research communications

Crystal structure of 1,2-bis[(1H-imidazol-2-yl)-methylidene]hydrazine and its one-dimensional hydrogen-bonding network

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In the title compound, $C_8H_8N_6$, two imidazolyl groups are separated by a zigzag –CH=N—N=CH– linkage. An inversion center is located at the mid-point of the N—N single bond and the complete molecule is generated by symmetry. In the crystal, each molecule forms four N—H···N hydrogen bonds with two neighbouring molecules to constitute a one-dimensional ladder-like structure propagating along the a-axis direction.

1. Chemical context

Supramolecular chemistry is a fascinating topic, and molecular assemblies *via* intermolecular non-covalent binding interactions (*i.e.* hydrogen bonding, ionic and π–π stacking interactions) have attracted much attentions in the field of crystal engineering over the last decade. In particular, hydrogen bonding, which is a powerful organizing force in designing a variety of supramolecular and solid-state architectures (Subramanian & Zaworotko, 1994), is not only used extensively to generate numerous network structures consisting of discrete organic and organometallic compounds (Desiraju, 2000), but is also responsible for interesting physical properties of these supramolecular arrangements, such as electrical, optical, magnetic, *etc*. (Bacchi & Pelagatti, 2016; Lindoy & Atkinson, 2000; Létard *et al.*, 1998).
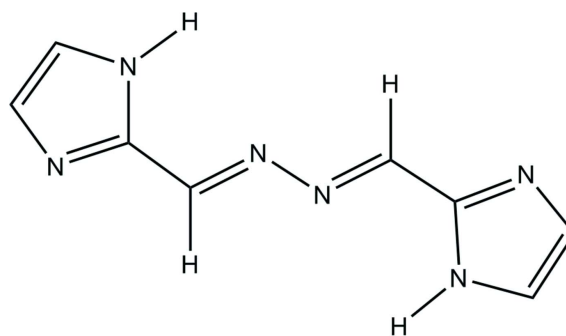
Imidazoles, containing two nitrogen atoms, possess both hydrogen-bond donating and accepting sites and are superior building blocks for supramolecular architectures. Many imidazole-containing polydentate ligands derived from hydrazine find a wide range of applications in coordination chemistry owing to their chelating ability (Zhou *et al.*, 2012). In this paper we report the synthesis of 1,2-bis[(1H-imidazol-2-yl)methylene]hydrazine (I), designed to consist of nitrogen donors and acceptors, and the supramolecular architecture it
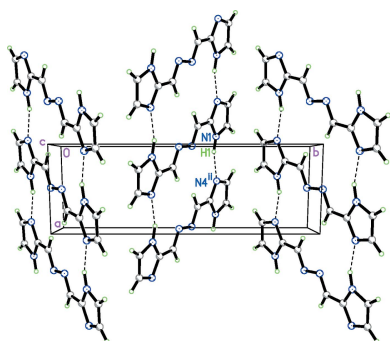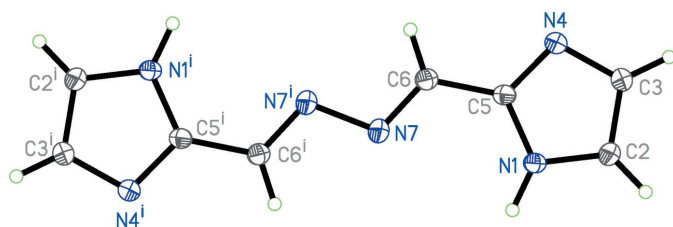
Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x$, $-y + 1$, $-z + 2$.]

gives rise to *via* hydrogen bonds. The functionality of molecule (I) as a bridge between metal centers for the formation of multi-dimensional structures will be discussed in subsequent publications.

2. Structural commentary

The molecular structure of the title compound consists of two imidazolyl groups linked by a zigzag –CH=N—N=CH– linkage (Fig. 1) and with $C5 \cdots C5^i = 5.937\,(3)$ Å [the distance between the centroids of the imidazolyl groups is 8.103 (3) Å]. The molecule possesses an inversion center located in the mid-point of the N—N single bond and the complete molecule is generated by symmetry. The molecule appears in a $Z(EE)Z$ configuration and its geometry is similar to that of 1,2-bis[(1H-imidazol-5-yl)methylene]hydrazine (Pinto *et al.*, 2013) and 1,2-bis[(thiophene-3-yl)methylene]hydrazine (Kim & Lee, 2008).

