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

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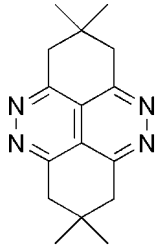
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.052; wR factor = 0.179; data-to-parameter ratio = 13.6.

The asymmetric unit of the title compound, $C_{16}H_{20}N_4$, contains two half-molecules, which are completed by crystallographic inversion symmetry. The pyridazine rings are conjugated and the cyclohexane rings adopt envelope conformations.

Related literature

For general background, see: Ischikawa *et al.* (1992); Labovitz *et al.* (1990); Mizutani, Shiroshita, Okuda *et al.* (1989); Patterson (1992); Coghlan *et al.* (1989); Mizutani, Shiroshita, Sakaki *et al.* (1989b); Munro & Bit (1987); Inoue *et al.* (1993); Tutsumi *et al.* (1992); Yokomoto *et al.* (1992); Miyamoto *et al.* (1990). For bond-length data, see: Allen *et al.* (1987). For ring-puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{16}H_{20}N_4$
M_r = 268.36
Monoclinic, $P2_1/n$
a = 12.819 (4) Å
b = 8.441 (3) Å
c = 13.310 (4) Å
β = 95.462 (5)°
V = 1433.7 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 (2) K
0.33 × 0.28 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.975, T_{max} = 0.984
7218 measured reflections
2518 independent reflections
1416 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.179
S = 1.04
2518 reflections
185 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2606).

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supplementary materials

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

J.-H. Peng, W.-J. Hao and S.-J. Tu

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 are widely used as agrochemical and pharmaceutical drugs (Ischikawa *et al.*, 1992; Labovitz *et al.*, 1990; Mizutani, Shiroshita, Okuda *et al.*, 1989; Patterson, 1992; Coghlan *et al.*, 1989; Mizutani, Shiroshita, Sakaki *et al.*, 1989; Munro & Bit, 1987). They can act as microbicides, pollen suppressants, fungicides and herbicides in agrochemistry. They can also be used as bactericides in pharmaceutical industry (Inoue *et al.*, 1993; Tutsumi *et al.*, 1992; Yokomoto *et al.*, 1992; Miyamoto *et al.*, 1990). The chemistry of cinnolines has received much attention based on the above facts.

The asymmetric unit of the title compound contains two-halves of centrosymmetric molecules (Fig. 1). The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The pyridazine rings A (N1/N2/C1-C3/C2A) and C (N3/N4/C9-C11/C10B) are, of course, planar and they are oriented at a dihedral angle of 43.89 (3)° [symmetry codes: (A) 2 - x, -y, -z; (B) 1 - x, -y, -z]. The cyclohexene rings B (C1/C2/C5/C6/C3A/C4A) and D (C9/C10/C13/C14/C11B/C12B), having total puckering amplitudes, Q_T, of 0.579 (3) and 0.566 Å, respectively, half-chair conformations [φ = -72.92 (3)° and θ = 103.84 (4)°; φ = 110.31 (4)° and θ = 74.14 (4)°] (Cremer & Pople, 1975) [symmetry codes: (A) 2 - x, -y, -z; (B) 1 - x, -y, -z].

Experimental

The title compound was prepared by the reaction of 3,4,6,7-tetrahydro- 3,3,6,6,9-pentamethyl-2*H*-xanthene-1,8(5*H*,9H)-dione (2 mmol) and hydrazine hydrate (8 mmol, 80%) in ethanol (8 ml), stirring at 353 K (yield; 88%, m.p. 562-563 K). Crystals suitable for X-ray analysis were obtained from an ethanol solution by slow evaporation.

Refinement

H atoms were positioned geometrically, with C-H = 0.97 and 0.96 Å for methylene and methyl H and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where x = 1.5 for methyl H and x = 1.2 for methylene H atoms.

Figures

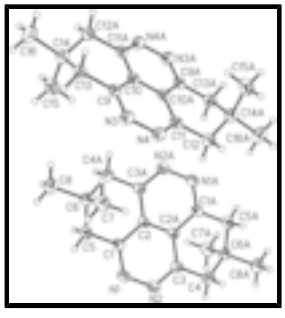


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry code (A): -x, -y, -z].

