

***N,N'*-Bis[1-(pyrazin-2-yl)ethylidene]-  
hydrazine**Abdurrahman Şengül,<sup>a</sup> Nevzat Karadayı<sup>b\*</sup> and Orhan Büyükgüngör<sup>b</sup><sup>a</sup>Department of Chemistry, Science and Literature Faculty, Karaelmas University, TR-67100 Zonguldak, Turkey, and <sup>b</sup>Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Samsun, Turkey  
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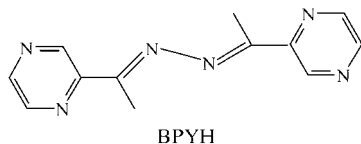
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Molecules of the title compound, C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>, contain both a diimine linkage and an N—N bond, and assume a planar structure. The compound lies about an inversion centre and there are three intramolecular C—H···N hydrogen bonds.

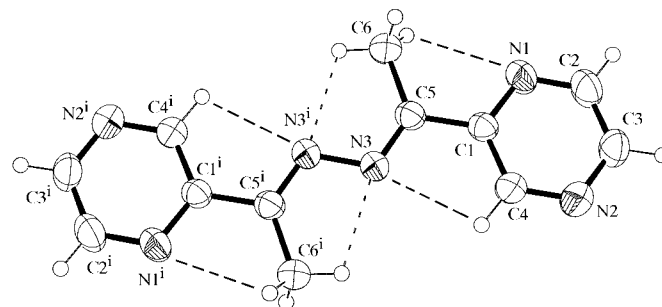
**Comment**

Supramolecular chemistry based on coordination chemistry is a vast area of current research. A particularly large number of such supramolecular complexes use oligomeric aromatic nitrogen-containing heterocycles as ligands, and the demand for multitopic (bridging) ligands provides a strong impetus for the synthesis of related compounds. Some approaches to the construction of supramolecular systems based on polyazines have been reported recently (Tuna *et al.*, 2003; Hamblin *et al.*, 2002; Matthews *et al.*, 2003). The recent interest in N<sub>2</sub>-diazine-bridged polyfunctional ligands mainly derives from the fact that the nature of the heterocyclic ring and the extent of the double-bond character in the N—N bond have been reported to play a crucial role in providing an intramolecular exchange pathway for spin-exchange interactions that are observed in the metal complexes of these ligands (Xu *et al.*, 1997). We report here the crystal structure of *N,N'*-bis[1-(pyrazin-2-yl)ethylidene]hydrazine (hereafter BPYH), in which the two pyrazinylimine binding units are linked directly (no spacer unit) through the imine N atoms.



The molecular structure of BPYH is shown in Fig. 1, and relevant bond distances and angles are listed in Table 1. The molecule is essentially planar and has a *trans* configuration.

The title molecule crystallizes in the *E,E* conformation, with the methyl groups on opposite sides of the N—N bond,

**Figure 1**

The molecular structure of BPYH, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed lines show possible hydrogen bonding (Table 2). [Symmetry code: (i)  $-x, 1 - y, -z$ .]

suggesting conjugation throughout the  $\pi$  systems. This configuration agrees with that commonly found in a number of azine compounds (Kesslen & Euler, 1999). The N3—N3<sup>i</sup> bond distance [1.398 (2) Å; symmetry code: (i)  $-x, 1 - y, -z$ ] is the same, within experimental error, as that found in free 2,4-dinitrophenylhydrazine [1.405 (6) Å; Okabe *et al.*, 1993], but is slightly shorter than that in hydrazine (1.449 Å; Kohata *et al.*, 1982), which suggests the existence of some double-bond character in the azine N—N bond.

The planarity in BPYH may arise as a result of several effects. Firstly, the N3···H6 distance is 2.7245 (18) Å, slightly less than the sum of the van der Waals radii for H and N atoms (2.75 Å), suggesting a possible interaction between these two atoms. The stereochemical influence of the nitrogen lone pairs is reflected in the bond angle; the C5—N3—N3<sup>i</sup> angle [113.64 (13)°] is significantly below the ideal  $sp^2$  value of 120°, a consequence of repulsion between the nitrogen lone pairs and the adjacent bonds.

