Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

4-Acetyl-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one hydrate

Karsten Gloe *et al.*

Electronic paper
This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4-Acetyl-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one hydrate

Karsten Gloe, Bieluonwu A. Uzoukwu and Otto Rademacher*

Institut für Anorganische Chemie, Technische Universität Dresden, D-01062 Dresden, Germany
Correspondence e-mail: otto.rademacher@chemie.tu-dresden.de

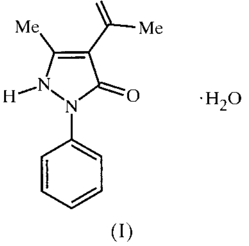
Received 2 October 2000
Accepted 23 October 2000

Data validation number: IUC0000305

The title compound, $C_{12}H_{12}O_2N_2\cdot H_2O$, is described. Although the keto–enol form of the ligand in solution is known, the compound crystallized in the orthorhombic space group $P2_12_12_1$ with only the monohydrated 1,3-diketo form. The intermolecular hydrogen bond between the imino N—H group of the ligand and O atom of the water molecule recorded an H···O distance of 1.73 (3) Å.

Comment

4-Acetyl-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one hydrate, (I), has been of versatile application in the extraction of transition metal ions from aqueous media (Bukowsky *et al.*, 1992; Uzoukwu *et al.*, 1998). The nature of the ligand in solution and its mode of interaction with metal ions have been studied mainly by spectroscopic methods (Okafor, 1984; Uzoukwu, 1995) because crystals of the ligand that are suitable for X-ray diffraction studies have been very difficult to obtain. Hence, X-ray diffraction studies of its complexes with metal ions have appeared in the literature (Pettinari *et al.*, 1994, 1998) with no X-ray diffraction report on the elusive structure of the ligand. No reference of a demonstrated method of obtaining good crystal form of (I) is apparently available. We report here the X-ray data of (I) and also a method for getting good crystals of the ligand.



(I)

Some selected bond length and angles of (I) are given in Table 1. The compound crystallized with a structural configuration in which the phenyl ring is twisted with a dihedral angle of 37.82 (6)° with respect to a plane defined by the pyrazole ring. The pyrazole ring and the O1/C4/C3/C11/O2 plane are nearly coplanar [dihedral angle 3.18 (14)°]. The C4=O1 carbonyl group usually participates in intraligand hydrogen bonding within the chelate ring of the keto–enol tautomer. In (I), it has a bond distance of 1.257 (3) Å that is much shorter than 1.319 (5) and 1.323 (3) Å reported for C—O single bond of the corresponding carbonyl groups in the 4-butanoyl (Uzoukwu *et al.*, 1993) and 4-benzyol derivatives (Akama *et al.*, 1995), respectively. This shows the double bond nature of the C4=O1 bond. The other carbonyl group, C11=O2, with a bond distance of 1.216 (3) Å is also shorter than the 1.256 (6) and 1.247 (3) Å reported for the corresponding carbonyl groups in the 4-butanoyl (Uzoukwu *et al.*, 1993) and 4-benzyol derivatives, and it has an approximate 180° orientation from the position of these carbonyl groups as well. The reduction in the bond distances of both carbonyl groups has been associated with the strain around the C11—C3—C2 and C11—C3—C4 carbon skeletons as a result of the close to 180° twist of the acyl group along the C3—C11 bond axis during the formation of the diketo tautomer. This may account for the longer N2—C4 bond distance of 1.375 (3) Å when compared with 1.348 (3) Å reported for a similar bond. There is an imino–water N—H···O intermolecular hydrogen bonding between the NH group of the ligand and water molecule, with an O3···H1 distance of 1.73 (3) Å. This intermolecular hydrogen bond is probably the most important bond formation that stabilized the crystallization of the compound as a 1,3-diketone rather than as a 1,3-keto–enol.

The UV spectrum of the compound in chloroform exhibited two absorption bands at 250 nm and 286 nm assigned to intramolecular π to π^* transitions. The IR spectrum indicated a very strong asymmetric C=O stretching frequency at 1635 cm^{-1}. Vibrational frequency bands due to O—H group of the water molecule appeared at 3300 cm^{-1} as a broad band. Another broad band centred at 2500 cm^{-1} has been assigned to stretching frequency of the intermolecular N—H···O hydrogen bond. The ^{1}H NMR data, however, showed that in an organic solvent the ligand rearranges to the keto–enol form with C4—O1—H species, for which the singlet at 10.38 p.p.m. was assigned to the O—H proton.