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

Crystal data

$C_{16}H_{20}N_4$	F_{000} = 576
M_r = 268.36	D_x = 1.243 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point = 562–563 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 12.819 (4) Å	Cell parameters from 1230 reflections
b = 8.441 (3) Å	θ = 2.3–23.2º
c = 13.310 (4) Å	μ = 0.08 mm^{-1}
β = 95.462 (5)º	T = 298 (2) K
V = 1433.7 (8) Å^3	Block, pale yellow
Z = 4	0.33 × 0.28 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2518 independent reflections
Radiation source: fine-focus sealed tube	1416 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.048
T = 298(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Bruker, 1998)	h = −15→15
T_{min} = 0.975, T_{max} = 0.984	k = −9→10
7218 measured reflections	l = −15→14

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.052	H-atom parameters constrained
$wR(F^2)$ = 0.179	$w = 1/[\sigma^2(F_o^2) + 0.3048P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
2518 reflections	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
185 parameters	$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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_{iso}*/U_{eq}
N1	1.11488 (18)	0.2369 (3)	0.00759 (19)	0.0510 (7)
N2	1.16426 (18)	0.1239 (3)	−0.04672 (19)	0.0513 (7)
N3	0.50653 (19)	0.2577 (3)	−0.08920 (17)	0.0469 (6)
N4	0.56253 (19)	0.1517 (3)	−0.14224 (17)	0.0470 (6)
C1	1.0250 (2)	0.2044 (3)	0.04438 (19)	0.0394 (7)
C2	0.97626 (18)	0.0553 (3)	0.02796 (18)	0.0350 (7)
C3	1.1205 (2)	−0.0146 (3)	−0.06568 (19)	0.0408 (7)
C4	1.1709 (2)	−0.1336 (3)	−0.1275 (2)	0.0522 (8)
H4A	1.2463	−0.1185	−0.1187	0.063*
H4B	1.1479	−0.1161	−0.1982	0.063*
C5	0.9742 (2)	0.3236 (4)	0.1053 (2)	0.0483 (8)
H5A	0.9906	0.4287	0.0819	0.058*
H5B	1.0030	0.3146	0.1752	0.058*
C6	0.8543 (2)	0.3047 (3)	0.0998 (2)	0.0456 (7)
C7	0.8054 (2)	0.3422 (4)	−0.0065 (2)	0.0602 (9)
H7A	0.8324	0.2704	−0.0536	0.090*
H7B	0.8224	0.4490	−0.0237	0.090*
H7C	0.7307	0.3308	−0.0091	0.090*
C8	0.8112 (3)	0.4183 (4)	0.1746 (3)	0.0705 (10)
H8A	0.7364	0.4078	0.1711	0.106*
H8B	0.8290	0.5251	0.1582	0.106*
H8C	0.8411	0.3935	0.2416	0.106*
C9	0.4617 (2)	0.2110 (3)	−0.00971 (19)	0.0380 (7)
C10	0.47112 (19)	0.0524 (3)	0.02548 (18)	0.0361 (7)
C11	0.5739 (2)	0.0028 (3)	−0.11235 (19)	0.0386 (7)
C12	0.6346 (2)	−0.1106 (3)	−0.1700 (2)	0.0460 (8)
H12A	0.7083	−0.1023	−0.1463	0.055*
H12B	0.6267	−0.0816	−0.2408	0.055*
C13	0.3987 (2)	0.3244 (3)	0.0462 (2)	0.0443 (7)
H13A	0.3267	0.3235	0.0162	0.053*
H13B	0.4261	0.4306	0.0394	0.053*
C14	0.4010 (2)	0.2827 (3)	0.1591 (2)	0.0448 (8)
C15	0.5115 (3)	0.3042 (4)	0.2106 (2)	0.0646 (10)

