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1*H*-Indole-3-carbaldehyde azine

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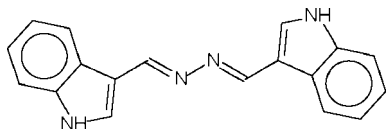
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 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.043; wR factor = 0.122; data-to-parameter ratio = 15.8.

The molecule of the title compound, $\text{C}_{18}\text{H}_{14}\text{N}_4$, lies on a center of inversion such that there is one half-molecule in the asymmetric unit. The N–N single bond adopts a *trans* configuration and the indole fused-ring system is nearly coplanar with the $-\text{CH}=\text{N}-\text{N}=\text{CH}-$ fragment [dihedral angle = $9.8(2)^\circ$]. Adjacent molecules are linked by indole–azine N–H \cdots N hydrogen bonds into a layer motif.

Related literature

For the synthesis, see: Alemany *et al.* (1970); Swaminathan & Narasimhan (1964). For the crystal structures of some aromatic azines, for example, benzalazine, see: Burke-Laing & Laing (1976); Mom & de With (1978); Sinha, (1970). For other heterocyclic aldehyde azines, see: Lin *et al.* (2001*a,b*); Wu *et al.* (2006).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{14}\text{N}_4$
 $M_r = 286.33$
 Monoclinic, $P2_1/c$
 $a = 5.0849(2)$ Å
 $b = 10.6708(4)$ Å
 $c = 13.4435(5)$ Å
 $\beta = 94.366(3)^\circ$

$V = 727.33(5)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 295(2)$ K
 $0.33 \times 0.27 \times 0.17$ mm

Data collection

Bruker APEX2 diffractometer
 Absorption correction: none
 5388 measured reflections

1659 independent reflections
 1085 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.121$
 $S = 1.01$
 1659 reflections
 105 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{N2}^i$	0.87 (2)	2.21 (2)	3.065 (2)	167 (2)

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2186).

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supplementary materials

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1*H*-Indole-3-carbaldehyde azine

M. R. Rizal, H. M. Ali and S. W. Ng

Comment

Azines are readily synthesized by condensing hydrazine with an aldehyde; the crystal structures of a large number of substituted benzaldehyde azines have been reported. The structure of the parent aromatic compound, benzalazine, has been known for a long time (Burke-Laing & Laing, 1976; Mom & de With, 1978; Sinha, 1970). There are few examples of heterocyclic azines, and their rarity can be attributed to the difficulty of synthesizing the starting aldehyde reactant. Among the few are, for example, unsubstituted and methyl-substituted thiophene-2-aldehyde azine (Lin *et al.*, 2001*a*, 2001*b*) and a pyrrole derivative has recently been reported (Wu *et al.*, 2006).

3-Indole azine has been known for some time; it was first synthesized from indole-3-carboxaldehyde and hydrazine in order to examine its psychopharmacological activity (Alemany *et al.*, 1970; Swaminathan Narasimhan, 1964). The title compound was the unexpected decomposition product of the Schiff base derived from the condensation of carbohydrazide and indole-3-carboxaldehyde. The molecule (Scheme I, Fig. 1) lies about a center-of-inversion such that there is half a molecule in the asymmetric unit. The N–N single-bond adopts a *trans* configuration and the indolyl fused-ring is nearly coplanar with the –CH=N–N=CH– fragment. Adjacent molecules are linked by an *N*–H_{indole}⋯N_{azine} hydrogen bonds into layer motif (Fig. 2).

Experimental

The reaction of carbohydrazide (0.3 g, 3.3 mmol) and indole-3-carboxaldehyde (1 g, 6.6 mmol) in ethanol under reflux for 2 h gave the corresponding Schiff base. This compound (0.2 g, 0.6 mmol), zinc acetate (0.06 g, 0.3 mmol) and several drops of triethylamine were dissolved in 10 ml ethanol. The contents were heated in a 25-ml, stainless-steel Paar bomb for 2 d at 373 K. The bomb was cooled to room temperature over several hours. Well formed crystals were isolated from the cooled bomb.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H 0.93 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2*U*(C). The amino H-atom was located in a difference Fourier map, and was freely refined.

Figures

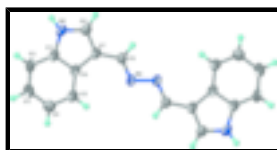


Fig. 1. Displacement ellipsoid plot of (I) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

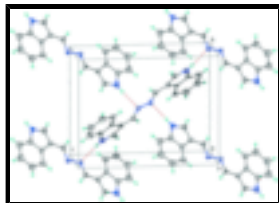


Fig. 2. Layer structure of (I).

