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1-[(2*RS*,3*RS*)-4-Acetyl-2-hydroxy-3-(5-methoxy-4-methyl-3-phenylpyrazol-1-ylamino)-2,5-dimethyl-2,3-dihydrofuran-3-yl]ethanone

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Key indicators

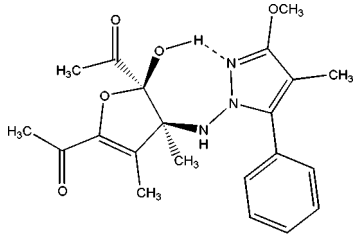
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.056
wR factor = 0.139
Data-to-parameter ratio = 13.1

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

The title compound, $C_{11}H_{23}N_3O_5$, contains a pyrazole ring and a dihydrofuran ring connected by an NH bridge. The pyrazole ring is planar, while the dihydrofuran ring adopts a twist conformation. The two rings are linked by an intramolecular O—H···N hydrogen bond. In the crystal structure, the intermolecular hydrogen-bond network forms chains parallel to the *b* axis.

Comment

Beside their synthetic utility, some 1-aminopyrazoles display interesting antidepressive, analgesic, antihistamine and spasmolitic actions (Adembri *et al.*, 1973; Jarrean & Koenig, 1981). Antifungal activity has been discovered for the 5-nitrofurfuryl derivative of *N*-aminopyrazole (Mester *et al.*, 1988). Structural features of the parent compound have recently been investigated both experimentally and computationally using *ab initio* methods (Jimenez *et al.*, 1999). The title product, (I), was obtained in quantitative yield and, to determine the relative configuration of the chiral centers, an X-ray diffraction analysis was carried out. As shown in the Scheme and in Fig. 1, an intramolecular hydrogen bond between the hydroxyl group, O1—H1, and atom N3 links the two rings and accounts for the stereoselectivity of the reaction.



(I)

The pyrazole ring is planar [maximum deviation from mean plane 0.010 (2) Å], and the bond lengths and angles do not differ significatly from those of similar compounds (Yamaguchi *et al.*, 1989). The mean plane of the pyrazole ring makes an angle of 40.0 (1)° with the phenyl ring bonded at C13 and is perpendicular to the C21—O5 bond of the methoxy group at C11 [torsion angle C21—O5—C11—C12 91.4 (4)°]. Atom N1 is pyramidal with the lone pair antiperiplanar with the N2—N3 bond [torsion angles N3—N2—N1—H1 −70.5 (3)° and N3—N2—N1—C2 58.5 (3)°]. This confirms a feature already observed for *N*-amino-pyrazole (Jimenez *et al.*, 1999) and some simple derivatives (Yamaguchi *et al.*, 1989).

The dihydrofuran ring (plane O1/C1/C2/C3/C4) adopts a twist conformation with puckering parameters (Cremer & Pople, 1975) $\varphi = -129.8\ (9)^\circ$ and $Q = 0.175\ (3)$ Å, and asym-