H15A	0.5326	0.4127	0.2047	0.097*
H15B	0.5590	0.2368	0.1790	0.097*
H15C	0.5124	0.2767	0.2807	0.097*
C16	0.3261 (3)	0.3920 (4)	0.2079 (2)	0.0652 (10)
H16A	0.3267	0.3663	0.2782	0.098*
H16B	0.2566	0.3788	0.1754	0.098*
H16C	0.3480	0.5000	0.2010	0.098*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0418 (15)	0.0440 (15)	0.0675 (17)	−0.0085 (12)	0.0070 (13)	−0.0044 (13)
N2	0.0442 (14)	0.0409 (15)	0.0702 (17)	−0.0060 (12)	0.0122 (12)	−0.0011 (13)
N3	0.0583 (16)	0.0392 (14)	0.0445 (14)	−0.0001 (12)	0.0117 (12)	0.0062 (11)
N4	0.0593 (16)	0.0392 (15)	0.0442 (14)	−0.0027 (12)	0.0133 (12)	0.0036 (11)
C1	0.0385 (16)	0.0370 (17)	0.0416 (16)	−0.0029 (13)	−0.0025 (13)	0.0016 (13)
C2	0.0322 (15)	0.0314 (15)	0.0402 (16)	−0.0019 (11)	−0.0026 (12)	0.0033 (11)
C3	0.0413 (16)	0.0387 (17)	0.0424 (16)	−0.0017 (14)	0.0045 (13)	0.0057 (13)
C4	0.0490 (18)	0.050 (2)	0.0595 (19)	0.0021 (15)	0.0164 (15)	0.0029 (15)
C5	0.0491 (18)	0.0458 (18)	0.0488 (17)	−0.0039 (15)	−0.0014 (14)	−0.0070 (14)
C6	0.0457 (17)	0.0406 (17)	0.0507 (17)	0.0024 (14)	0.0067 (14)	−0.0028 (14)
C7	0.055 (2)	0.052 (2)	0.071 (2)	0.0062 (16)	−0.0062 (16)	0.0042 (17)
C8	0.068 (2)	0.061 (2)	0.084 (3)	0.0038 (19)	0.0189 (19)	−0.0165 (19)
C9	0.0411 (16)	0.0354 (17)	0.0370 (15)	−0.0034 (13)	0.0004 (12)	0.0020 (13)
C10	0.0367 (15)	0.0380 (17)	0.0331 (15)	−0.0046 (12)	0.0008 (11)	0.0016 (11)
C11	0.0412 (16)	0.0380 (17)	0.0366 (15)	−0.0045 (13)	0.0033 (12)	0.0039 (13)
C12	0.0470 (17)	0.0492 (19)	0.0429 (16)	0.0018 (14)	0.0091 (13)	0.0031 (14)
C13	0.0459 (17)	0.0349 (16)	0.0518 (17)	−0.0025 (13)	0.0030 (13)	0.0026 (14)
C14	0.0489 (18)	0.0416 (18)	0.0438 (16)	0.0031 (14)	0.0053 (14)	−0.0027 (13)
C15	0.064 (2)	0.061 (2)	0.065 (2)	−0.0014 (18)	−0.0099 (17)	−0.0108 (18)
C16	0.081 (2)	0.060 (2)	0.057 (2)	0.0161 (19)	0.0187 (18)	−0.0003 (17)

Geometric parameters (Å, °)

