

Ismail Yıldırım,^a Namık
Özdemir,^{b*} Yunus Akçamur,^a
Muharrem Dinçer^b and
Ömer Andaç^c^aErciyes University, Arts and Sciences Faculty,
Department of Chemistry, 38039 Kayseri,
Turkey, ^bOndokuz Mayıs University, Arts and
Sciences Faculty, Department of Physics, 55139
Samsun, Turkey, and ^cOndokuz Mayıs
University, Arts and Sciences Faculty,
Department of Chemistry, 55139 Samsun,
Turkey

Correspondence e-mail: namiko@omu.edu.tr

Key indicators

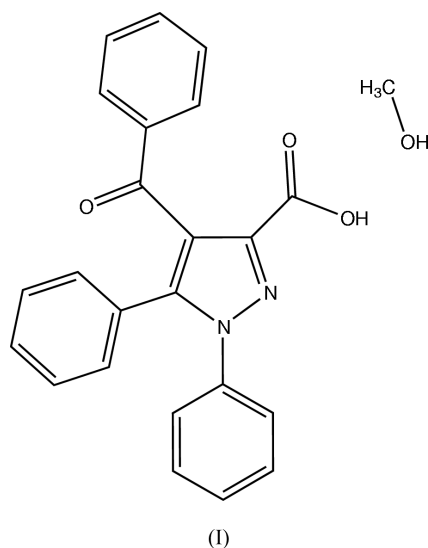
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Disorder in main residue
 R factor = 0.043
 wR factor = 0.079
Data-to-parameter ratio = 12.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4-Benzoyl-1,5-diphenyl-1*H*-pyrazole-3-
carboxylic acid methanol solvateIn the title compound, $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_3 \cdot \text{CH}_4\text{O}$, the N—N bond distance in the pyrazole ring, which is planar within 0.008 \AA , is $1.3634(18)\text{ \AA}$. The crystal packing is stabilized by O—H \cdots O, O—H \cdots N and C—H \cdots O intermolecular hydrogen bonds.

Received 20 December 2004

Accepted 24 December 2004

Online 8 January 2005

Comment

Derivatives of pyrazole continue to attract interest because of their wide spectrum of biological, medicinal (Badawey & El-Ashmawey, 1998) and agricultural (Thomson, 1997) activities. Some pyrazoles have been reported to possess significant antimicrobial (Mahajan *et al.*, 1991), antiviral (Baraldi *et al.*, 1998), antitumor (Hatheway *et al.*, 1978; Katayama & Oshiyama, 1997), antifungal (Chen & Li, 1998), pesticidal (Londershausen, 1996), anticonvulsant (Lepage & Hublot, 1992), antihistaminic (Mishra *et al.*, 1998) and antidepressant activities (Bailey *et al.*, 1985), as well as interesting properties in commercially important dyestuffs (Baroni & Kovyrzina, 1961; Neunhoeffer *et al.*, 1959). Recyclization reactions of 4-benzoyl-5-phenyl-2,3-dihydro-2,3-furandione with various phenylhydrazones and phenylhydrazine lead to pyrazole-carboxylic acid and pyridazinones (Akçamur *et al.*, 1986, 1997; Şener *et al.*, 2002, 2004; Verişen & Erturan, 1998). As part of our ongoing study of the relationship between the molecular and crystal structures of pyrazole derivatives, a crystal structure determination of the title compound, (I), has been undertaken and the results are presented here.Previously, we have reported closely related compounds, namely methyl 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylate, (II) (Dinçer, Özdemir, Yıldırım, Demir, Akçamur & Işık, 2004), and 4-benzoyl-*N*-methyl-1,5-diphenyl-1*H*-pyra-