The molecule (I) has a planar (r.m.s. deviation = 0.012 Å) structure which, in addition to the observed bond distances, suggests partial delocalization of the π electrons over the
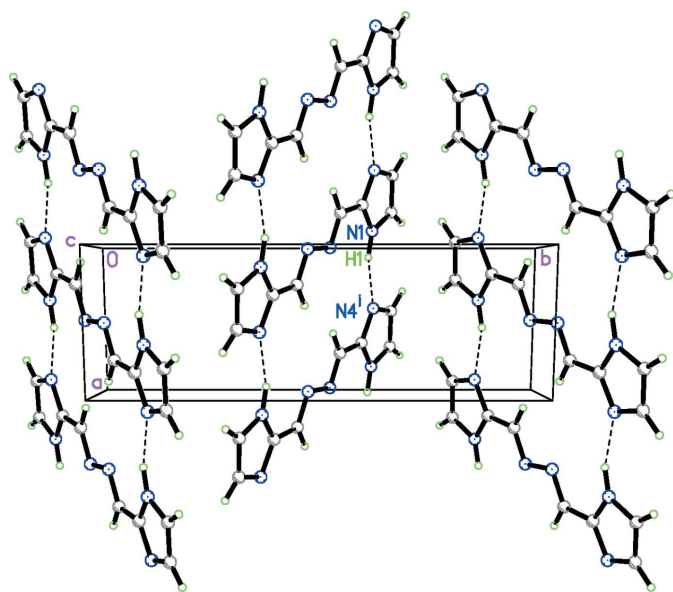
whole molecule. The geometric parameters, *viz.*, the N—N single bond [$N7$—$N7^i = 1.409\,(2)$ Å; symmetry code: (i) $-x$, $-y + 1$, $-z + 2$] , C=N double bond [$C6$—$N7 = 1.2795\,(19)$ Å] and C=N—N bond angle [$C6=N7$—$N7^i = 111.41\,(15)°$], are comparable to the corresponding parameters found in 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene [Dong *et al.*, 2000] and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene [Ciurtin *et al.*, 2001].

3. Supramolecular features

In the crystal structure of (I), each molecule is involved in four N—H$\cdots$N hydrogen bonds (*i.e.*: two donor and two acceptor interactions) and interacts with two neighboring molecules, resulting in a one-dimensional ladder-like structure along the a axis (Fig. 2). Numerical details of the hydrogen-bonding geometry are tabulated in Table 1.

As a comparison, the related compound 1,2-bis[(1H-imidazol-5-yl)methylene]hydrazine (Pinto *et al.*, 2013) is a planar molecule which constitutes corrugated layers parallel

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
$N1$—$H1\cdots N4^i$	0.95 (2)	1.95 (2)	2.8493 (17)	157.9 (19)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_8N_6$
M_r	188.20
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	5.0618 (3), 14.6282 (8), 6.1294 (4)
β (°)	106.321 (2)
V (Å^3)	435.56 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	$0.35 \times 0.10 \times 0.03$
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.702, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2614, 999, 903
R_{int}	0.014
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.117, 1.12
No. of reflections	999
No. of parameters	68
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.31, -0.26

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

Figure 2
A packing diagram for (I), viewed along the c axis. Dashed lines represent hydrogen bonds. [Symmetry code: (i) $x + 1$, y, z.]

to the (101) plane, as a result of both hydrogen bonding and π–π stacking interactions with adjacent molecules. In the present case of (I), instead, there are no significant π–π stacking interactions.

4. Synthesis and crystallization

A methanol solution (10 mL) of imidazole-2-carboxaldehyde (2.48 g, 25.8 mmol) was added to a methanol solution (10 mL) of hydrazine monohydrate (0.64 ml, 12.9 mmol). The mixture was stirred for 3 h and the precipitate was collected by filtration. Single crystals suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether into a DMSO solution of the title compound (I). Yield: 2.21 g (91%).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were located in difference-Fourier maps. For the H atom bounded to atom N1, the atomic coordinates and U_{iso} were refined, giving an N—H distance of 0.95 (2) Å. The C-bound H atoms were subsequently treated as riding atoms in geometrically idealized positions: C—H distances of 0.95 Å with $U_{iso}(H) = 1.2U_{eq}(C)$.

