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5,10-dihydroxy-5*H*,10*H*-diimidazo[1,2-*a*:1′,2′-*d*]pyrazine

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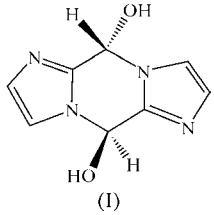
Crystallization of the title compound, $C_8H_8N_4O_2$, results in the formation of one-dimensional chains of imidazole (im) molecules linked together by strong hydrogen bonds. The O···N(im) separation and O—H(···N) distance are 2.6906 (17) and 1.74 (2) Å, respectively, and the O—H···N angle is 173 (2)°. The one-dimensional chains are weakly π stacked along the *b* axis, with centroid-to-centroid separations of 3.678 (2) Å between five- and six-membered rings and 3.963 (2) Å between six-membered rings. Each molecule is arranged around an inversion center.

Comment

Solid-state supramolecular assemblies are often stabilized by hydrogen bonding, hydrophobic and hydrophilic interactions, π–π stacking, and electrostatic interactions between ionic groups (Desiraju, 1995; MacDonald & Whitesides, 1994; Krische & Lehn, 2000). The present study expands our interest in utilizing imidazole compounds in supramolecular chemistry. We (Cheruzel *et al.*, 2003, 2005; Mashuta *et al.*, 2002) and others (Cromer *et al.*, 1987) have shown that imidazole compounds readily form strong π stacks and hydrogen bonds



(I)

with proton donor and/or acceptor compounds in the solid state, making these compounds excellent synthons for stabilizing supramolecular structures. The study described here illustrates our latest efforts to prepare imidazole compounds that form one-dimensional hydrogen-bonded chain structures. Compound (I) is the first fused tricyclic azafulvalene-containing imidazole to be crystallographically characterized. Compound (I) has a nearly planar centrosymmetric tricyclic structure, containing fused five- and six-membered rings, which is structurally similar to other 1-azafulvalenes (Galeazzi *et al.*, 1993). The title compound, which was synthesized by the base-assisted cyclization of imidazole-2-carbaldehyde, has C_i symmetry and two stereocenters.

The structure of (I) is shown in Fig. 1, and selected geometric parameters are given in Table 1. The five-membered aromatic imidazole rings are planar [the largest deviation from the mean plane of the N and C atoms is 0.005 (1) Å for atom C1]. The imidazole C—C/C—N distances and C—C—N/C—N—C angles of (I) are normal and consistent with those of other *N*-alkylated imidazole compounds (Mashuta *et al.*, 2002). The six-membered ring, on the other hand, is slightly puckered, as reflected in both the torsion angles [N1—C1—C4—N1′ = 7.7 (2)° and C4′—N1—C1—C4 = −9.2 (2)°] and the 0.029 (1) Å deviation of atom C4 from the plane defined by the other atoms.

Each of the stereocenters contains a hydroxy group (O1—H1O) and a methine H atom (H4) arranged in an *anti* conformation, which are related by inversion. The stereocenter at C4 is assigned an *R* configuration, while the center at C4′ is assigned an *S* configuration. Therefore, (I) is achiral and a *meso* form of the compound. Each molecule of (I) is strongly hydrogen bonded and π stacked with neighboring molecules related by inversion symmetry and translation, respectively

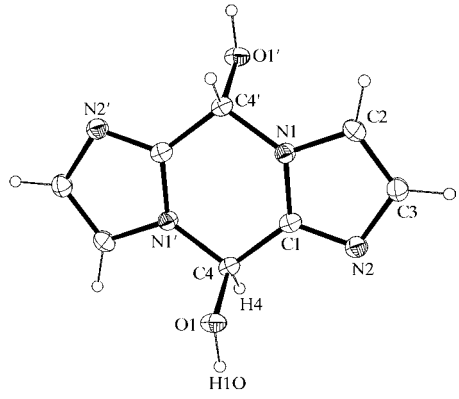


Figure 1
An *ORTEP-3* (Farrugia, 1997) plot of (I), showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