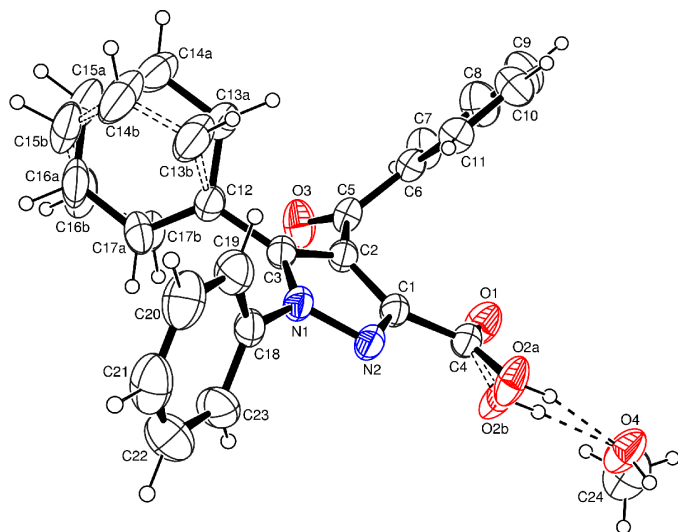


Figure 1

An ORTEP-3 (Farrugia, 1997) drawing of the title compound, (I), with the atomic numbering scheme; both disordered components are shown. Displacement ellipsoids of non-H atoms are drawn at the 30% probability level. The intermolecular O—H···O hydrogen bonds are represented by dashed lines.

zole-3-carboxamide, (III) (Dinçer, Özdemir, Yıldırım, Demir & Işık, 2004). The main aim of the present investigation is to study the differences between the structures of (I), (II) and (III), and to determine the type of hydrogen bonding.

The conformation of (I), together with the atom-numbering scheme, is shown in Fig. 1. In the structure, the phenyl ring at the 5-position and the O atom (O2) belonging to the carboxylic acid group show positional disorder and the refined site-occupancy factors of the disordered components (C13a—C17a and C13b—C17b, and O2a and O2b) are 0.51 (1) and 0.49 (1), respectively. The planes of the C13a—C17a and C13b—C17b parts seem to be rotated with respect to each other about the C12···C15 vector. The dihedral angle between these two planes, including atom C12, is 36.7 (8)°.

As expected, all five rings [A (N1/N2/C1—C3), B (C6—C11), C (C12—C17a), C' (C12—C17b) and D (C18—C23)] are essentially planar. The maximum deviations from the least-squares plane of the pyrazole ring is 0.008 (1) Å for atom N2. However, all fragments in the structure do not share a common plane. The dihedral angles between the mean planes of the rings are 71.45 (A/B), 65.67 (A/C), 77.90 (A/C'), 66.70 (A/D), 85.48 (B/C), 78.53 (B/C'), 43.37 (B/D), 67.59 (C/D) and 77.17° (C'/D). The Φ_{CN} torsion angle (C12—C3—N1—C18) is 4.0 (4)°, which shows that the conformation about the C3—N1 bond is (+)synperiplanar. The Φ_{CC} (C5—C2—C3—C12 and C4—C1—C2—C5) torsion angles are -4.3 (4) and -1.8 (4)°, respectively, showing that the conformations about the C2—C3 and C1—C2 bonds are (-)synperiplanar.

The N—N bond distance is 1.363 (2) Å. Comparison of the bond lengths and angles of the pyrazole rings in (I), (II) and (III) shows that there are no important differences in (I) with respect to the others. The crystal structure contains intermolecular hydrogen bonds (Table 2). As can be seen in Fig. 2, the methanol solvent molecule plays an active role in linking

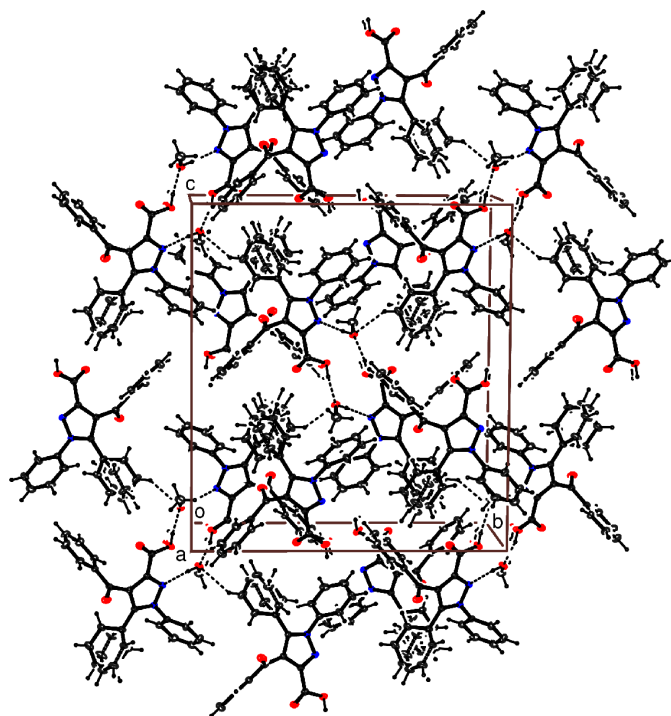


Figure 2

A projection of the crystal structure of (I) approximately along the *a* axis. Dashed lines show the intermolecular interactions.