The C=N—N=C linkage is planar. The C5—N3 bond [1.2816 (16) Å] is longer than the mean distance (1.273 Å) for related azine compounds (Kesslen & Euler, 1999; Hagen *et al.*, 1977; Chen *et al.*, 1994), which, together with the short N—N bond, implies a small degree of delocalization through the azine  $\pi$  system. The C1—N1 bond distance [1.3281 (16) Å] is shorter than the distance [1.335 (2) Å] reported by Zhang *et al.* (2001). The plane of the C1/C5/N3/C6 group is rotated by 3.62 (1)° from the plane of the C1/N1/C2/C3/N2/C4 ring. The structure arises from a combination of packing effects, steric effects and very weak intramolecular hydrogen contacts; the molecule contains three C—H···N hydrogen bonds (Table 2).

**Experimental**

BPYH was synthesized by the reaction of 2-acetylpyrazine with hydrazine hydrate in a refluxing ethanol/HCl solution, using a procedure similar to that reported for the synthesis of 2-pyridine-aldehydeazine by Kesslen & Euler (1999). Crystallization was performed twice (from ethanol and acetonitrile), yielding orange crystals suitable for X-ray analysis. A single crystal was selected, mounted on a glass fibre using epoxy cement and used for data collection.

Crystal data

$C_{12}H_{12}N_6$	$D_x = 1.339 \text{ Mg m}^{-3}$
$M_r = 240.28$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3509 reflections
$a = 4.4395 (7) \text{ \AA}$	$\theta = 2.3\text{--}28.5^\circ$
$b = 7.4724 (7) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 17.972 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.304 (13)^\circ$	Block, pale yellow
$V = 596.04 (15) \text{ \AA}^3$	$0.50 \times 0.30 \times 0.20 \text{ mm}$
$Z = 2$	

Data collection

Stoe IPDS-II diffractometer	$R_{\text{int}} = 0.086$
$\omega$ scans	$\theta_{\text{max}} = 26.0^\circ$
4249 measured reflections	$h = -5 \rightarrow 5$
1174 independent reflections	$k = -9 \rightarrow 9$
877 reflections with $I > 2\sigma(I)$	$l = -22 \rightarrow 22$

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.112$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
1174 reflections	$\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$
96 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.090 (14)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C1—C4	1.391 (2)	C5—N3	1.2816 (16)
C1—C5	1.4841 (18)	C5—C6	1.491 (2)
N1—C1—C5	117.37 (12)	C1—C5—C6	118.82 (11)
C4—C1—C5	121.87 (11)	C1—N1—C2	116.02 (13)
N3—C5—C1	114.94 (12)	C4—N2—C3	116.02 (13)
N3—C5—C6	126.24 (12)		
N1—C1—C5—N3	176.64 (12)	C4—C1—C5—C6	176.14 (14)

The H atoms bonded to atom C6 were refined as riding, with C—H distances of 0.96  $\text{\AA}$  and  $U_{\text{iso}}(\text{H})$  values of  $1.5U_{\text{eq}}(\text{C})$ . All other H atoms were refined isotropically; the C—H bond distances are in the range 0.920 (19)–0.971 (17)  $\text{\AA}$ .

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s)

Table 2

Hydrogen-bonding and short-contact geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C6—H6B $\cdots$ N1	0.96	2.63	2.8173 (19)	91
C4—H4 $\cdots$ N3	0.953 (17)	2.449 (17)	2.7598 (18)	98.8 (12)
C6—H6A $\cdots$ N3 <sup>i</sup>	0.96	2.31	2.7245 (18)	105

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

used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1007). Services for accessing these data are described at the back of the journal.

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