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1,2,3,6,7,8-Hexahydrocinnolino[5,4,3-*cde*]cinnoline

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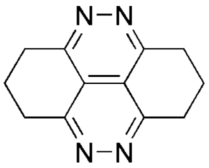
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.123; data-to-parameter ratio = 9.2.

The title compound, $C_{12}H_{12}N_4$, was synthesized by the reaction of hydrazine hydrate and 9-methyl-3,4,6,7-tetrahydro-2*H*-xanthene-1,8(5*H*,9*H*)-dione in ethanol. In the crystal, the molecule lies across an inversion centre. The pyridazine rings are coplanar and the C_6 rings adopt envelope conformations.

Related literature

For the biological properties of cinnoline and its derivatives, see: Abdelrazek *et al.* (2006); Gomtsyan *et al.* (2005); Inoue *et al.* (1993); Lewgowd & Stanczak (2007); Lewgowd *et al.* (2005); Singh *et al.* (2003); Stefanska *et al.* (2003); Tutsumi *et al.* (1992).



Experimental

Crystal data

$C_{12}H_{12}N_4$	M_r = 212.26
Monoclinic, $P2_1/c$	Z = 2
a = 9.698 (5) Å	Mo $K\alpha$ radiation
b = 5.875 (3) Å	μ = 0.09 mm^{-1}
c = 10.023 (5) Å	T = 298 (2) K
β = 117.314 (6)°	0.55 × 0.41 × 0.09 mm
V = 507.4 (4) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	2508 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	890 independent reflections
T_{min} = 0.953, T_{max} = 0.992	575 reflections with $I > 2\sigma(I)$
	R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041	97 parameters
$wR(F^2)$ = 0.123	All H-atom parameters refined
S = 1.01	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
890 reflections	$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2750).

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supporting information

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1,2,3,6,7,8-Hexahydrocinnolino[5,4,3-*cde*]cinnoline

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S1. Comment

It is well known that six-membered nitrogen-containing heterocycles are abundant in numerous natural products that exhibit important biological properties. For example, cinnolines and their derivatives exhibit a diverse range of biological properties (Lewgowd & Stanczak, 2007) such as molluscicidal activity (Abdelrazek *et al.*, 2006), cytotoxic activity (Lewgowd *et al.*, 2005), transient receptor potential vanilloid 1 (TRPV1) receptor antagonists (Gomtsyan *et al.*, 2005), and topoisomerase I (TOP1)-targeting activity and cytotoxicity (Singh *et al.*, 2003). They also acted as anticancer agents active on a multidrug resistant cell line (Stefanska *et al.*, 2003). They can also be used as bactericides in pharmaceutical industry (Inoue *et al.*, 1993; Tutsumi *et al.*,1992). The chemistry of cinnolines has received much attention based on the above facts.

The title molecule lies across an inversion centre (Fig. 1). The two pyridazine rings (C1/C2/C2A/C3A/N2/N1 and C1A/C2A/C2/C3/N2A/N1A) are conjugated and are coplanar. The two cyclohexene rings (C1—C6 and C1A—C6A) adopt envelope conformations, with atoms C5 and C5A deviate from the C1/C2/C3/C4/C6 and C1A/C2A/C3A/C4A/C6A planes by 0.656 (3) and 0.656 (3) Å, respectively.

A view of the crystal packing is shown in Fig.2.

S2. Experimental

The title compound was prepared by the reaction of 3,4,6,7-tetrahydro -9-methyl-2*H*-xanthene-1,8(5*H*,9H)-dione (2 mmol) and hydrazine hydrate 80% (8 mmol) in ethanol (8 ml) stirring at 353 K (yield 84%; m.p. 543–544 K). Single crystals suitable for X-ray diffraction were obtained from an ethanol solution by slow evaporation.

S3. Refinement

All H atoms were located in a difference Fourier map and refined freely [C-H = 0.95 (2)-1.04 (2) Å].