the molecules. The hydrogen bonds between atoms O2 and O4, acting both as donors and acceptors, together with O—H···N hydrogen bonds form an *R*(14) ring. These interactions along with the C—H···O interactions (Table 2) generate a two-dimensional network.

Experimental

4-Benzoyl-5-phenyl-2,3-dihydro-2,3-furandione (2 g, 7.15 mmol) (Ziegler *et al.*, 1967) and phenylhydrazine (0.81 g, 7.16 mmol), as described by Akçamur *et al.* (1986), were refluxed in boiling benzene (30 ml) for 1–1.5 h. The solvent was removed by evaporation and the oily residue was triturated with dry diethyl ether to give a crude solid, which was then recrystallized from methanol, yielding pure 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic acid, (I) (1.31 g, 49%; m.p. 468–470 K). Solvents were dried by refluxing with the appropriate drying agents and distilled before use. All other reagents were purchased from Merck, Fluka, Aldrich or the Acros Chemical Co., and used without further purification. Analysis calculated for C₂₃H₁₆N₂O₃: C 74.99, H 4.38, N 7.60%; found: C 75.20, H 4.50, N 7.47%.

Crystal data

C₂₃H₁₆N₂O₃·CH₄O
M_r = 400.42
 Orthorhombic, *Pcab*
a = 10.8731 (9) Å
b = 18.7861 (14) Å
c = 20.5836 (19) Å
V = 4204.5 (6) Å³
Z = 8
D_x = 1.265 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 8043 reflections
 θ = 2.0–24.5°
 μ = 0.09 mm⁻¹
T = 293 (2) K
 Prism, colorless
 0.50 × 0.33 × 0.21 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: integration
 (*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.965$, $T_{\max} = 0.984$
 27 164 measured reflections
 3914 independent reflections

1743 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.099$
 $\theta_{\text{max}} = 25.5^\circ$
 $h = -13 \rightarrow 13$
 $k = -22 \rightarrow 22$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.079$
 $S = 1.00$
 3914 reflections
 327 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0154P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.11 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{Å}^{-3}$

Table 1
 Selected geometric parameters (Å, °).

| | | | |
|---------------|-------------|--------------|-------------|
| O1—C4 | 1.186 (2) | N1—C18 | 1.449 (2) |
| O2a—C4 | 1.300 (6) | N2—C1 | 1.331 (2) |
| O2b—C4 | 1.308 (8) | C1—C2 | 1.398 (3) |
| O3—C5 | 1.218 (2) | C1—C4 | 1.502 (3) |
| O4—C24 | 1.385 (3) | C2—C3 | 1.388 (2) |
| N1—C3 | 1.346 (2) | C2—C5 | 1.475 (3) |
| N1—N2 | 1.3634 (18) | C3—C12 | 1.483 (3) |
| C3—N1—N2 | 112.36 (15) | N1—C3—C2 | 107.07 (17) |
| C3—N1—C18 | 130.22 (16) | N1—C3—C12 | 123.02 (17) |
| N2—N1—C18 | 117.33 (18) | C2—C3—C12 | 129.9 (2) |
| C1—N2—N1 | 103.84 (16) | O1—C4—O2a | 124.5 (4) |
| N2—C1—C2 | 112.77 (15) | O1—C4—O2b | 125.5 (5) |
| N2—C1—C4 | 119.16 (19) | O1—C4—C1 | 122.7 (2) |
| C2—C1—C4 | 127.9 (2) | O2a—C4—C1 | 112.3 (4) |
| C3—C2—C1 | 103.93 (18) | O2b—C4—C1 | 111.0 (5) |
| C3—C2—C5 | 126.19 (18) | O3—C5—C2 | 119.6 (2) |
| C1—C2—C5 | 129.81 (17) | O3—C5—C6 | 121.0 (2) |
| C4—C1—C2—C5 | −1.8 (4) | C5—C2—C3—C12 | −4.3 (4) |
| C18—N1—C3—C12 | 4.0 (4) | | |

