

**(5Z)-4-Amino-2-(4-hydroxyphenyl)-
1H-imidazol-5(2H)-one oxime 3-oxide**Xue-Qin Cao,^a Zhan-Xiong Li,^a Guo-Qiang Chen^{a*} and
De-Chun Zhang^b^aSchool of Materials Engineering, Suzhou University, Suzhou 215021, People's Republic of China, and ^bDepartment of Chemistry, Suzhou University, Suzhou 215123, People's Republic of China

Correspondence e-mail: chenguojiang@suda.edu.cn

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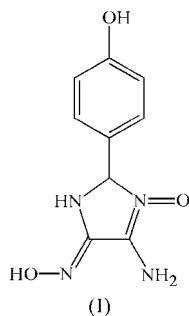
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The title molecule, C₉H₁₀N₄O₃, consists of benzene and imidazole rings which are almost perpendicular to each other. A hydroxyimino group is directly linked to the imidazole ring with a double C=N bond, which is the first example in this type of compound. The double bond may be a good location for the initiation of various reactions with a wide range of potential applications. In the crystal structure, there are π - π interactions between molecules related by a centre of symmetry, with the imidazole and benzene rings almost completely overlapped. The molecules are hydrogen bonded in each direction and form a three-dimensional hydrogen-bond network.

Comment

Having attempted to synthesize a new Schiff base by the reaction of 3,4-diaminoglyoxime and 4-hydroxybenzaldehyde, we unexpectedly obtained mainly the title compound, (I), and its molecular structure was finally confirmed by single-crystal structure determination after conventional IR, NMR, MS and elemental analyses.

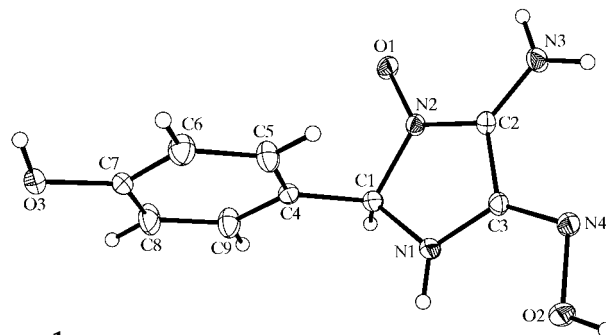


Compound (I) (Fig. 1) is a nitron (Popov *et al.*, 2004). It is well known that nitrones are typical examples of 1,3-dipoles easily participating in cycloaddition reaction with a wide variety of multiple-bond systems, to provide various heterocyclic five-membered ring systems (Coskun & Yilmaz, 2004). Besides their synthetic applications, nitrones have a wide

spectrum of biological activity (Voinov *et al.*, 2000). The cycloadducts of di- and triarylimidazoline 3-oxides with many dipolarophiles give bicyclic compounds with potentially interesting biological activity (Coskun *et al.*, 2006). The derivatives of 2,5-dihydro-1*H*-imidazole 3-oxide are magnetic (Roschupkina *et al.*, 2004). Furthermore, the oxidation of these compounds can yield stable nitroxyl radicals (Martin & Volodarskii, 1979). Nitroxyl radicals are normally used as spin carriers, due to their exceptional stability and ease of chemical modification (Li *et al.*, 2004). Nitroxide radical ligands based on the pyrazole ring are of great interest in understanding the role of the hydrogen bond as a pathway for magnetic exchange (Catala *et al.*, 2001). Molecule-based magnetic materials are becoming more and more interesting because the combination of metal ions and organic radicals has often been used to construct assembled systems (Oshio *et al.*, 2001). In the field of molecular magnetism, the synthesis and study of transition metal complexes incorporating organic free radicals is a major research aim (Kahn, 1993). Therefore, it is our belief that the novel structure of the title compound must bring about new findings in cycloaddition reactions and applications of nitrones. Work towards these aims is now in progress in our laboratory. We present here the results of our study of the molecular structure of (I) and a brief analysis of the molecular packing.

The molecule of (I) consists of a benzene ring and an imidazole ring. The dihedral angle between the two ring planes is 87.9 (1)°. While the two rings are almost perpendicular, atoms O1, N3 and N4 are almost coplanar with the imidazole ring (to within 0.03 Å). In addition, the N4-C3 bond length is 1.286 (2) Å and the four atoms N4, C3, C2 and N1 are nearly coplanar (the maximum deviation from the least-squares plane is 0.03 Å), which shows that the N-OH group is directly linked to the imidazole ring *via* a C=N double bond. In this respect, compound (I) is the first example in this family of compounds, confirmed by a search of the Cambridge Structural Database (*CONQUEST*, Version 1.8; Allen, 2002). The double bond may be a good location for the initiation of various reactions having wide-ranging potential applications.

In the title crystal, molecules are paired through π - π interactions (Desiraju, 1989). There are two noticeable cases

**Figure 1**

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

(Fig. 2) involving both the imidazole and benzene rings. For the reference molecule and its equivalent related by a centre of symmetry (symmetry code: $1 - x, -y, -z$), the distances between the imidazole rings and their centroids are 3.354 and 3.603 Å, respectively, which shows that the ring planes are almost completely overlapped. For the benzene–benzene interaction, involving the reference molecule and another related by a centre of symmetry (symmetry code: $-x, -y, 1 - z$), the corresponding values are 3.693 and 3.719 Å, respectively.

In the crystal structure, N–H...N, N–H...O and O–H...O hydrogen bonds (Table 3 and Fig. 2) link the molecules to form a three-dimensional network.

