

5,5-Dimethyl-3-(5-methyl-1*H*-pyrazol-3-ylamino)cyclohex-3-en-1-one

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The molecules of the title compound, C₁₂H₁₇N₃O, are linked by two N—H···O hydrogen bonds to form a three-dimensional network. The N···O distances are 2.804 (3) and 2.766 (3) Å, both involving a common acceptor O atom.

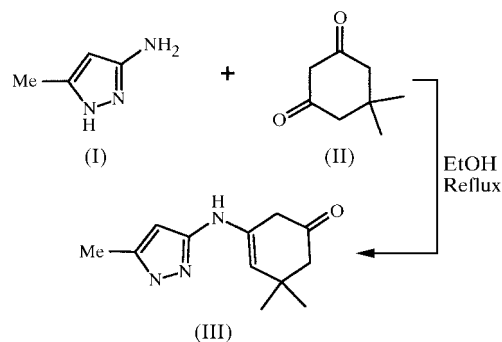
Comment

Recently, we reported the structures of several pyrazolo[3,4-*b*]pyridines prepared from 3-aminopyrazoles and substituted cyanochalcones (Quiroga *et al.*, 1999). Continuing the study of the reactions of 3-aminopyrazoles as intermediates in the preparation of fused pyrazole heterocycles, we have carried out reactions between these compounds and 1,3-diketones. Pyrazolo[3,4-*c*]pyridines have been prepared from arylidene-aminopyrazoles and 1,3-dicarbonyl derivatives such as dimedone. The title compound, (III), results from the reaction of 3-amino-5-methylpyrazole, (I), with dimedone, (II), as shown in the scheme below. 3-*N*-Substituted diaminopyrazole derivatives have been reported to be a target for neuropeptide Y antagonists (Fumaki, Fukuroda, Kanatani & Ihara, 1996*a*) and hence are used in the treatment of bulimia, obesity and diabetes (Fumaki, Fukuroda, Kanatani & Ihara, 1996*b*) or as an anticonvulsant (Lankau *et al.*, 1999).

The pyrazole ring in (III) is strictly planar with the atoms attached directly to it and shows high aromaticity, although there is a slight suggestion of double-bond character, as shown in the scheme below. This arises because, due to the presence of the N6—H fragment attached to C4, there is no delocalization of the lone pair on N6 towards the pyrazole ring; C4—N6 [1.400 (3) Å] is clearly a single bond.

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The cyclohexenone ring is disordered, with atoms C10, C11, C12 and C14 occupying two alternate components. The major component has an occupancy of 0.760 (5) and the minor component an occupancy of 0.240 (5). In the following description, the minor atom names are given in brackets. The two positions for C13 overlap each other. In both of these components, all atoms except C11 (C11') are nearly coplanar, the maximum and minimum deviations being 0.035 (2) Å for C8 [0.092 (5) Å for C9] and −0.033 (2) Å for C7 [−0.086 (3) Å for C8]. Atom C11 in the major component is 0.641 (7) Å below the plane of the other five atoms and in the minor component, 0.56 (2) Å above the plane of the other five atoms. This means that the molecule adopts each of the two possible sofa conformations involving C11 (C11'). The mean planes of these two disordered rings, consisting of the five ring atoms but omitting C11 (C11'), are inclined to one another at an angle of 17.7°.



Another structural feature is that the lone pair on N6 is delocalized to the α,β -unsaturated ketone showing amide vinylogous behaviour, as shown by the bond distances N6—C7 of 1.343 (3), C7—C8 of 1.372 (3), C8—C9 of 1.413 (3) and C9—O91 of 1.255 (3) Å, and the torsion angle N6—C7—C8—C9 of −178.8 (2)°. This π system, defined by the mean plane of N6, C7, C8, C9 and O91, is isolated from the pyrazole ring and both planes are inclined to one another at 28.61 (12)°. Selected bond lengths are given in Table 1.

The molecules are linked by two strong N—H···O hydrogen bonds, each involving O91 as an acceptor, to form a three-dimensional network of intersecting infinite chains. Atom O91 at $(2 - x, 1 - y, z - \frac{1}{2})$ acts as an acceptor for the

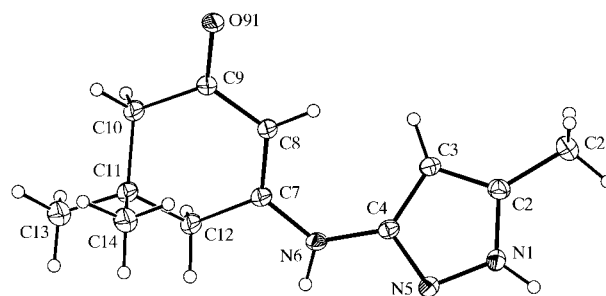


Figure 1

A view of the major component of (III) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

donor atom N1, with an $N \cdots O$ distance of 2.804 (3) Å. Atom O91 at $(\frac{3}{2} - x, \frac{1}{2} + y, z - \frac{1}{2})$ acts as an acceptor for atom N6, with an $N \cdots O$ distance of 2.766 (3) Å. The former gives rise to a primary $C(9)$ motif, which when translated by the screw axis at $(1, \frac{1}{2}, z)$ gives an infinite spiral chain (Fig. 2). The latter gives a $C(6)$ chain motif, producing an infinite chain running parallel to [011], produced by the action of the n -glide plane at $\frac{3}{4}$ along a . Full hydrogen-bond data are given in Table 2.

Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

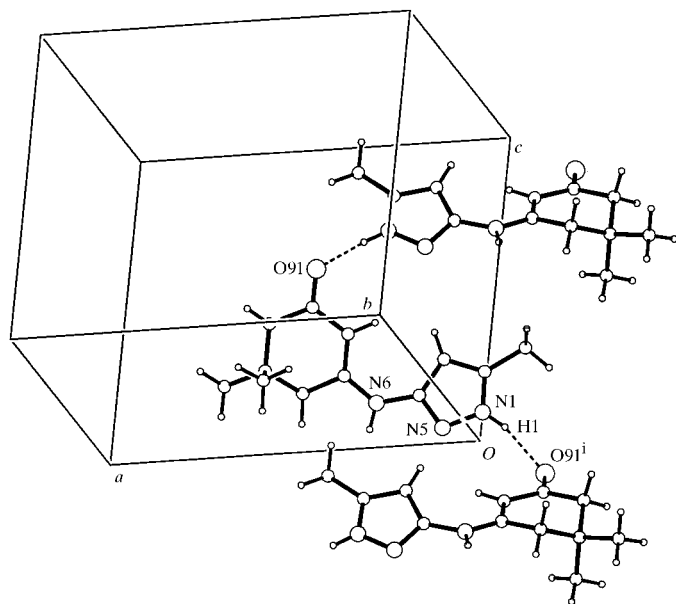


Figure 2

A view of the crystal structure of (III) showing the infinite spiral chain parallel to [001] arising from the $C(9)$ primary motif. Only the major component is shown [symmetry code: (i) $2 - x, 1 - y, z - \frac{1}{2}$].

Experimental

A solution of 3-amino-5-methylpyrazole, (I) (3.1 mmol), and dime-done, (II) (3.1 mmol), in ethanol (5 ml) was heated to reflux for 30 min. Cooling the solution to room temperature afforded yellow crystals of (III) which were filtered off, washed with fresh ethanol and dried. Crystals suitable for X-ray diffraction were obtained after recrystallization from ethanol (yield 75%, m.p. 516–518 K). Analysis calculated for $C_{12}H_{17}N_3O$: C 65.73, H 7.81, N 19.16%; found C 65.53, H 7.75, N 19.29%.

Crystal data

$C_{12}H_{17}N_3O$
 $M_r = 219.29$
 Orthorhombic, $Pna2_1$
 $a = 12.5130$ (3) Å
 $b = 9.4275$ (3) Å
 $c = 10.6441$ (3) Å
 $V = 1255.65$ (6) Å³
 $Z = 4$
 $D_x = 1.160$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 1515 reflections
 $\theta = 3.25$ – 27.39°
 $\mu = 0.076$ mm⁻¹
 $T = 150$ (2) K
 Plate, colourless
 $0.25 \times 0.15 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans with κ offsets
 Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
 $T_{\min} = 0.981$, $T_{\max} = 0.996$
 13 142 measured reflections
 1515 independent reflections

1360 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 27.39^\circ$
 $h = -16 \rightarrow 15$
 $k = -12 \rightarrow 12$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.122$
 $S = 1.053$
 1515 reflections
 148 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.3673P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C4—N6	1.400 (3)	C8—C9	1.413 (3)
N6—C7	1.343 (3)	C9—O91	1.255 (3)
C7—C8	1.372 (3)		
N6—C7—C8—C9	−178.8 (2)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots O91 ⁱ	0.88	1.95	2.804 (3)	162
N6—H6 \cdots O91 ⁱⁱ	0.88	1.90	2.766 (3)	168

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

H atoms were treated as riding, with $C-H = 0.93$ – 0.99 Å and $N-H = 0.88$ Å. Since no atom heavier than O was present in the structure, the absolute structure could not be determined and Friedel pairs were merged. The disordered atoms of the cyclohexenone ring were refined using the following restraints: all bonds involving C10, C11, C12, C13 and C14 of the major component, and C10', C11', C12', C13' and C14' of the minor component were given a *DFIX* restraint (*SHELXL97*; Sheldrick, 1997) with a target value of 1.54 (2) Å, and the C7—C12 and C7—C12' bonds were given a *DFIX* value of 1.52 (2) Å, these being the 'normal' bond lengths for the two types of C—C bond present, according to Ladd & Palmer (1994). These restraints were designed to bring the minor component bond lengths into line with those of the major component without putting too large a restraint on the major component bonds. The cyclohexenone ring atoms C10 (C10') to C12 (C12') were allowed to refine anisotropically but with their atomic displacement parameters constrained to be equal. A similar but separate constraint was applied to the methyl atoms attached to the cyclohexenone ring.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service at the University of Southampton. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1111). Services for accessing these data are described at the back of the journal.

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