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4-[(3-Hydroxy-5-phenyl-1*H*-pyrazol-4-yl)-methyl]-5-phenyl-1*H*-pyrazol-3(2*H*)-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.124
Data-to-parameter ratio = 12.5

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

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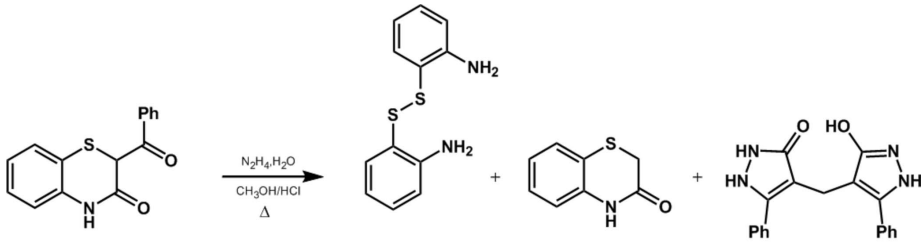
The solid-state structure of the title compound, $C_{19}H_{16}N_4O_2$, is dominated by the keto–enol tautomerization of its two 1*H*-pyrazol-3-one moieties. Since all H atoms could be located in a difference Fourier synthesis, it was possible to distinguish the enol form from the keto form unambiguously. As a result of this tautomerization, an intramolecular hydrogen bond embedded in an eight-membered ring is formed. The two-dimensional hydrogen-bonding system results from three additional intermolecular hydrogen bonds of different strengths, all involved in eight- and ten-membered ring systems.

Comment

From the literature, it is known that the reaction of diketones with hydrazine results in the formation of the corresponding pyrazole derivatives. In the present case, the condensation of 2-benzoyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine, (I), with an excess of hydrazine hydrate in boiling aqueous methanol containing hydrochloric acid gave 2,2′-dithiodianiline, (II), 3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine, (III), and 4-[(3-hydroxy-5-phenyl-1*H*-pyrazol-4-yl)methyl]-5-phenyl-1*H*-pyrazol-3(2*H*)-one, (IV) (see scheme). The title compound, (IV), has been isolated from the reaction mixture and characterized in solution by ^{1}H and ^{13}C NMR spectroscopy. Single crystals were grown from ethanol.



I II III IV

The solid state structure of (IV) (Fig. 1) is characterized by the capability of the –NH—CO– group of a 1*H*-pyrazol-3-one moiety to undergo a keto–enol tautomerization. The keto form is observed in moiety 1 (N11/N12/C13–C15) and the enol form in moiety 2 (N21/N22/C23–C25). This assignment has been confirmed from the location of all H atoms in a difference Fourier synthesis and from the C—O bond lengths. The C—O bond length of the keto group is significantly shorter [1.284 (2) Å] than that of the hydroxyl group [1.353 (3) Å], in accordance with the formulation of a double or single C—O bond, respectively. As a result of this tautomerization, an intramolecular hydrogen bond is formed (Table 2), which

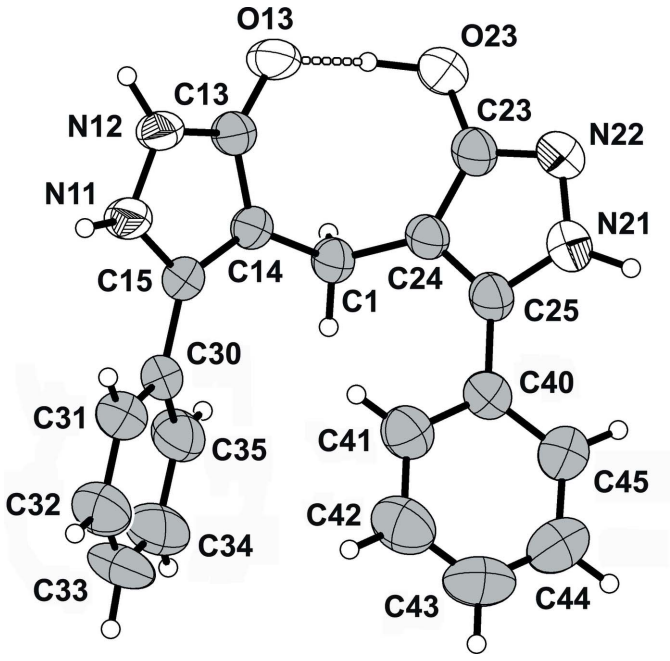


Figure 1
The molecular structure of compound (IV), with the numbering scheme used. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary size. The dotted line indicates the intramolecular hydrogen bond.

leads to the formation of an eight-membered ring system in which the two pyrazole groups are involved.

In the literature, there is only one further compound, 1,1-bis(3-methyl-3-pyrazolin-5-one-4-yl)-1-desoxy-D-galactose, which exhibits the same structural features (*i.e.* a keto–enol tautomerization and an intramolecular hydrogen bond within an eight-membered ring system). In this compound, similar variations of the C—O bond lengths were found [1.297 and 1.361 Å; Sadybakasov *et al.*, 1989].

