Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

3-Hydroxy-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole

Hong-Jun Zhu,* Dan-Dan Wang and Ji Ma

Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China

Correspondence e-mail: zhuhj@njut.edu.cn

Received 28 September 2004
Accepted 21 October 2004
Online 30 October 2004

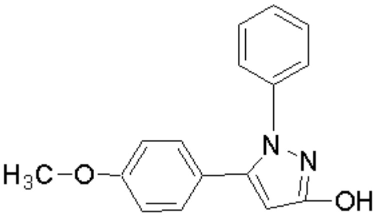
In the title compound, $C_{16}H_{14}N_2O_2$, the two crystallographically independent molecules in the asymmetric unit have different orientations of the phenyl and methoxyphenyl substituents with respect to the pyrazole ring. Both independent molecules exist as O—H···N hydrogen-bonded dimers, which are interlinked *via* C—H···N hydrogen bonds to form one-dimensional double-stranded chains. A three-dimensional network is formed *via* C—H···π interactions.

Key indicators
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.004 Å
R factor = 0.053
wR factor = 0.138
Data-to-parameter ratio = 14.7

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

Comment

The structure of pyrazole molecules, containing the fragment ═N—N(H)—, is favourable for the formation of various hydrogen-bonded complexes and assemblies in solid-state cyclic dimers, trimers, tetramers, linear chains and helical chains, depending on the substituents (Claramunt *et al.*, 1997; Elguero *et al.*, 1994; Llamas-Saiz *et al.*, 1994). The variety of association forms, and of structural and spectroscopic properties, allows the study of the effects of substitution on the geometry and thermodynamic characteristics of complexes and assemblies, the effects of the mutual influence of several conjugated hydrogen bonds, the splitting of and appearance of complex structure in ν(NH) bands in the IR spectra, chemical shifts and spin–spin interaction in the NMR spectra, and the effects of H/D substitution. The existence of cyclic assemblies gives the unique possibility of measuring the kinetic characteristics of degenerate H-atom transfer in rings of different dimensions and separating the contribution of the H-atom tunnelling effect. Helical assemblies, because of their special chiral geometric features and their occurrence in biological species, have also received increasing attention (Nozaki *et al.*, 1998; Gier *et al.*, 1998; Mamula *et al.*, 1998). Based on the above considerations, we synthesized the title compound, (I), and now report its crystal structure.



(I)

The asymmetric unit of (I) consists of two independent molecules, which have different orientations of the phenyl and methoxyphenyl substituents with respect to the pyrazole ring (Fig. 1). The bond lengths in the pyrazole ring show partial

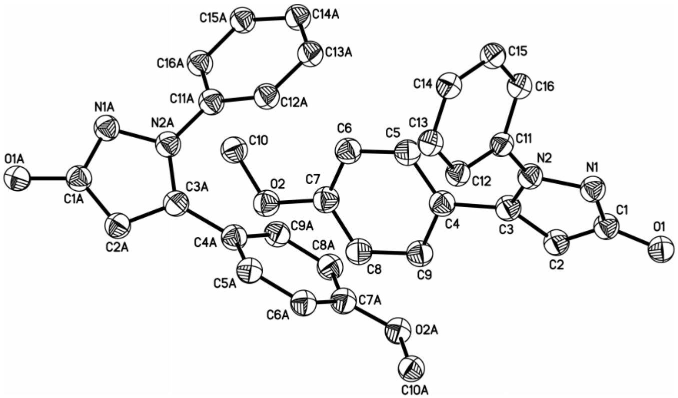


Figure 1
The structures of the two independent molecules of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

aromatic character, which suggests a delocalized π-electron system throughout the ring. It is likely that the two substituent groups at the 1- and 5-positions of the pyrazole ring influence the aromaticity of that ring. The presence of a phenyl ring at the 1-position results in a lengthening of the N—N bonds. The N—C distances [1.328 and 1.385 (3) Å] deviate significantly from the mean value of N—C distances in pyrazole rings [1.357 (12) Å; Infants *et al.*, 1998; Jimenez-Cruz *et al.*, 2003; Quiroga-Puello *et al.*, 1997]. The phenyl and methoxyphenyl rings of the two molecules are oriented at angles of 60.5 (1) and 40.1 (1)°, and 29.7 (1) and 46.4 (1)°, respectively, to the pyrazole ring. The dihedral angles between the phenyl and methoxyphenyl rings are 66.4 (1) and 51.3 (1)°.

