0.913 (2) Å (Fig. 2a). Although compound (II) does contain a conventional N—
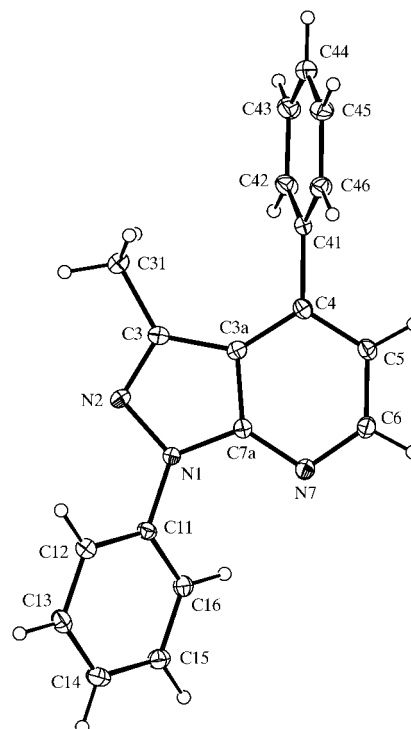

Figure 1
View of (I) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level.

H···N hydrogen bond, there is similar π–π stacking between the pyridine rings related by the centre of inversion at (0,1,1), with a Cg···Cg distance of 3.701 (3) Å, a perpendicular distance of 3.552 Å and an offset between the centres of 1.04 Å. Fig. 2(b) shows the stacking in (II), labelled in this case with the numbering system used for (I). Figs. 2(a) and 2(b) show the differences in the stacking in the two compounds. These differences result from the different polarizations of the pyridine rings in the two compounds, which result from the presence of the amino and cyano substituents in compound (II).

There are two C—H···π interactions involving each of phenyl rings 3 (atoms C11–C16, centroid $Cg3$) and 4 (atoms C41–C46, centroid $Cg4$). The C43—H43···$Cg3^{ii}$ interaction (Table 2) links the molecules into centrosymmetrically related dimers via the centre of inversion at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ [symmetry code:
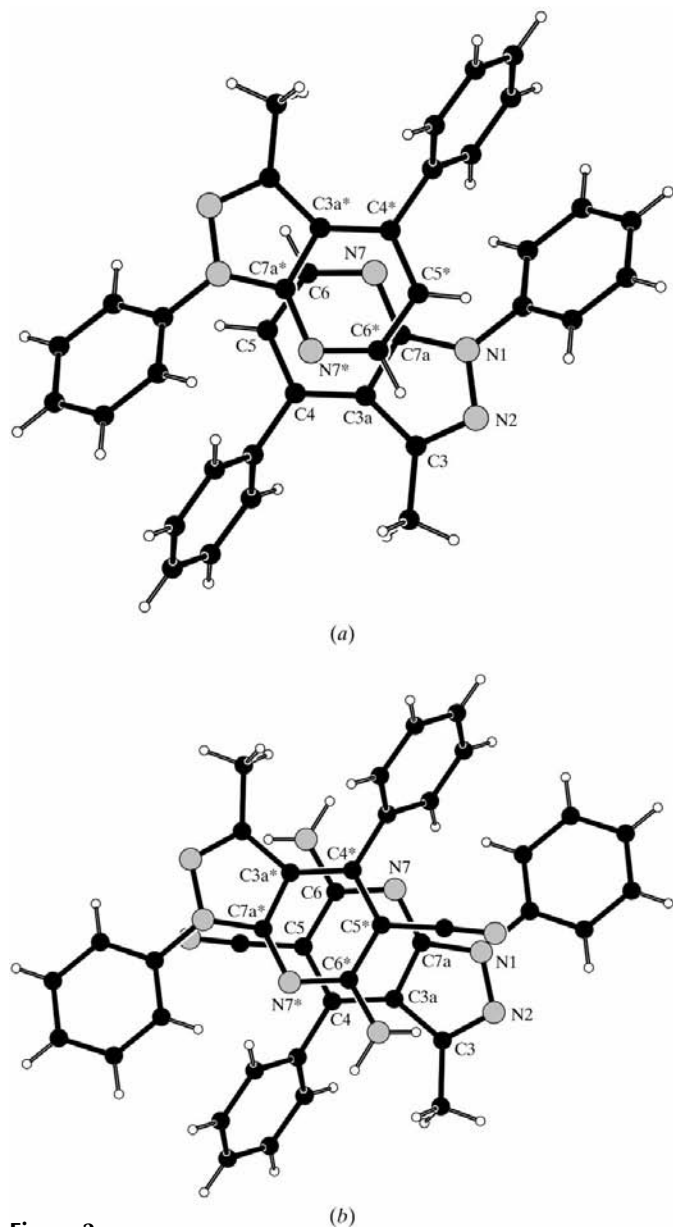

