

Double π - π stacking in 2-[(*E*)-(3,5-dimethylisoxazol-4-yl)diazenyl]benzoic acid

Luis Alvarez-Thon,^{a*} Carlos Bustos,^b Eduardo Schott,^b Christian Sanchez^b and Andres Ibañez^c

^aDepartamento de Química, Universidad Andrés Bello, Santiago de Chile, Chile,

^bDepartamento de Química, Universidad Austral de Chile, Valdivia, Chile, and ^cCIMAT, Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago de Chile, Chile

Correspondence e-mail: quaternionic@gmail.com

Molecules of the title compound, C₁₂H₁₁N₃O₃, are linked into zigzag chains by O—H···N hydrogen bonds. The crystal structure is further stabilized by π - π stacking interactions.

Comment

In the past few years, synthesis of isoxazole-related compounds has been the subject of many investigations due to the versatility of their properties. Some uses or properties are anti-inflammatory, analgesic and ulcerogenic (Daidone *et al.*, 1999), antimicrobial and antifungal (Bhatt *et al.*, 1998), inhibition of cyclooxygenase-2 (Talley, 1999; Talley *et al.*, 2000), anticancer activity (Li *et al.*, 2003), selective agonist of dopamine D4 receptors (Rowley *et al.*, 1996) and antagonist of GABA (Frolund *et al.*, 2002).

Key indicators

Single-crystal X-ray study

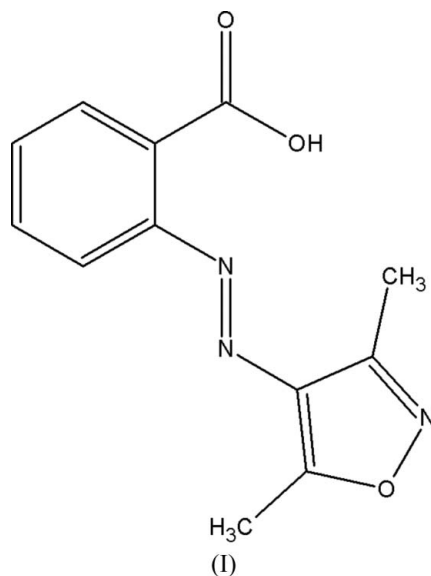
T = 298 K

Mean σ (C—C) = 0.004 Å

R factor = 0.043

wR factor = 0.074

Data-to-parameter ratio = 9.5



A perspective view of the title compound is shown in Fig. 1. The dihedral angle between the mean planes formed by the two rings is 25.20 (15)°. The bond lengths of the isoxazole ring (Table 1) are in very good agreement with the usual values for isoxazoles (Allen *et al.*, 1987).

Zigzag chains, which run in the [010] direction (Fig. 2), are formed *via* an intermolecular O—H···N hydrogen bond. The structure is further stabilized by π - π stacking interactions. The isoxazole ring at (*x*, *y*, *z*) shows two stacking interactions: with the benzene ring at ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$), with a distance of 3.9343 (18) Å between the ring centroids, and with that at ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$), with a distance between the ring centroids of 3.6700 (18) Å. Columns are formed along the *a* axis *via* these π - π stacking interactions (Fig. 3).

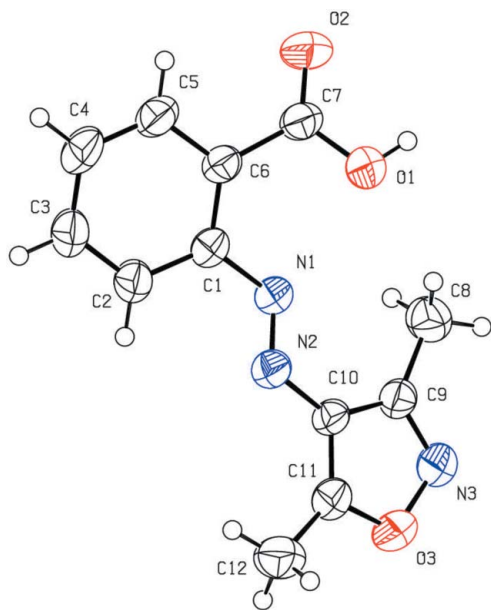


Figure 1

A view of the molecule of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms drawn as circles of arbitrary size.

Experimental

In a 100 ml round-bottomed flask were mixed 2-[(2*Z*)-2-(1-methyl-3-oxobutylidene)hydrazino]benzoic acid (0.005 mol), ethanol (25 ml), glacial acetic acid (2 ml) and hydroxylamine hydrochloride (0.005 mol, 0.35 g). The mixture was then stirred and heated under reflux for 18 h. After cooling to room temperature, H₂O (30 ml) was added, allowing the precipitation of an abundant quantity of orange solid. The product was collected by suction, washed twice with H₂O and dried under vacuum at 313 K. The crude compound was recrystallized by diffusion of *n*-hexane into a concentrated solution in *n*-hexane/chloroform (1:3 v/v).