Both crystallographically independent molecules exist as O—H···N hydrogen-bonded dimers (Table 2). These crystallographically independent dimers are interlinked *via* C—H···N hydrogen bonds to form one-dimensional double-stranded chain structures (Fig. 2); C—H···π interactions interlink the chains into a three-dimensional network.

Experimental

5-(4-Methoxyphenyl)-1-phenylpyrazolidin-3-one, (II), was first prepared and recrystallized from ethyl acetate, according to the method of Masahiko & Kazuyoshi (1999). Analysis calculated for $C_{16}H_{16}N_2O_2$: C 71.61, N 10.44, H 6.02%; found: C 71.37, N 10.35, H 5.72%; IR (KBr, ν, cm^{-1}): 3300, 3045, 2902, 2835, 1691, 1595, 1511, 1491, 1245; ^{1}H NMR (CDCl$_3$, δ, p.p.m.): 2.5 (*q*, 1H, CH$_2$CO), 3.3 (*q*, 1H, CH$_2$CO), 3.8 (*s*, 3H, CH$_3$O), 4.9 (*s*, 1H, CH—N), 6.9–7.4 (*m*, 9H, aromatic), 7.9 (*s*, 1H, NHCO). To prepare (I), compound (II) (4.0 g, 15 mmol) was dissolved in dimethylformamide (100 ml) and mixed with FeCl$_3$ (0.3 g, 1.5 mmol). The mixture was heated to 353 K and maintained at that temperature for 1 h, and then stirred for 12 h without heating. The reaction mixture was then poured into water (500 ml). The precipitate which formed was filtered off, washed with water and dried under reduced pressure. The crude product was then crystallized from ethanol–water (1:1.5) to give (I) (yield 2.5 g, 9.5 mmol). Crystals of (I) suitable for diffraction measurements were grown by slow evaporation of a solution in C_2H_5OH at room temperature. Analysis calculated for $C_{16}H_{14}N_2O_2$: C 72.17, H 5.30, N 10.52%; found: C 72.03, H 5.32, N 10.64%; IR (KBr, ν, cm^{-1}): 3433, 3005, 2843, 1612, 1579, 1599, 1526, 1321, 1247, 1179, 1033, 834,767; ^{1}H NMR (acetone-d_6, δ, p.p.m.): 3.8 (*s*, 3H, OCH$_3$), 5.8 (*d*, 1H, CH,), 6.8–7.4 (*m*, 9H, aromatic), 10.2 (*s*, 1H, OH).

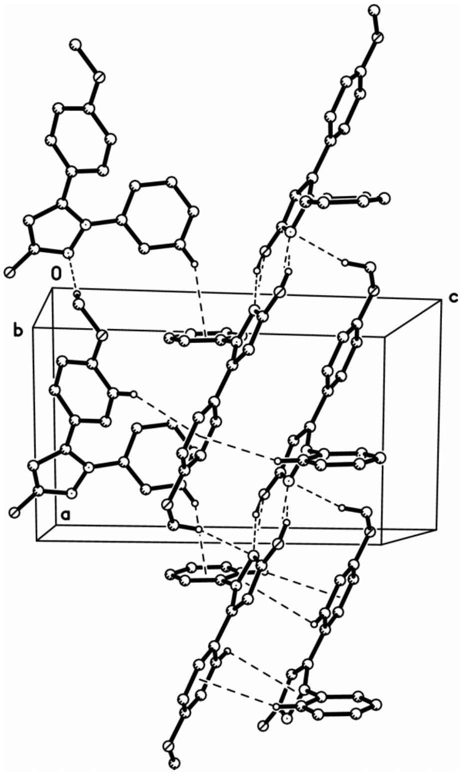


Figure 2
The crystal packing of (I). Dashed lines indicate hydrogen bonds. H atoms not involved in the hydrogen bonding have been omitted for clarity.