Figure 2
View of the π–π stacking between the molecules in (a) (I) and (b) (II).
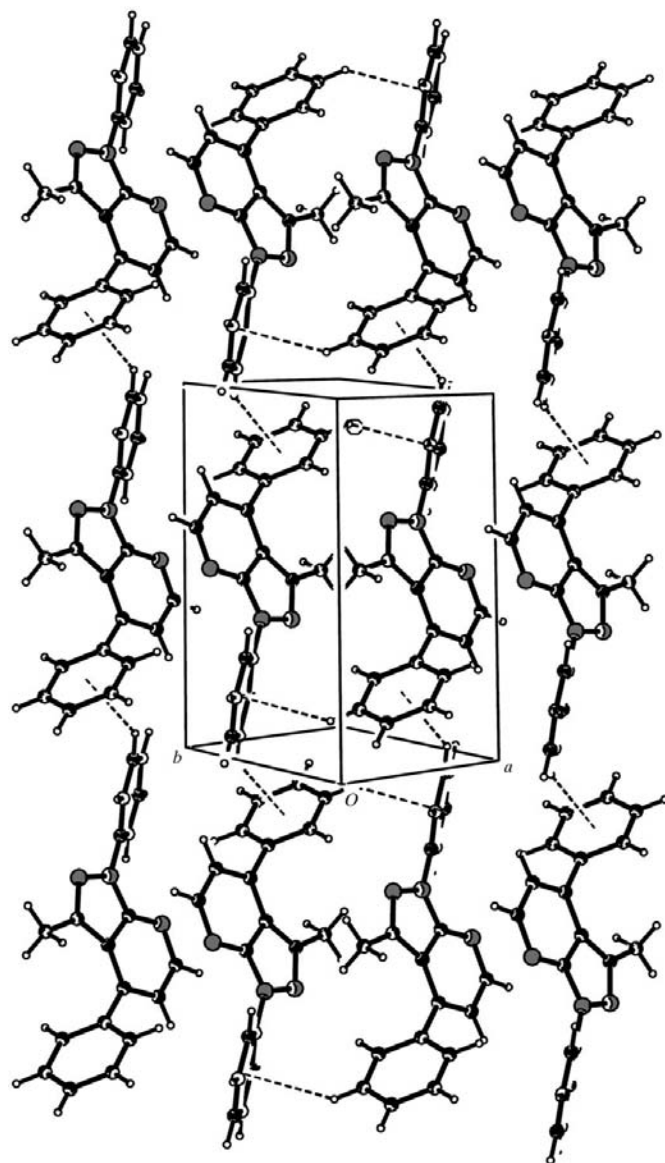

Figure 3
View of the linked dimer chains and sheet formed by the π–π stacking in (I).

(ii) $1 - x$, $1 - y$, $1 - z$]. These dimers are then linked by a C13—H13···$Cg4^{i}$ interaction and the equivalent interaction via the centre at $(\frac{1}{2},\frac{1}{2},0)$, so forming chains of dimers running parallel to [001] [symmetry code: (i) x, y, $-1 + z$]. These C—H···π and π–π interactions link the molecules into two-dimensional sheets lying parallel to (110) (Fig. 3). In (II), the equivalent ring to ring 3 is involved in a C—H···π interaction. In this case, the atom equivalent to H42 is involved in an interaction with the ring in the molecule at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, with an H···$Cg$ distance of 2.85 Å, a C···Cg distance of 3.735 (5) Å and an angle at H of 160°.

Experimental

An ethanol solution containing equimolar quantities of 5-(3-phenyl-2-propenylidene)-2,2-dimethyl-[1,3]dioxane-4,6-dione and 5-amino-3-methyl-1-phenylpyrazole in ethanol was heated under reflux for

2 h. The solvent was then removed under vacuum and the resulting crude solid was purified by silica-gel column chromatography using hexane/ethyl acetate (1:1 v/v) as eluant, yielding (I) (55%, m.p. 408 K). Analysis, found: C 79.9, H 5.2, N 14.7%; $C_{19}H_{15}N_3$ requires: C 80.0, H 5.3, N 14.7%. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from a chloroform solution.

Crystal data

$C_{19}H_{15}N_3$
$M_r = 285.34$
Triclinic, $P\bar{1}$
$a = 8.1392 (4)$ Å
$b = 8.4351 (4)$ Å
$c = 11.3852 (6)$ Å
$\alpha = 77.951 (3)°$
$\beta = 81.192 (2)°$
$\gamma = 70.681 (2)°$
$V = 718.39 (6)$ Å^3

$Z = 2$
$D_x = 1.319$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3135 reflections
$\theta = 3.1–27.4°$
$\mu = 0.08$ mm^{-1}
$T = 120 (1)$ K
Block, yellow
$0.20 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.944$, $T_{max} = 0.994$
9243 measured reflections
3135 independent reflections

1682 reflections with $I > 2\sigma(I)$
$R_{int} = 0.092$
$\theta_{max} = 27.4°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.123$
$S = 0.94$
3135 reflections
200 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected torsion angles (°).

C7a—N1—C11—C12	135.2 (2)	C5—C4—C41—C46	−66.5 (3)
N2—N1—C11—C12	−39.0 (3)	C3a—C4—C41—C46	111.6 (2)
C7a—N1—C11—C16	−45.1 (3)	C5—C4—C41—C42	112.8 (2)
N2—N1—C11—C16	140.78 (18)	C3a—C4—C41—C42	−69.1 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

$Cg3$ and $Cg4$ are the centroids of the C11–C16 and C41–C46 rings, respectively.

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
C13—H13$\cdots$$Cg4^i$	0.95	2.74	3.543 (3)	142
C43—H43$\cdots$$Cg3^{ii}$	0.95	2.79	3.579 (3)	142

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

Compound (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H distances of 0.95 (aromatic) and 0.98 Å (methyl).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and WordPerfect macro *PRPKAPPA* (Ferguson, 1999).

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