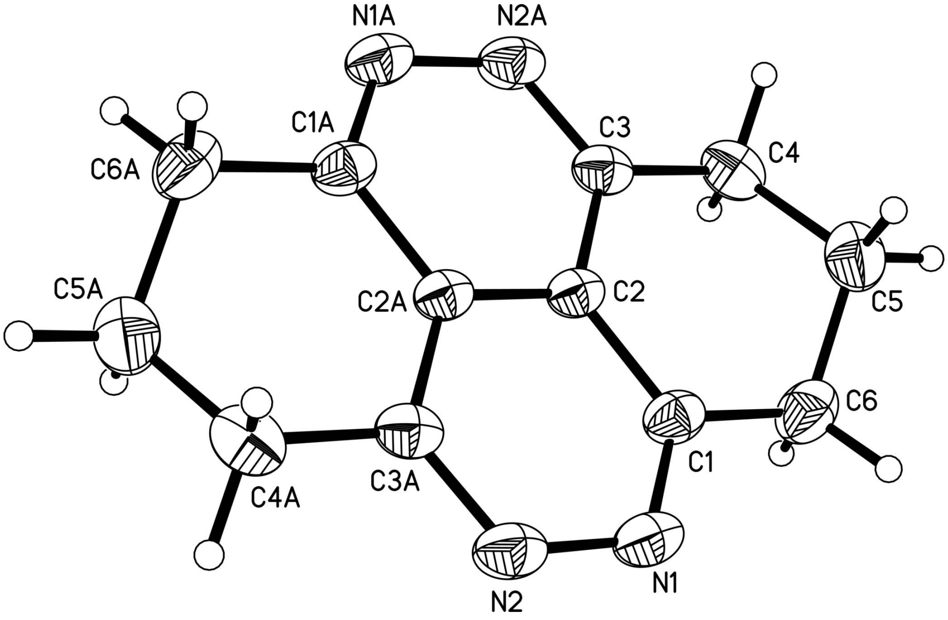

Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with the suffix A are generated by the symmetry operation (1-x, -y, 1-z).

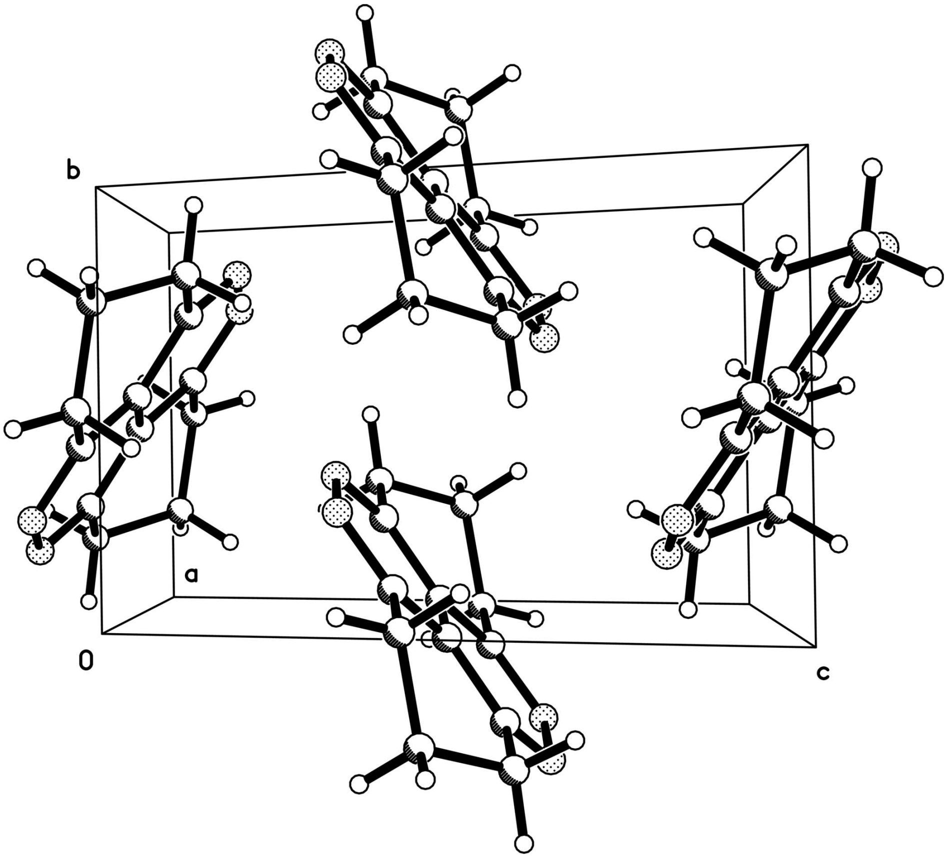

Figure 2

Molecular packing in the title compound, viewed approximately along the *a* axis.