Experimental

Compound (I) was synthesized and purified as reported elsewhere (Jensen, 1959). The diketo crystal was grown as follows. A warm ethanol solution of the ligand (1 g in 50 ml) was obtained. Warm water (200 ml) was poured into the ethanol solution and the white suspension was decanted. It was redissolved in 200 ml of warm water in a beaker with addition of drops of ethanol, covered with a dish and kept aside for one week for the crystals to grow.

e580 Karsten Gloe *et al.* • $C_{12}H_{12}N_2O_2\cdot H_2O$ *Acta Cryst.* (2000). C**56**, e580–e581

Crystal data

$C_{12}H_{12}N_2O_2\cdot H_2O$
$M_r = 234.25$
Orthorhombic, $P2_12_12_1$
$a = 7.419\ (4)$ Å
$b = 7.522\ (4)$ Å
$c = 21.814\ (8)$ Å
$V = 1217.2\ (10)$ Å^3
$Z = 4$
$D_x = 1.278$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 19.77$–$28.22°$
$\mu = 0.093$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
$1.00 \times 0.58 \times 0.58$ mm

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
2346 measured reflections
2130 independent reflections
1907 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 24.99°$

$h = -8 \rightarrow 8$
$k = -8 \rightarrow 0$
$l = -25 \rightarrow 0$
3 standard reflections
every 400 reflections
frequency: 120 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.103$
$S = 1.059$
1264 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.0872P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.016 (3)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.495 (3)	C4—N2	1.376 (3)
C2—N1	1.328 (3)	C5—N2	1.430 (3)
C2—C3	1.384 (3)	C11—O2	1.217 (3)
C3—C4	1.431 (3)	C11—C12	1.489 (4)
C3—C11	1.458 (3)	N1—N2	1.381 (3)
C4—O1	1.256 (3)		
N1—C2—C3	109.3 (2)	O2—C11—C3	120.6 (3)
N1—C2—C1	119.7 (2)	O2—C11—C12	120.0 (3)
C3—C2—C1	131.1 (2)	C3—C11—C12	119.3 (2)
O1—C4—N2	122.8 (2)	C4—N2—N1	108.86 (17)
O1—C4—C3	131.4 (2)	C4—N2—C5	129.56 (18)
N2—C4—C3	105.75 (19)	N1—N2—C5	120.94 (17)

Friedel pairs were merged because anomalous dispersion effects are negligible. The H atoms bonded to N and O were located in difference Fourier maps and refined freely isotropically [N—H = 0.97 (3) Å, and O—H = 0.82 (5) and 0.84 (4) Å], all other were included in the refinement in calculated positions (C—H = 0.93 and 0.96 Å), riding on their carrier atoms.

Data collection: *CAD*-4 *EXPRESS* (Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4/*PC* (Harms, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

The authors wish to thank Alexander von Humboldt–Stiftung for a Research Fellowship to BAU.

References

Akama, Y., Shiro, M., Ueda, T. & Kajitani, M. (1995). *Acta Cryst.* C**51**, 1310–1314.

Bukowsky, H., Uhlemann, E., Gloe, K. & Mühl, P. (1992). *Anal. Chim. Acta*, **257**, 105–109.

Harms, K. (1996). *XCAD*4/*PC*. University of Marburg, Germany.

Jensen, B. S. (1959). *Acta Chem. Scand.* **13**, 1668–1670.

Nonius (1992). *CAD*-4 *EXPRESS*. Nonius BV, Delft, The Netherlands.

Okafor, E. C. (1984). *Spectrochim. Acta Ser. A*, **40**, 397–402.

Pettinari, C., Accorroni, F., Cingolani, A., Marchetti, F., Cassetta, A. & Barba, L. (1998). *J. Organomet. Chem.* **566**, 187–201.

Pettinari, C., Marchetti, F., Cingolani, A., Mariciante, C., Spagna, R. & Colapietro, M. (1994). *Polyhedron*, **13**, 939–950.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Uzoukwu, B. A (1995). *Spectrochim. Acta Ser. A*, **51**, 1081–1082.

Uzoukwu, B. A., Al-Juaid, S. S., Hitchcock, P. B. & Smith, J. D. (1993). *Polyhedron*, **12**, 2719–2724.

Uzoukwu, B. A., Gloe, K. & Duddeck, H. (1998). *Solvent Extraction and Ion Exchange*, **16**, 751–774.