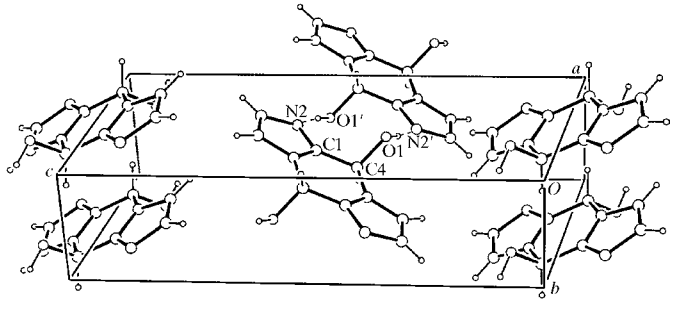


Figure 2
A packing diagram showing the hydrogen-bonding interactions between imidazole molecules and π stacking interactions between imidazole rings. [Symmetry code: (′) $2-x, 1-y, 1-z$.]

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(Fig. 2). Hydroxy groups (O1—H1O and O1′—H1O′) on opposing *R* and *S* stereocenters of molecules related by inversion symmetry are hydrogen bonded to respective imidazole N atoms (N2 and N2′). The hydrogen-bond parameters (Table 2) are consistent with the formation of strong hydrogen bonds. The two pairs of O1—H1O···N hydrogen bonds link molecules together, forming ten-membered rings, and the bifunctional nature of (I) results in the formation of infinite one-dimensional hydrogen-bonded chains projected along the crystallographic *a* axis.

The one-dimensional chains of (I) also form slipped π stacks (Janiak, 2000), with neighboring chains related by translation along the crystallographic *b* axis. The closest contact between imidazole rings in a double layer is 3.516 (2) Å, between C1 at (x, y, z) and C2 at $(x, 1 + y, z)$. There are centroid–centroid separations of 3.678 (2) Å between five- and six-membered rings at (x, y, z) and $(1 - x, -y, 1 - z)$, respectively, and 3.963 (2) Å between six-membered rings also at (x, y, z) and $(1 - x, -y, 1 - z)$. The overall packing arrangement of the hydrogen-bonded chains and π stacks resembles a herring-bone pattern.

Experimental

Imidazole-2-carbaldehyde (1 mmol) was added to an aqueous methanol (5 ml) solution (5:1) containing NaOH (1.5 mmol), and the mixture was stirred for 1 h. The mixture was then extracted three times with CH_2Cl_2 (5 ml) and the combined extracts were allowed to evaporate slowly in air, producing colorless single crystals.

Crystal data

$C_8H_8N_4O_2$
M_r = 192.18
Monoclinic, $P2_1/c$
a = 6.6274 (19) Å
b = 3.9625 (11) Å
c = 15.260 (4) Å
β = 100.615 (5)°
V = 393.89 (19) Å^3
Z = 2
D_x = 1.620 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 835 reflections
θ = 2.7–24.6°
μ = 0.12 mm^{-1}
T = 100 (2) K
Block, colorless
0.12 × 0.11 × 0.05 mm

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.3967 (17)	N2—C3	1.3854 (19)
N1—C1	1.3568 (18)	C1—C4	1.501 (2)
N1—C2	1.3779 (19)	C2—C3	1.353 (2)
N2—C1	1.3156 (19)		
N1^{i}—C4—C1	107.90 (11)		

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N2^{ii}	0.95 (2)	1.74 (2)	2.6906 (17)	173 (2)

Symmetry code: (ii) $-x + 2, -y + 1, -z + 1$.

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996).
T_{min} = 0.956, T_{max} = 0.989
3097 measured reflections
881 independent reflections
688 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 27.5°
$h = -8 \rightarrow 8$
$k = -5 \rightarrow 5$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.071
S = 1.08
881 reflections
78 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0139P)^2 + 0.291P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

H atoms were located in difference maps. Imidazole H atoms were refined isotropically. The positions for the hydroxy and methine H atoms were refined, while their U_{iso}(H) values were assigned as $1.2U_{eq}$(parent atom).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1086). Services for accessing these data are described at the back of the journal.

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