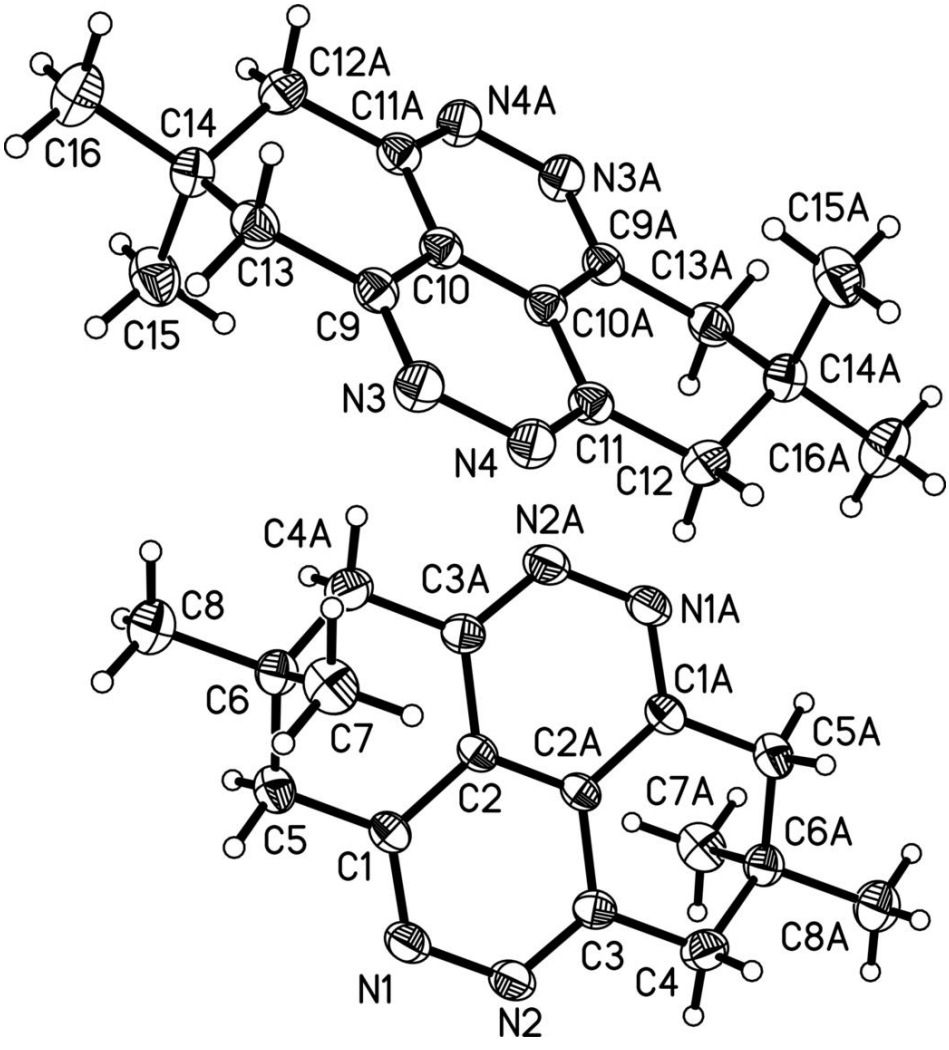
N1—C1	1.322 (3)	C8—H8A	0.9600
N1—N2	1.386 (3)	C8—H8B	0.9600
N2—C3	1.311 (3)	C8—H8C	0.9600
N3—C9	1.312 (3)	C9—C10	1.420 (4)
N3—N4	1.382 (3)	C9—C13	1.495 (4)
N4—C11	1.323 (4)	C10—C10^{ii}	1.373 (5)
C1—C2	1.413 (3)	C10—C11^{ii}	1.419 (3)
C1—C5	1.482 (4)	C11—C10^{ii}	1.419 (3)
C2—C2^{i}	1.371 (5)	C11—C12	1.491 (4)
C2—C3^{i}	1.423 (3)	C12—C14^{ii}	1.534 (4)
C3—C2^{i}	1.423 (3)	C12—H12A	0.9700
C3—C4	1.485 (4)	C12—H12B	0.9700
C4—C6^{i}	1.533 (4)	C13—C14	1.541 (4)