1*H*-Indole-3-carbaldehyde azine

Crystal data

$C_{18}H_{14}N_4$

$M_r = 286.33$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 5.0849\ (2)\ \text{\AA}$

$b = 10.6708\ (4)\ \text{\AA}$

$c = 13.4435\ (5)\ \text{\AA}$

$\beta = 94.366\ (3)^\circ$

$V = 727.33\ (5)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 300$

$D_x = 1.307\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1012 reflections

$\theta = 2.3\text{--}23.6^\circ$

$\mu = 0.08\ \text{mm}^{-1}$

$T = 295\ (2)\ \text{K}$

Irregular block, green–yellow

$0.33 \times 0.27 \times 0.17\ \text{mm}$

Data collection

Bruker APEX2
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 295\ (2)\ \text{K}$

φ and ω scans

Absorption correction: none

5388 measured reflections

1659 independent reflections

1085 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 2.4^\circ$

$h = -6 \rightarrow 6$

$k = -9 \rightarrow 13$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.121$

$S = 1.01$

1659 reflections

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 +]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.17\ \text{e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.16\ \text{e \AA}^{-3}$

105 parameters

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.016 (6)

Secondary atom site location: difference Fourier map

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.4730 (3)	0.8059 (1)	0.1978 (1)	0.0484 (4)
N2	0.4464 (2)	0.5165 (1)	0.4519 (1)	0.0422 (4)
C1	0.2718 (3)	0.7222 (1)	0.1726 (1)	0.0425 (4)
C2	0.1064 (3)	0.7130 (2)	0.0860 (1)	0.0538 (5)
C3	-0.0787 (3)	0.6201 (2)	0.0817 (1)	0.0579 (5)
C4	-0.1034 (4)	0.5384 (2)	0.1612 (1)	0.0546 (4)
C5	0.0606 (3)	0.5473 (1)	0.2473 (1)	0.0454 (4)
C6	0.2548 (3)	0.6396 (1)	0.2540 (1)	0.0388 (4)
C7	0.4578 (3)	0.6773 (1)	0.3285 (1)	0.0400 (4)
C8	0.5819 (3)	0.7783 (1)	0.2901 (1)	0.0466 (4)
C9	0.5376 (3)	0.6213 (1)	0.4228 (1)	0.0411 (4)
H1	0.524 (3)	0.865 (2)	0.159 (1)	0.062 (5)*
H2	0.1210	0.7680	0.0330	0.065*
H3	-0.1911	0.6111	0.0243	0.070*
H4	-0.2329	0.4767	0.1561	0.065*
H5	0.0419	0.4926	0.3002	0.054*
H8	0.7215	0.8217	0.3228	0.056*
H9	0.6619	0.6629	0.4650	0.049*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.061 (1)	0.041 (1)	0.043 (1)	-0.002 (1)	0.005 (1)	0.012 (1)
N2	0.063 (1)	0.036 (1)	0.027 (1)	-0.001 (1)	-0.003 (1)	0.001 (1)
C1	0.049 (1)	0.039 (1)	0.039 (1)	0.006 (1)	0.006 (1)	0.005 (1)
C2	0.062 (1)	0.058 (1)	0.040 (1)	0.007 (1)	-0.001 (1)	0.014 (1)
C3	0.060 (1)	0.065 (1)	0.047 (1)	0.005 (1)	-0.008 (1)	0.003 (1)
C4	0.054 (1)	0.050 (1)	0.059 (1)	-0.003 (1)	-0.001 (1)	0.000 (1)
C5	0.052 (1)	0.040 (1)	0.045 (1)	0.003 (1)	0.006 (1)	0.004 (1)
C6	0.046 (1)	0.035 (1)	0.036 (1)	0.007 (1)	0.007 (1)	0.003 (1)
C7	0.052 (1)	0.034 (1)	0.034 (1)	0.004 (1)	0.004 (1)	0.001 (1)
C8	0.059 (1)	0.040 (1)	0.041 (1)	-0.002 (1)	0.001 (1)	0.003 (1)
C9	0.056 (1)	0.036 (1)	0.032 (1)	-0.003 (1)	-0.001 (1)	-0.003 (1)

Geometric parameters (\AA , $^\circ$)

