organic compounds

2-(1H-Tetrazol-1-yl)benzoic acid

Alexander S. Lyakhov, Pavel N. Gaponik, Sergei V. Voitekhovich, Ludmila S. Ivashkevich,* Alexander A. Kulak and Oleg A. Ivashkevich

Institute of Physico-Chemical Problems, Belarusian State University, Leningradskaya Str. 14, Minsk 220050, Belarus
Correspondence e-mail: iva@fhp.bsu.unibel.by

In the title compound, $C_8H_6N_4O_2$, the tetrazole and benzene rings are planar to within 0.001 (1) and 0.007 (1) Å, respectively. These rings are not coplanar in the molecule, the dihedral angle between them being 52.90 (4)°. Molecules are connected together by O—H···N and C—H···O hydrogen bonds, forming two-dimensional networks parallel to the xz plane with van der Waals interactions between them.

Comment

This work is part of a systematic investigation of the molecular and crystal structures of 1-aryltetrazoles, which are of great interest in the field of theoretical and experimental chemistry. To date, the structures of the following 1-aryltetrazoles have been reported: 1-phenyltetrazole (Matsunaga *et al.*, 1999), 1-(2,4,6-trimethylphenyl)tetrazole (Lyakhov *et al.*, 2000) and 4-nitro-2-(1H-tetrazol-1-yl)phenol (Lyakhov *et al.*, 2001). In this paper, we present the crystal structure of 2-(1H-tetrazol-1-yl)benzoic acid, (I) (Fig. 1).

(I)
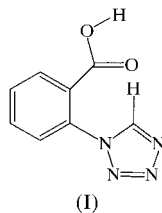
The tetrazole ring is planar to within 0.001 (1) Å. The endocyclic angles vary from 106.2 (1) to 109.1 (1)°. The N1—N2 and N3—N4 bonds are similar and longer than N2—N3, while the N1—C5 bond length is somewhat longer than N4—C5 (Table 1). This is a typical geometry for the 1-substituted tetrazole ring. All the bond lengths and angles of the ring are within the ranges found for tetrazole-containing structures generated by a search of the Cambridge Structural Database (Allen & Kennard, 1993). The tetrazole-ring geometry shows that there is strong π-delocalization in the N1—C5—N4 fragment, whereas discrete single and double bonds exist in the remainder of the ring.
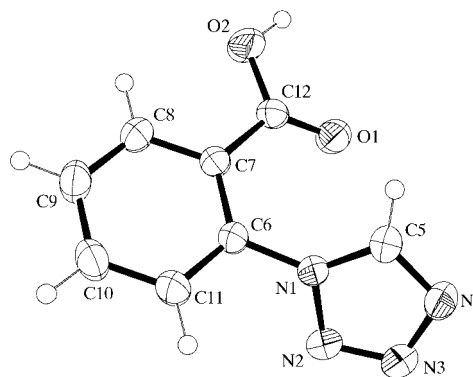

Figure 1
ORTEP-3 drawing (Farrugia, 1997) of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The benzene ring is planar to within 0.007 (1) Å. The bond distances and angles are consistent with those observed previously for benzene rings. The bond lengths and angles of the carboxyl group also have typical values (Table 1). The dihedral angle between the COO plane and the least-squares plane of the benzene ring is 11.8 (2)°. The bridge N1—C6 bond lies almost in the planes of the tetrazole and benzene rings. The angles between the N1—C6 bond and the least-squares planes of the benzene and tetrazole rings are 1.62 (7) and 5.22 (7)°, respectively.

The benzene and tetrazole rings are not coplanar in the molecule, the dihedral angle between the rings being 52.90 (4)°. It is interesting to compare this value with that of a
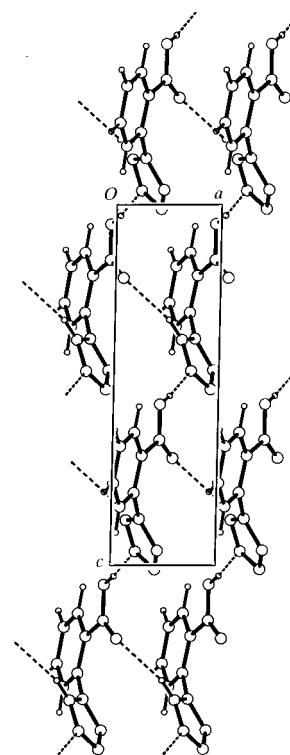

Figure 2
The hydrogen-bonded two-dimensional network in the structure of (I) viewed along the [010] direction.

free molecule of (I). The *ab initio* calculations were performed on an isolated molecule using the HF/6-311G** basis set with the *GAMESS* program (Schmidt *et al.*, 1993). Geometry optimization with respect to all variables results in a dihedral angle between the benzene and tetrazole rings of 69.5°. This value is somewhat larger than that in the crystal of (I). The data obtained confirm a presumption (Lyakhov *et al.*, 2001) that the decrease in the dihedral angle in the crystals of 1-aryltetrazoles is due to molecular packing.

Inspection of the packing of the molecules in (I) reveals that there are two types of hydrogen bonds, O2—H2···N4 and C5—H5···O1 (Desiraju, 1996), between the molecules (Table 2). O2—H2···N4 bridges are responsible for the formation of infinite one-dimensional zigzag chains parallel to the [10$\bar{1}$] direction. These chains are linked together by C5—H5···O1 hydrogen bonds, forming two-dimensional networks parallel to the *xz* plane (Fig. 2). Only van der Waals interactions exist between these networks in the structure.

Experimental

The title compound was prepared by heterocyclization of anthranilic acid and 2-amino-4-nitrophenol with ethyl orthoformate and sodium azide in acetic acid (Voitekhovich *et al.*, 2001). Single crystals were grown by slow crystallization from an acetonitrile solution.

Crystal data

$C_8H_6N_4O_2$	$D_x = 1.546$ Mg m^{-3}
$M_r = 190.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 3.8410$ (10) Å	reflections
$b = 16.073$ (4) Å	$\theta = 17.9–24.1°$
$c = 13.234$ (3) Å	$\mu = 0.12$ mm^{-1}
$\beta = 91.15$ (2)°	$T = 293$ (2) K
$V = 816.9$ (3) Å^3	Prism, colourless
$Z = 4$	$0.74 \times 0.30 \times 0.18$ mm

Data collection

Nicolet *R3m* four-circle diffractometer	$\theta_{max} = 30.1°$
	$h = 0 \rightarrow 5$
$\omega/2\theta$ scans	$k = 0 \rightarrow 22$
2822 measured reflections	$l = -18 \rightarrow 18$
2410 independent reflections	3 standard reflections
1888 reflections with $I > 2\sigma(I)$	every 100 reflections
$R_{int} = 0.019$	intensity decay: 2.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0582P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$+ 0.1169P]$
$wR(F^2) = 0.113$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2410 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
152 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.077 (7)

Table 1
Selected bond lengths (Å).

N1—C5	1.332 (1)	N4—C5	1.307 (2)
N1—N2	1.357 (1)	C7—C12	1.496 (1)
N1—C6	1.434 (1)	C12—O1	1.205 (1)
N2—N3	1.289 (1)	C12—O2	1.316 (1)
N3—N4	1.359 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N4^i	0.92 (2)	1.83 (2)	2.729 (1)	169 (2)
C5—H5···O1^{ii}	0.96 (2)	2.31 (2)	3.112 (2)	141 (1)

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

H-atom positions were found from the ΔF map and all associated parameters were refined freely [C—H = 0.93 (2)–0.99 (2) Å].

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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