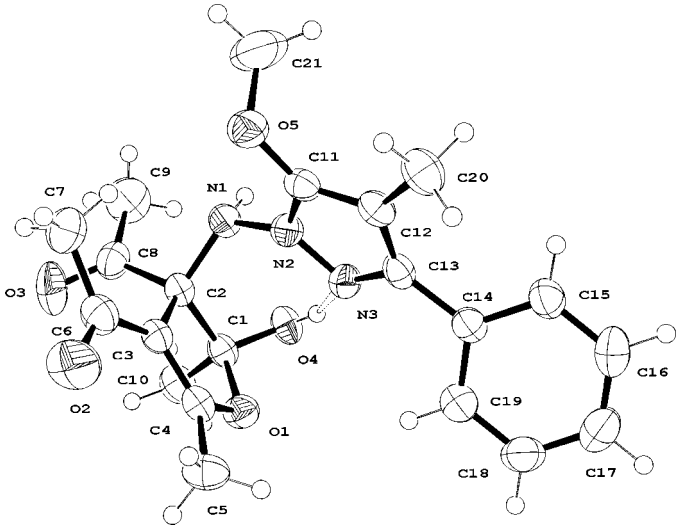


Figure 1
View of (I) with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

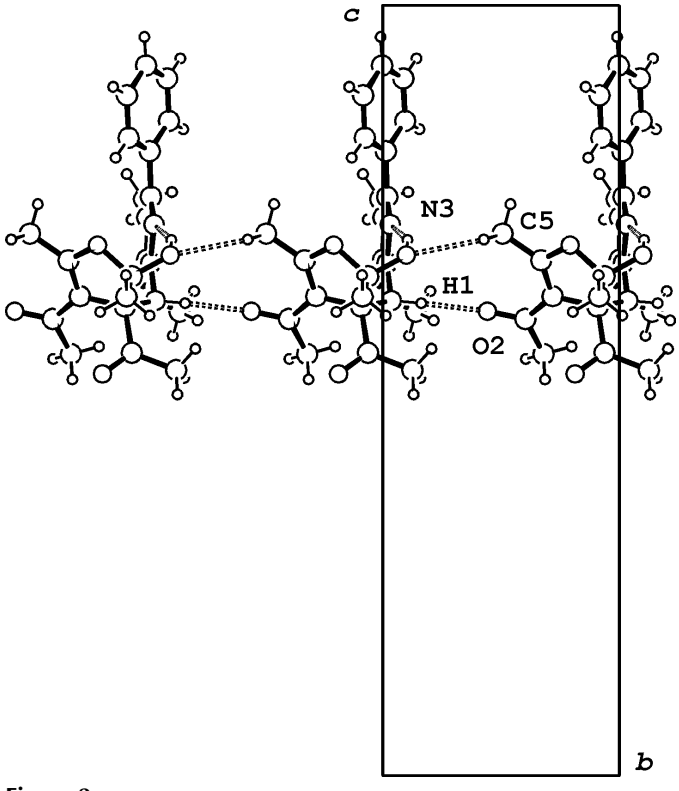


Figure 2
(100) projection of molecules linked by hydrogen bonds. Symmetry-related chains have been omitted for clarity.

metry parameter (Nardelli, 1983) Δ_2(C4) = 0.007 (1). The plane of the acetyl group (C3/C6/O2/C7) makes an angle of 14.7 (1)° with the plane of the furan ring.

The most significant intermolecular interaction is a hydrogen bond occurring between atoms H1 and O4 of the molecule translated by a unit cell along the *b* axis. Hence, the crystal structure is characterized as chains of parallel molecules. These chains appear to be further linked by a non-conventional hydrogen bond between atom O4 and the C5 methyl group (Table 2). This hydrogen-bond network is depicted in Fig. 2.

Experimental

3,4-Diacetylhex-3-ene-2,5-dione (0.196 g, 1 mmol; Adembri *et al.*, 1997) and 5-methoxy-4-methyl-3-phenylpyrazol-1-ylamine (0,203 g, 1 mol; Adembri *et al.*, 1972) were dissolved in dichloromethane (10 ml) and left at room temperature for 24 h. The solid, obtained in quantitative yield, was filtered off and recrystallized from diethyl ether (m.p. 387 K).

Crystal data

$C_{21}H_{25}N_3O_5$
M_r = 399.44
Monoclinic, $P2_1/c$
a = 11.339 (3) Å
b = 7.444 (2) Å
c = 24.546 (4) Å
β = 97.61 (1)°
V = 2053.6 (8) Å^3
Z = 4
D_x = 1.292 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 35 reflections
θ = 4–38°
μ = 0.09 mm^{-1}
T = 293 (2) K
Block, colourless
0.4 × 0.2 × 0.2 mm

Data collection

Siemens $P4$ diffractometer
ω scans
4895 measured reflections
3612 independent reflections
1988 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25°
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 8$
$l = -29 \rightarrow 29$
3 standard reflections
every 97 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.139
S = 1.01
3612 reflections
276 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.0883P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.011
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.345 (3)	N3—C13	1.334 (3)
O1—C1	1.469 (3)	C12—C11	1.373 (4)
O5—C11	1.349 (3)	C12—C13	1.415 (4)
N2—C11	1.349 (4)	C3—C4	1.357 (4)
N2—N3	1.355 (3)	C3—C2	1.508 (4)
N2—N1	1.400 (3)	C1—C2	1.599 (4)
N1—C2	1.484 (4)		
C4—O1—C1	108.9 (2)	N3—C13—C12	111.7 (2)
N3—N2—N1	122.2 (2)	N2—C11—C12	107.9 (3)
N2—N1—C2	116.0 (2)	O1—C1—C2	103.4 (2)
C13—N3—N2	104.8 (2)	C3—C2—C1	101.5 (2)
C4—C3—C2	108.1 (3)		
N3—N2—N1—C2	58.5 (3)	N2—N1—C2—C1	−69.5 (3)
C21—O5—C11—N2	−92.7 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.98	2.17	3.056 (3)	150
O4—H4···N3	0.82	1.97	2.720 (3)	152
C5—H5*C*···O4^{ii}	0.96	2.52	3.293 (4)	138

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

The H atoms were introduced at calculated positions as riding atoms, with bond lengths of 0.82 (O—H), 0.98 (N—H), 0.93 (C—H aromatic) and 0.96 Å (CH_3). The O—H, N—H and aromatic C—H H-atom displacement parameters were refined. The displacement parameters for the methyl group H atoms were set equal to 1.2 times U_{eq} of the parent atoms.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1999).

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