Crystal data

$C_{16}H_{14}N_2O_2$
$M_r = 266.29$
Triclinic, $P\bar{1}$
$a = 9.4266$ (19) Å
$b = 9.938$ (2) Å
$c = 15.347$ (3) Å
$\alpha = 88.90$ (3)°
$\beta = 86.63$ (3)°
$\gamma = 70.37$ (3)°
$V = 1351.9$ (5) Å^3
$Z = 4$
$D_x = 1.308$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.0$–24.1°
$\mu = 0.09$ mm^{-1}
$T = 291$ (2) K
Block, white
0.20 × 0.18 × 0.18 mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL*; Bruker, 2000)
$T_{\min} = 0.97$, $T_{\max} = 0.98$
5322 measured reflections
5322 independent reflections
3789 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 26.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.138$
$S = 1.01$
5322 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.44P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.307 (3)	N2—C3	1.328 (3)
O2—C10	1.368 (3)	C1—C2	1.384 (4)
O2—C7	1.410 (3)	C2—C3	1.423 (3)
N1—N2	1.411 (3)		
C10—O2—C7	116.6 (2)	O1—C1—C2	123.6 (2)
C1—N1—N2	103.7 (2)	C1—C2—C3	102.9 (2)
C3—N2—N1	110.4 (2)		

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

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 denote the centroids of rings N1/N2/C1–C3, N1*A*/N2*A*/C1*A*–C3*A*, C4–C9 and C11–C16, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1^{i}	0.82	1.91	2.718 (3)	169
O1*A*—H1*A*···N1*A*^{ii}	0.82	1.89	2.707 (3)	174
C10—H10*C*···N1^{iii}	0.96	2.57	3.461 (4)	154
C10*A*—H10*F*···N1*A*^{iv}	0.96	2.61	3.551 (3)	166
C5—H5···*Cg*1^{v}	0.93	3.07	3.495 (3)	110
C5*A*—H5*A*···*Cg*2^{vi}	0.93	2.97	3.434 (3)	113
C8*A*—H8*A*···*Cg*3	0.93	2.91	3.682 (3)	142
C10—H10*C*···*Cg*1^{vii}	0.96	2.76	3.553 (3)	141
C10*A*—H10*F*···*Cg*2^{iv}	0.96	2.85	3.646 (3)	141
C15*A*—H15*A*···*Cg*4^{iii}	0.93	2.81	3.660 (3)	152

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $2-x, 2-y, -z$; (iii) $1+x, y, z$; (iv) $x-1, y, z$; (v) $1-x, 1-y, 1-z$; (vi) $1-x, 2-y, -z$; (vii) $1+x, 1+y, z$.

All H atoms were placed in calculated positions, with O—H = 0.82 Å and C—H = 0.93–0.97 Å, and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(O)$ for the hydroxyl H atoms and $1.2U_{eq}(C)$ for the remaining H atoms.

Data collection: *XSCANS* (Bruker, 2000); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank the Centre of Test and Analysis, Zhengzhou University, for support.

References

Bruker (2000). *XSCANS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Claramunt, R. M., Sanz, D., López, C., Jiménez, J. A. (1997). *Magn. Res. Chem.* **35**, 35–75.

Elguero, J., Cano, F. H., Foces-Foces, C., Llamas-Saiz, A. L., Limbach, H. H., Aguilar-Parrilla, F., Claramunt, R. M. & López, C. (1994). *J. Heterocycl. Chem.* **31**, 695–700.

Gier, T. E., Bu, X., Feng, P. & Stucky, G. D. (1998). *Nature* (*London*), **395**, 154–157.

Infants, L., Foces-Foces, C., Claramunt, R. M., Lopez C. & Elguero, J. (1998). *J. Mol. Struct.* **447**, 71–79.

Jimenez-Cruz, F., Hernandez-Ortega, S. & Rios-Olivares, H. (2003). *J. Mol. Struct.* **650**, 223–231.

Llamas-Saiz, A. L., Foces-Foces, C. & Elguero, J. (1994). *J. Mol. Struct.* **319**, 231–260.

Mamula, O., Zelewsky, A. V., Bernardinelli, G. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 289–293.

Masahiko, T. & Kazuyoshi, Y. (1999). Jpn Pat. 11 060 559.

Nozaki, K., Terakawa, T., Takaya, H. & Hiyama, T. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 131–133.

Quiroga-Puello, J., Insuasty Obando, B., Foces-Foces, C., Infantes, L., Claramunt, R. M., Cabildo, P., Jimínez, J. A. & Elguero, J. (1997). *Tetrahedron*, **53**, 10783–10802.