C4—H4A	0.9700	C13—H13A	0.9700
C4—H4B	0.9700	C13—H13B	0.9700
C5—C6	1.540 (4)	C14—C16	1.521 (4)
C5—H5A	0.9700	C14—C15	1.525 (4)
C5—H5B	0.9700	C14—C12^{ii}	1.534 (4)
C6—C8	1.524 (4)	C15—H15A	0.9600
C6—C7	1.525 (4)	C15—H15B	0.9600
C6—C4^{i}	1.533 (4)	C15—H15C	0.9600
C7—H7A	0.9600	C16—H16A	0.9600
C7—H7B	0.9600	C16—H16B	0.9600
C7—H7C	0.9600	C16—H16C	0.9600
C1—N1—N2	120.5 (2)	H8A—C8—H8C	109.5
C3—N2—N1	120.4 (2)	H8B—C8—H8C	109.5
C9—N3—N4	120.4 (2)	N3—C9—C10	121.3 (2)
C11—N4—N3	120.6 (2)	N3—C9—C13	120.5 (2)
N1—C1—C2	121.0 (2)	C10—C9—C13	118.2 (2)
N1—C1—C5	120.4 (2)	C10^{ii}—C10—C11^{ii}	118.1 (3)
C2—C1—C5	118.6 (2)	C10^{ii}—C10—C9	118.5 (3)
C2^{i}—C2—C1	118.5 (3)	C11^{ii}—C10—C9	123.4 (2)
C2^{i}—C2—C3^{i}	118.3 (3)	N4—C11—C10^{ii}	121.0 (2)
C1—C2—C3^{i}	123.2 (2)	N4—C11—C12	120.2 (2)
N2—C3—C2^{i}	121.2 (2)	C10^{ii}—C11—C12	118.8 (2)
N2—C3—C4	120.5 (2)	C11—C12—C14^{ii}	112.6 (2)
C2^{i}—C3—C4	118.2 (2)	C11—C12—H12A	109.1
C3—C4—C6^{i}	113.0 (2)	C14^{ii}—C12—H12A	109.1
C3—C4—H4A	109.0	C11—C12—H12B	109.1
C6^{i}—C4—H4A	109.0	C14^{ii}—C12—H12B	109.1
C3—C4—H4B	109.0	H12A—C12—H12B	107.8
C6^{i}—C4—H4B	109.0	C9—C13—C14	112.2 (2)
H4A—C4—H4B	107.8	C9—C13—H13A	109.2
C1—C5—C6	113.1 (2)	C14—C13—H13A	109.2
C1—C5—H5A	109.0	C9—C13—H13B	109.2
C6—C5—H5A	109.0	C14—C13—H13B	109.2
C1—C5—H5B	109.0	H13A—C13—H13B	107.9
C6—C5—H5B	109.0	C16—C14—C15	109.4 (3)
H5A—C5—H5B	107.8	C16—C14—C12^{ii}	109.2 (2)
C8—C6—C7	109.5 (3)	C15—C14—C12^{ii}	110.0 (2)
C8—C6—C4^{i}	109.7 (2)	C16—C14—C13	108.9 (2)
C7—C6—C4^{i}	110.0 (2)	C15—C14—C13	110.0 (2)
C8—C6—C5	109.0 (2)	C12^{ii}—C14—C13	109.3 (2)
C7—C6—C5	110.1 (2)	C14—C15—H15A	109.5
C4^{i}—C6—C5	108.6 (2)	C14—C15—H15B	109.5
C6—C7—H7A	109.5	H15A—C15—H15B	109.5
C6—C7—H7B	109.5	C14—C15—H15C	109.5
H7A—C7—H7B	109.5	H15A—C15—H15C	109.5

C6—C7—H7C	109.5	H15B—C15—H15C	109.5
H7A—C7—H7C	109.5	C14—C16—H16A	109.5
H7B—C7—H7C	109.5	C14—C16—H16B	109.5
C6—C8—H8A	109.5	H16A—C16—H16B	109.5
C6—C8—H8B	109.5	C14—C16—H16C	109.5
H8A—C8—H8B	109.5	H16A—C16—H16C	109.5
C6—C8—H8C	109.5	H16B—C16—H16C	109.5

Symmetry codes: (i) −*x*+2, −*y*, −*z*; (ii) −*x*+1, −*y*, −*z*.

Fig. 1


C12A
C11A
N4A
C14
C16
N3A
C15A
C9A
C13A
C13
C10
C10A
C15
C9
C14A
N3
N4
C11
C12
C16A
C4A
N2A
C3A
C8
N1A
C1A
C6
C7
C5A
C2A
C2
C7A
C5
C1
C6A
C3
C8A
C4
N1
N2