Details of the intermolecular hydrogen-bonding scheme are listed in Table 2. In summary, there are three classical hydrogen bonds of different strengths, all involved in eight- and ten-membered intermolecular rings (Fig. 2), resulting in a double layer parallel to the $(\bar{1}01)$ plane. The strongest one is between the two 1*H*-pyrazol-3-one rings of two neighbouring molecules. A centrosymmetric nearly planar eight-membered ring results, with atom O13 being the acceptor and N12—H12 the donor function. The medium strength and weak hydrogen bonds are involved in non-centrosymmetric non-planar ten-membered rings, which are completed by the intramolecular hydrogen bond described above. A medium strength hydrogen bond exists between the N11—H11 group and atom N22 of two neighbouring molecules, and a weak one between the N21—H21 group of the second molecule and atom O23 of a third molecule (Table 2). In addition, there are two C—H···O interactions of this O atom with H atoms [H31($\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$), O···H = 2.412 Å and O···H—C = 155°; H45($-\frac{1}{2}+x,\frac{3}{2}-y,-\frac{1}{2}+z$), O···H = 2.573 Å and O···H—C = 156°] of two different phenyl rings.

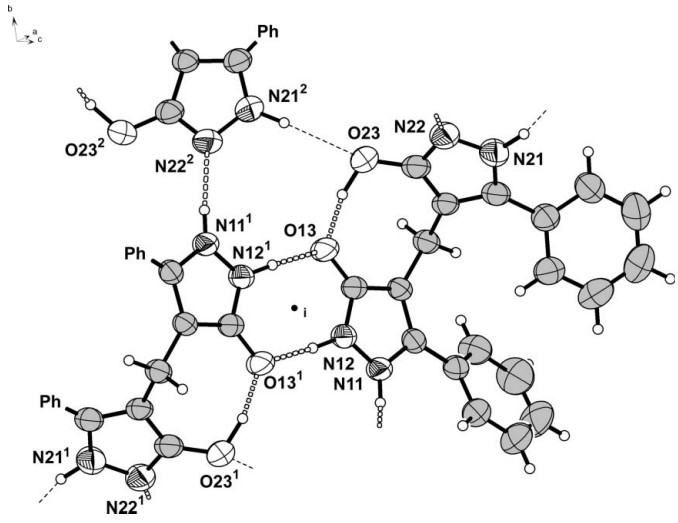


Figure 2
Part of the crystal structure of compound (IV), showing the main structural features of the hydrogen-bonding system. Dotted and dashed lines indicate hydrogen bonds. A crystallographic centre of symmetry is indicated. [Symmetry codes: (1) $1-x,-y,-z$; (2) $-\frac{1}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z$.]

Experimental

To a solution containing compound (I) (1 g, 3.7 mmol) and concentrated hydrochloric acid (0.5 ml) in methanol (50 ml), hydrazine hydrate (5 ml) was added dropwise. The mixture was heated under reflux for 24 h. After cooling, the solvent was evaporated *in vacuo*. A crystalline product was obtained, which on recrystallization from ethanol gave bright-yellow single crystals of the title compound, (IV) (yield 0.18 g, 15%; m.p. 499–501 K). IR (ATR, ν, cm^{-1}): 3427, 1615, 1589; ^{1}H NMR (300 MHz, d_6-DMSO, δ, p.p.m.): 3.47 (*s*, 2H, CH_2), 6.94–7.30 (*m*, 10H, H_{arom}); ^{13}C NMR (75 MHz, d_6-DMSO, δ, p.p.m.): 15.8, 101.9, 128.1, 128.6, 129.1, 131.1, 136.0, 142.6, 154.0, 162.5. The filtrate was concentrated under reduced pressure and the resulting residue was chromatographed on a silica-gel column (dichloromethane–diethyl ether), affording the compounds (II) and (III) in that order.

Crystal data

$C_{19}H_{16}N_4O_2$
M_r = 332.36
Monoclinic, $P2_1/n$
a = 9.2908 (10) Å
b = 16.4731 (15) Å
c = 11.0153 (13) Å
β = 106.903 (8)°
V = 1613.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
0.40 × 0.37 × 0.28 mm

Data collection

Bruker *P*4 diffractometer
Absorption correction: none
3662 measured reflections
2843 independent reflections
1855 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
3 standard reflections
every 97 reflections
intensity decay: 2.3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.124
S = 1.00
2843 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—C15	1.358 (3)	N21—C25	1.357 (3)
N11—N12	1.362 (2)	N21—N22	1.370 (2)
N12—C13	1.341 (3)	N22—C23	1.327 (3)
C13—O13	1.284 (2)	C23—O23	1.353 (3)
C13—C14	1.417 (3)	C23—C24	1.406 (3)
C14—C15	1.391 (3)	C24—C25	1.380 (3)
C15—N11—N12	108.44 (17)	C25—N21—N22	113.01 (18)
C13—N12—N11	109.63 (17)	C23—N22—N21	102.89 (18)
O13—C13—N12	122.20 (19)	O23—C23—N22	118.96 (19)
O13—C13—C14	130.2 (2)	O23—C23—C24	127.5 (2)
N12—C13—C14	107.60 (18)	N22—C23—C24	113.46 (19)
C15—C14—C13	105.98 (18)	C25—C24—C23	104.12 (19)
N11—C15—C14	108.30 (18)	N21—C25—C24	106.51 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···N22^{i}	0.93	1.99	2.911 (3)	172
N12—H12···O13^{ii}	0.93	1.77	2.689 (2)	172
N21—H21···O23^{iii}	0.93	2.58	3.329 (2)	139
O23—H23···O13	1.03	1.54	2.551 (2)	169

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

All H atoms were initially found in a difference Fourier synthesis. In order to maximize the data:parameter ratio, H atoms bonded to carbon and nitrogen were placed in geometrically idealized positions, with C—H = 0.93–0.98 Å and N—H = 0.93 Å, and constrained to ride on their parent atoms, with U_{iso}(H) refined freely. The H atom of the OH group was also constrained, using the position found in a difference Fourier synthesis.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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