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Crystal structure of 1,2-bis[(1*H*-imidazol-2-yl)methylidene]hydrazine and its one-dimensional hydrogen-bonding network

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Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

1,2-Bis[(1*H*-imidazol-2-yl)methylidene]hydrazine

Crystal data

$C_8H_8N_6$	$F(000) = 196$
$M_r = 188.20$	$D_x = 1.435$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.0618$ (3) Å	Cell parameters from 2074 reflections
$b = 14.6282$ (8) Å	$\theta = 2.8–27.5°$
$c = 6.1294$ (4) Å	$\mu = 0.10$ mm^{-1}
$\beta = 106.321$ (2)°	$T = 150$ K
$V = 435.56$ (5) Å^3	Needle, colourless
$Z = 2$	$0.35 \times 0.10 \times 0.03$ mm

Data collection

Bruker D8 VENTURE diffractometer	999 independent reflections
φ and ω scans	903 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)	$R_{int} = 0.014$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.8°$
$T_{min} = 0.702$, $T_{max} = 0.746$	$h = -6 \rightarrow 6$
2614 measured reflections	$k = -18 \rightarrow 19$
	$l = -7 \rightarrow 6$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.042$	
$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.2863P]$
$S = 1.12$	where $P = (F_o^2 + 2F_c^2)/3$
999 reflections	$(\Delta/\sigma)_{max} < 0.001$
68 parameters	$\Delta\rho_{max} = 0.31$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	−0.1374 (2)	0.62851 (8)	0.4802 (2)	0.0175 (3)
H1	0.055 (5)	0.6193 (14)	0.515 (4)	0.037 (6)*
C2	−0.2801 (3)	0.67725 (10)	0.2944 (2)	0.0204 (4)
H2	−0.2082	0.7044	0.1823	0.025*
C3	−0.5481 (3)	0.67920 (10)	0.3022 (2)	0.0197 (3)
H3	−0.6956	0.7084	0.1937	0.024*
N4	−0.5714 (2)	0.63279 (8)	0.4899 (2)	0.0187 (3)
C5	−0.3193 (3)	0.60313 (10)	0.5944 (2)	0.0162 (3)
C6	−0.2539 (3)	0.55035 (10)	0.8020 (2)	0.0180 (3)
H6	−0.3975	0.5336	0.8659	0.022*
N7	−0.0068 (3)	0.52574 (8)	0.9014 (2)	0.0195 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0139 (6)	0.0223 (6)	0.0170 (6)	0.0001 (5)	0.0052 (5)	0.0008 (5)
C2	0.0187 (7)	0.0264 (8)	0.0165 (7)	0.0001 (6)	0.0055 (5)	0.0039 (5)
C3	0.0168 (7)	0.0227 (7)	0.0187 (7)	0.0013 (5)	0.0037 (5)	0.0040 (5)
N4	0.0152 (6)	0.0220 (6)	0.0188 (6)	0.0006 (5)	0.0046 (5)	0.0027 (5)
C5	0.0141 (7)	0.0180 (7)	0.0167 (7)	−0.0007 (5)	0.0049 (5)	−0.0013 (5)
C6	0.0166 (7)	0.0205 (7)	0.0173 (7)	−0.0005 (5)	0.0054 (5)	0.0004 (5)
N7	0.0198 (6)	0.0224 (6)	0.0159 (6)	0.0003 (5)	0.0043 (5)	0.0030 (5)

Geometric parameters (Å, º)

N1—C5	1.3557 (18)	C3—H3	0.9500
N1—C2	1.3656 (18)	N4—C5	1.3295 (18)
N1—H1	0.95 (2)	C5—C6	1.445 (2)
C2—C3	1.371 (2)	C6—N7	1.2795 (19)
C2—H2	0.9500	C6—H6	0.9500
C3—N4	1.3689 (19)	N7—N7^i	1.409 (2)
C5—N1—C2	107.26 (12)	C5—N4—C3	105.60 (12)
C5—N1—H1	130.4 (13)	N4—C5—N1	111.18 (13)
C2—N1—H1	122.3 (13)	N4—C5—C6	123.37 (13)
N1—C2—C3	106.15 (12)	N1—C5—C6	125.46 (13)
N1—C2—H2	126.9	N7—C6—C5	121.43 (13)
C3—C2—H2	126.9	N7—C6—H6	119.3
N4—C3—C2	109.81 (13)	C5—C6—H6	119.3

N4—C3—H3	125.1	C6—N7—N7ⁱ	111.41 (15)
C2—C3—H3	125.1		

C5—N1—C2—C3	−0.35 (16)	C2—N1—C5—N4	0.38 (17)
N1—C2—C3—N4	0.21 (17)	C2—N1—C5—C6	−179.95 (14)
C2—C3—N4—C5	0.02 (17)	N4—C5—C6—N7	−177.58 (13)
C3—N4—C5—N1	−0.25 (16)	N1—C5—C6—N7	2.8 (2)
C3—N4—C5—C6	−179.93 (13)	C5—C6—N7—N7ⁱ	−179.35 (14)

Symmetry code: (i) −*x*, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N4ⁱⁱ	0.95 (2)	1.95 (2)	2.8493 (17)	157.9 (19)

Symmetry code: (ii) *x*+1, *y*, *z*.