1,2,3,6,7,8-Hexahydrocinnolino[5,4,3-cde]cinnoline

Crystal data

$C_{12}H_{12}N_4$
M_r = 212.26
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.698 (5) Å
b = 5.875 (3) Å
c = 10.023 (5) Å
β = 117.314 (6)°
V = 507.4 (4) Å^3
Z = 2
$F(000)$ = 224
D_x = 1.389 Mg m^{-3}
Melting point = 543–544 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 734 reflections
θ = 2.4–26.3°
μ = 0.09 mm^{-1}
T = 298 K
Plate, colourless
0.55 × 0.41 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.953, $T_{\max}$ = 0.992
2508 measured reflections
890 independent reflections
575 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 25.0°, $\theta_{\min}$ = 4.1°
$h = -11 \rightarrow 11$
$k = -6 \rightarrow 6$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.123
S = 1.01
890 reflections
97 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 0.0552P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\min}$ = −0.15 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
N1	0.7159 (2)	−0.2597 (3)	0.65617 (19)	0.0547 (6)

N2	0.5861 (2)	−0.3398 (3)	0.66438 (18)	0.0555 (6)
C1	0.7050 (2)	−0.0820 (4)	0.5729 (2)	0.0466 (6)
C2	0.56377 (19)	0.0384 (3)	0.49395 (18)	0.0390 (5)
C3	0.5474 (2)	0.2352 (3)	0.4062 (2)	0.0450 (5)
C4	0.6864 (3)	0.3211 (5)	0.3949 (3)	0.0581 (7)
C5	0.8354 (3)	0.2567 (4)	0.5326 (3)	0.0647 (7)
C6	0.8445 (3)	0.0004 (4)	0.5597 (3)	0.0621 (7)
H1	0.682 (2)	0.250 (4)	0.305 (3)	0.065 (6)*
H2	0.678 (2)	0.487 (4)	0.382 (2)	0.076 (7)*
H3	0.930 (3)	0.308 (4)	0.522 (3)	0.086 (8)*
H4	0.839 (3)	0.340 (4)	0.623 (3)	0.079 (7)*
H5	0.846 (2)	−0.086 (4)	0.470 (2)	0.072 (7)*
H6	0.936 (3)	−0.039 (4)	0.649 (3)	0.081 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0567 (12)	0.0508 (12)	0.0500 (10)	0.0164 (9)	0.0187 (9)	0.0061 (8)
N2	0.0652 (12)	0.0458 (11)	0.0474 (11)	0.0115 (9)	0.0189 (9)	0.0086 (8)
C1	0.0501 (12)	0.0467 (12)	0.0395 (10)	0.0102 (10)	0.0175 (9)	−0.0019 (10)
C2	0.0445 (11)	0.0386 (11)	0.0306 (9)	0.0072 (8)	0.0146 (8)	−0.0029 (8)
C3	0.0574 (13)	0.0386 (12)	0.0351 (10)	0.0051 (10)	0.0178 (9)	−0.0010 (9)
C4	0.0737 (17)	0.0505 (15)	0.0555 (14)	−0.0061 (12)	0.0344 (13)	−0.0027 (12)
C5	0.0595 (15)	0.0680 (17)	0.0681 (16)	−0.0087 (13)	0.0306 (13)	−0.0101 (13)
C6	0.0484 (14)	0.0707 (18)	0.0650 (16)	0.0111 (11)	0.0242 (13)	−0.0033 (12)

Geometric parameters (Å, º)

N1—C1	1.310 (3)	C4—C5	1.518 (3)
N1—N2	1.381 (2)	C4—H1	0.98 (2)
N2—C3^{i}	1.309 (3)	C4—H2	0.98 (2)
C1—C2	1.417 (3)	C5—C6	1.526 (3)
C1—C6	1.499 (3)	C5—H3	1.01 (2)
C2—C2^{i}	1.373 (3)	C5—H4	1.01 (2)
C2—C3	1.417 (3)	C6—H5	1.04 (2)
C3—N2^{i}	1.309 (3)	C6—H6	0.95 (2)
C3—C4	1.492 (3)		
C1—N1—N2	120.01 (17)	C5—C4—H2	111.0 (13)
C3^{i}—N2—N1	120.67 (18)	H1—C4—H2	109.4 (18)
N1—C1—C2	121.89 (19)	C4—C5—C6	111.2 (2)
N1—C1—C6	120.07 (18)	C4—C5—H3	111.1 (13)
C2—C1—C6	118.0 (2)	C6—C5—H3	109.2 (14)
C2^{i}—C2—C3	118.3 (2)	C4—C5—H4	108.6 (14)
C2^{i}—C2—C1	117.8 (2)	C6—C5—H4	110.1 (13)
C3—C2—C1	123.94 (17)	H3—C5—H4	106.5 (19)
N2^{i}—C3—C2	121.33 (19)	C1—C6—C5	110.70 (19)
N2^{i}—C3—C4	120.3 (2)	C1—C6—H5	107.1 (12)

C2—C3—C4	118.39 (18)	C5—C6—H5	110.5 (12)
C3—C4—C5	111.3 (2)	C1—C6—H6	109.2 (14)
C3—C4—H1	105.8 (12)	C5—C6—H6	111.1 (15)
C5—C4—H1	110.6 (12)	H5—C6—H6	108.2 (19)
C3—C4—H2	108.6 (13)		

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