N1—C8	1.351 (2)	C6—C7	1.440 (2)
N1—C1	1.381 (2)	C7—C8	1.370 (2)
N2—C9	1.283 (2)	C7—C9	1.432 (2)
N2—N2 ⁱ	1.409 (2)	N1—H1	0.87 (2)

supplementary materials

C1—C2	1.387 (2)	C2—H2	0.9300
C1—C6	1.412 (2)	C3—H3	0.9300
C2—C3	1.365 (2)	C4—H4	0.9300
C3—C4	1.393 (2)	C5—H5	0.9300
C4—C5	1.377 (2)	C8—H8	0.9300
C5—C6	1.393 (2)	C9—H9	0.9300
C8—N1—C1	109.2 (1)	N2—C9—C7	123.4 (1)
C9—N2—N2 ⁱ	112.0 (1)	C8—N1—H1	126 (1)
N1—C1—C2	129.9 (1)	C1—N1—H1	125 (1)
N1—C1—C6	107.6 (1)	C3—C2—H2	121.4
C2—C1—C6	122.5 (2)	C1—C2—H2	121.4
C3—C2—C1	117.3 (2)	C2—C3—H3	119.2
C2—C3—C4	121.7 (2)	C4—C3—H3	119.2
C5—C4—C3	121.2 (2)	C5—C4—H4	119.4
C4—C5—C6	118.9 (1)	C3—C4—H4	119.4
C5—C6—C1	118.5 (1)	C4—C5—H5	120.5
C5—C6—C7	135.2 (1)	C6—C5—H5	120.5
C1—C6—C7	106.3 (1)	N1—C8—H8	124.8
C8—C7—C9	123.7 (1)	C7—C8—H8	124.8
C8—C7—C6	106.5 (1)	N2—C9—H9	118.3
C9—C7—C6	129.7 (1)	C7—C9—H9	118.3
N1—C8—C7	110.5 (1)		
C8—N1—C1—C2	-179.5 (2)	C2—C1—C6—C7	179.4 (1)
C8—N1—C1—C6	0.5 (2)	C5—C6—C7—C8	-178.6 (2)
N1—C1—C2—C3	-179.6 (2)	C1—C6—C7—C8	0.5 (2)
C6—C1—C2—C3	0.4 (2)	C5—C6—C7—C9	5.1 (3)
C1—C2—C3—C4	0.7 (3)	C1—C6—C7—C9	-175.9 (2)
C2—C3—C4—C5	-0.7 (3)	C1—N1—C8—C7	-0.2 (2)
C3—C4—C5—C6	-0.3 (2)	C9—C7—C8—N1	176.5 (1)
C4—C5—C6—C1	1.3 (2)	C6—C7—C8—N1	-0.2 (2)
C4—C5—C6—C7	-179.7 (2)	N2 ⁱ —N2—C9—C7	-178.9 (1)
N1—C1—C6—C5	178.6 (1)	C8—C7—C9—N2	-169.5 (1)
C2—C1—C6—C5	-1.4 (2)	C6—C7—C9—N2	6.3 (3)
N1—C1—C6—C7	-0.6 (2)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots N2 ⁱⁱ	0.87 (2)	2.21 (2)	3.065 (2)	167 (2)

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

Fig. 1

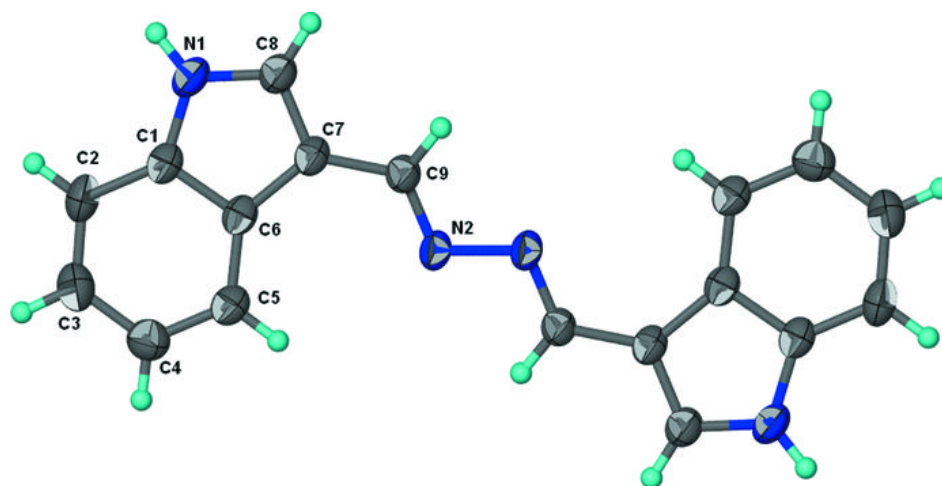


Fig. 2