Crystal data

C₁₂H₁₁N₃O₃
M_r = 245.24
 Orthorhombic, *P*2₁2₁2₁
a = 7.3550 (10) Å
b = 11.6182 (15) Å
c = 13.6335 (17) Å
V = 1165.0 (3) Å³
Z = 4
D_x = 1.398 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 999 reflections
 $\theta = 2.3\text{--}27.9^\circ$
 $\mu = 0.10\text{ mm}^{-1}$
T = 298 K
 Polyhedron, orange
 0.26 × 0.20 × 0.18 mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 8600 measured reflections
 1569 independent reflections

945 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.073$
 $\theta_{\text{max}} = 27.9^\circ$
 $h = -9 \rightarrow 9$
 $k = -14 \rightarrow 15$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.074$
S = 0.91
 1569 reflections
 165 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0217P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.019$
 $\Delta\rho_{\text{max}} = 0.14\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.10\text{ e \AA}^{-3}$

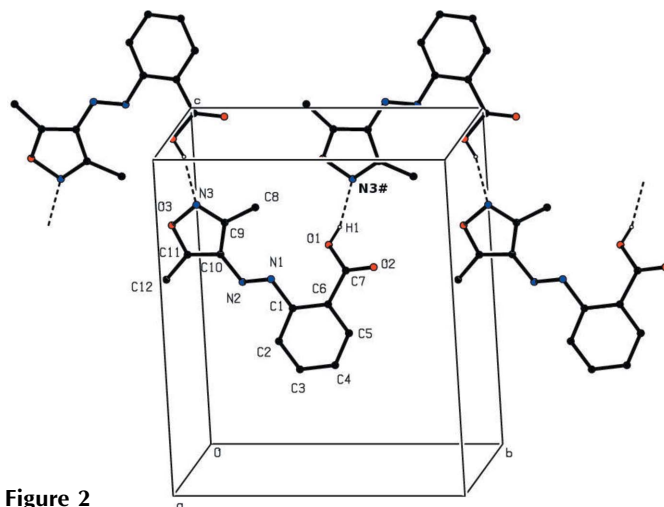


Figure 2

Part of the crystal structure, showing the formation of a zigzag chain along [010]. The dashed lines represent hydrogen bonds. H atoms not involved in hydrogen bonds have been omitted. [Symmetry code: (#) $-x, \frac{1}{2} + y, \frac{3}{2} - z$.]

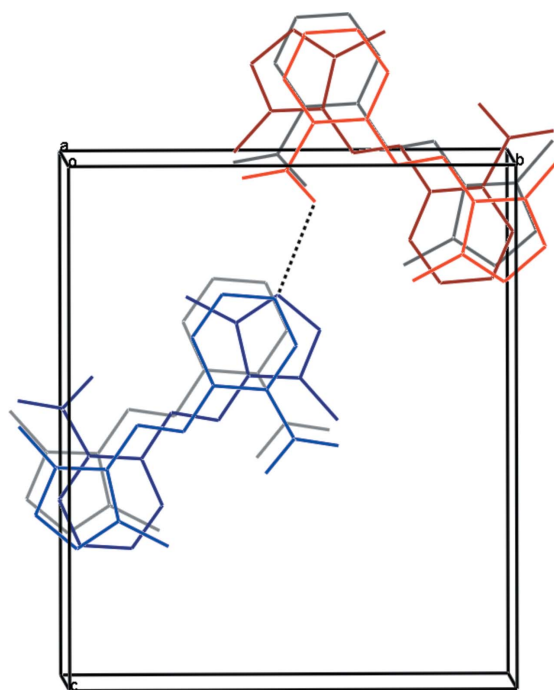


Figure 3

View approximately along the [100] direction, showing the π - π stacking. H atoms have been omitted.

Table 1

Selected geometric parameters (Å, °).

O3—N3	1.424 (3)	C9—C10	1.418 (4)
O3—C11	1.352 (3)	C10—C11	1.347 (3)
N3—C9	1.301 (3)	N1—N2	1.254 (3)
N2—N1—C1	113.0 (2)	N1—N2—C10	113.2 (2)
C1—N1—N2—C10	176.6 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1\cdots N3^i$	0.82	1.94	2.735 (3)	163

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with aromatic C–H = 0.93 Å, methyl C–H = 0.96 Å and O–H = 0.82 Å. The methyl groups were allowed to rotate but not to tip. In the absence of significant anomalous dispersion effects, Friedel pairs were merged prior to final refinement.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-PC* (Sheldrick, 1994); software used to prepare material for publication: *PLATON* (Spek, 2003).

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