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

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| O4—H4...N2 ⁱ | 0.82 | 1.99 | 2.804 (2) | 176 |
| O2b—H2b...O4 | 0.82 | 1.77 | 2.583 (10) | 171 |
| O2a—H2a...O4 | 0.82 | 1.77 | 2.576 (8) | 165 |
| C10—H10...O1 ⁱⁱ | 0.93 | 2.46 | 3.339 (3) | 158 |
| C14a—H14a...O4 ⁱⁱⁱ | 0.93 | 2.53 | 3.334 (6) | 145 |

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

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.82 Å for O-bound H atoms, 0.93 Å

for the benzene ring H atoms and 0.96 Å for the methyl group H atoms. The displacement parameters of the H atoms were constrained as $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ (1.5 U_{eq} for methyl atoms) of the carrier atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

This study was supported financially by the Research Center of Ondokuz Mayıs University and the Research Center of Erciyes University.

References

Akçamar, Y., Penn, G., Ziegler, E., Sterk, H., Kollenz, G., Peters, K., Peters, E.-M. & von Schnering, H. G. (1986). *Monatsh. Chem.* **117**, 231–245.
 Akçamar, Y., Şener, A., İpekoğlu, A. M. & Kollenz, G. (1997). *J. Heterocycl. Chem.* **34**, 221–224.
 Badawey, E. & El-Ashmawey, I. M. (1998). *Eur. J. Med. Chem.* **33**, 349–361.
 Bailley, D. M., Hansen, P. E., Hlavac, A. G., Baizman, E. R., Pearl, J., Defelice, A. F. & Feigenson, M. E. (1985). *J. Med. Chem.* **28**, 256–263.
 Baraldi, P. G., Manfredini, S., Romagnoli, R., Stevanato, L., Zaid, A. N. & Manservigi, R. (1998). *Nucleosides Nucleotides*, **17**, 2165–2171.
 Baroni, E. E. & Kovyrzina, K. A. (1961). *Zh. Obshch. Khim.* **31**, 1641–1645.
 Chen, H. S. & Li, Z. M. (1998). *Chem. J. Chin. Univ.* **19**, 572–576.
 Dinçer, M., Özdemir, N., Yıldırım, I., Demir, E., Akçamar, Y. & Işık, Ş. (2004). *Acta Cryst.* **E60**, o317–o319.
 Dinçer, M., Özdemir, N., Yıldırım, I., Demir, E. & Işık, Ş. (2004). *Acta Cryst.* **E60**, o946–o948.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Hatheway, G. J., Hansch, C., Kim, K. H., Milstein, S. R., Schimidt, C. L., Smith, R. N. & Quin, F. R. (1978). *J. Med. Chem.* **21**, 563–567.
 Katayama, H. & Oshiyama, T. (1997). *Can. J. Chem.* **75**, 913–919.
 Lepage, F. & Hublot, B. (1992). European Patent Application EP 459 887; *Chem. Abstr.* **116**, 128917.
 Londershausen, M. (1996). *Pestic. Sci.* **48**, 269–274.
 Mahajan, R. N., Havaladar, F. H. & Fernandes, P. S. (1991). *J. Indian Chem. Soc.* **68**, 245–249.
 Mishra, P. D., Wahidullah, S. & Kamat, S. Y. (1998). *Indian J. Chem. Sec. B*, **37**, 199.
 Neunhoeffer, O., Alsdorf, G. & Ulrich, H. (1959). *Chem. Ber.* **92**, 252–256.
 Şener, A., Akbaş, E. & Şener, M. K. (2004). *Turk. J. Chem.* **28**, 271–277.
 Şener, A., Kasımoğulları, R., Şener, M. K., Bildirici, I. & Akçamar, Y. (2002). *J. Heterocycl. Chem.* **39**, 869–875.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
 Thomson, W. T. (1997). *Agricultural Chemicals – Book II Herbicides*, 13th ed., pp. 268, 269–278. California, USA: Thomson Publications.
 Veriřen, M. & Erturan, S. (1998). *Turk. J. Chem.* **22**, 335–340.
 Ziegler, E., Eder, M., Beleggratis, C. & Prewedourakis, E. (1967). *Monatsh. Chem.* **98**, 2249–2251.