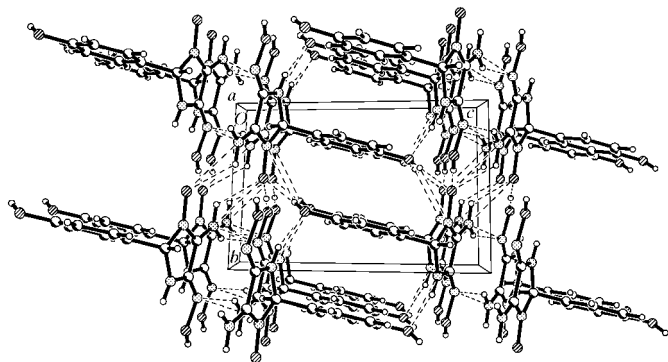


Figure 2
A packing diagram for (I), viewed down the *a* axis.

Experimental

4-Hydrobenzaldehyde (3 mmol) and *p*-toluenesulfonic acid (0.175 mmol) were added to a solution of 3,4-diaminoglyoxime (2.5 mmol) in anhydrous ethanol (30 ml) with stirring at 328 K. The resulting mixture was stirred for 2 h at this temperature, then filtered and washed twice with anhydrous ethanol (yield 0.4662 g, 84%; white solid). Colourless crystals of (I) suitable for single-crystal X-ray study were obtained by slow evaporation from dimethyl sulfoxide at room temperature after 10 d. Elemental analysis (EA1110 CHNO-S analyzer) calculated for $C_9H_{10}N_4O_3$: C 48.65, H 4.50, N 25.23%; found: C 48.16, H 4.68, N 24.73%. IR (FT-IR spectrometer with KBr pellets, ν , cm^{-1}): 3325 (*s*), 3176 (*s*), 3015 (*s*), 1710 (*s*), 1689 (*s*), 1610 (*m*), 1514 (*m*), 1473 (*m*), 1385 (*m*), 1223 (*s*), 933 (*m*). 1H NMR (UNITYNOVA400 NMR spectrometer, DMSO as solvent, ambient temperature): δ 1.06 (*s*, 1H), 5.57 (*s*, 1H), 5.64 (*s*, 1H), 6.28 (*s*, 2H), 6.75–7.39 (*m*, 4H), 10.19 (*s*, 1H).

Crystal data

$C_9H_{10}N_4O_3$	$\gamma = 66.596$ (11)°
$M_r = 222.21$	$V = 488.09$ (17) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.6739$ (11) Å	Mo $K\alpha$ radiation
$b = 7.5697$ (16) Å	$\mu = 0.12$ mm ⁻¹
$c = 10.899$ (2) Å	$T = 193$ (2) K
$\alpha = 85.036$ (18)°	$0.55 \times 0.18 \times 0.16$ mm
$\beta = 75.039$ (15)°	

Data collection

Rigaku Mercury diffractometer	4751 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	1768 independent reflections
$T_{min} = 0.927$, $T_{max} = 0.981$	1469 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	148 parameters
$wR(F^2) = 0.108$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.21$ e Å ⁻³
1768 reflections	$\Delta\rho_{min} = -0.21$ e Å ⁻³

Table 1

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>
N3–H3B...N4 ⁱ	0.88	2.17	2.944 (2)	146
N3–H3A...O1 ⁱⁱ	0.88	2.21	2.825 (2)	127
N1–H1A...O3 ⁱⁱⁱ	0.88	1.99	2.843 (2)	163
O3–H3...O1 ^{iv}	0.84	1.80	2.598 (2)	159
O2–H2...O1 ^v	0.84	1.88	2.6949 (19)	163

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

H atoms were positioned geometrically and treated as riding, with O–H = 0.84 Å, N–H = 0.88 Å and C–H = 0.95–1.00 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(O)$.

Data collection: *CrystalClear* (Rigaku/MSC, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3047). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Catala, L., Feher, R., Amabilino, D. B., Wurst, K. & Veciana, J. (2001). *Polyhedron*, **20**, 1563–1569.
- Coskun, N., Mert, H. & Arikan, N. (2006). *Tetrahedron*, **62**, 1351–1359.
- Coskun, N. & Yilmaz, B. (2004). *Synth. Commun.* **34**, 9, 1617–1623.
- Desiraju, G. R. (1989). *Crystal Engineering*, ch. 9, pp. 225–260. Oxford: Elsevier Science.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Jacobson, R. (1998). Private communication to Rigaku Corporation, Tokyo, Japan.
- Kahn, O. (1993). *Molecular Magnetism*. New York: VCH.
- Li, L., Liao, D. Z., Bai, L. J., Jiang, Z. H. & Yan, S. P. (2004). *J. Mol. Struct.* **569**, 179–183.
- Martin, V. V. & Volodarskii, L. B. (1979). *Khim. Geterotsykl. Soedin.* **1**, 103–109.
- Oshio, H., Yamamoto, M., Hoshino, N. & Ito, T. (2001). *Polyhedron*, **20**, 1621–1625.
- Popov, S. A., Andreev, R. V., Romanenko, G. V., Ovchaenko, V. I. & Reznikov, V. A. (2004). *J. Mol. Struct.* **697**, 49–60.
- Rigaku/MSC (1999). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.
- Rigaku/MSC (2003). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
- Roschupkina, G. I., Rybalova, T. V., Gatilov, Y. V. & Reznikov, V. A. (2004). *J. Struct. Chem.* **45**, 356–359.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1990). *XP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Voinov, M. A., Grigorev, I. A. & Volodarsky, L. B. (2000). *Tetrahedron*, **56**, 4071–4077.