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6*H*,13*H*-5,12:7,14-Dimethano-dinaphtho[2,3-*d*:2,3-*i*][1,3,6,8]tetra-azecine

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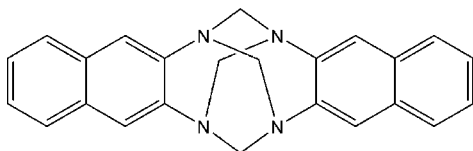
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.027; wR factor = 0.077; data-to-parameter ratio = 5.4.

In the title compound, $\text{C}_{24}\text{H}_{20}\text{N}_4$, obtained through the condensation of naphthalene-2,3-diamine with formaldehyde in methanol, the molecule is located on a special position of site symmetry $\bar{4}$. Due to symmetry considerations, the aromatic rings are strictly perpendicular to each other. In the crystal, molecules are linked by pairs of $\text{C}-\text{H}\cdots\pi$ interactions into columns along [110].

Related literature

For chemical background to the synthesis of the title compound, see: Volpp (1962). For related structures, see: Murray-Rust & Smith (1975); Rivera *et al.* (2009, 2011). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{24}\text{H}_{20}\text{N}_4$	$Z = 2$
$M_r = 364.5$	Cu $K\alpha$ radiation
Tetragonal, $I\bar{4}2m$	$\mu = 0.63$ mm ⁻¹
$a = 7.1996$ (2) Å	$T = 120$ K
$c = 17.4511$ (5) Å	$0.45 \times 0.22 \times 0.15$ mm
$V = 904.56$ (6) Å ³	

Data collection

Agilent Xcalibur diffractometer with an Atlas (Gemini ultra Cu) detector	4873 measured reflections
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2010)	273 independent reflections
$T_{\min} = 0.50$, $T_{\max} = 0.90$	268 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	51 parameters
$wR(F^2) = 0.077$	Only H-atom coordinates refined
$S = 1.85$	$\Delta\rho_{\text{max}} = 0.08$ e Å ⁻³
273 reflections	$\Delta\rho_{\text{min}} = -0.15$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$\text{Cg}1$ and $\text{Cg}2$ are the centroids of the $\text{C}2-\text{C}4/\text{C}2'-\text{C}4'$ and $\text{C}4-\text{C}6/\text{C}4'-\text{C}6'$ rings, respectively.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}3-\text{H}3\cdots\text{Cg}2^i$	1.042 (18)	2.648 (14)	3.6921 (14)	178.2 (15)
$\text{C}5-\text{H}5\cdots\text{Cg}1^i$	1.047 (18)	2.652 (14)	3.6979 (14)	178.0 (16)

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

Data collection: CrysAlis PRO (Agilent, 2010); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2003); program(s) used to refine structure: JANA2006 (Petříček *et al.*, 2006); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: JANA2006.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2445).

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6*H*,13*H*-5,12:7,14-Dimethanodinaphtho[2,3-*d*:2,3-*i*][1,3,6,8]tetraazecine

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S1. Comment

We have as a general goal the design and synthesis of new macrocyclic saturated ring-fused amins, of considerable interest as useful intermediates for the synthesis of *N*-containing heterocyclic compounds. These amins comprise a family of preformed electrophilic reagents which have been utilized in condensation reactions with electron-rich aromatic compounds in a variant of the Mannich reaction. These ring-fused amins are frequently prepared by reaction of 1,2-diamines with formaldehyde (Volpp, 1962). By an analogous route we prepared for the first time 6*H*,13*H*-5,12:7,14-dimethanodinaphtho[2,3-*d*:2,3-*i*][1,3,6,8]tetraazecine (**I**).

The molecular structure and atom-numbering scheme for (**I**) are shown in Fig. 1. Unlike the related structures, which crystallized in orthorhombic space groups *Aba2* (Rivera *et al.*, 2009, 2011) and *Pbcn* (Murray-Rust & Smith, 1975), the title compound (**I**) crystallizes in the tetragonal $I\bar{4}2m$ space group with one quarter-molecule in the asymmetric unit (located on a special position of site symmetry $\bar{4}$). The X-ray structure of **I** shows similar features to other ring-fused amins. So, the bond lengths and angles are normal (Allen *et al.*, 1987) and similar to those observed for related structures (Murray-Rust & Smith, 1975; Rivera *et al.*, 2009; Rivera *et al.*, 2011).

Due to symmetry considerations the aromatic rings are strictly perpendicular to each other. In the crystal packing (Fig. 2), the molecules are linked by a pair of C—H $\cdots\pi$ interactions (Table 1) into columns along [110].

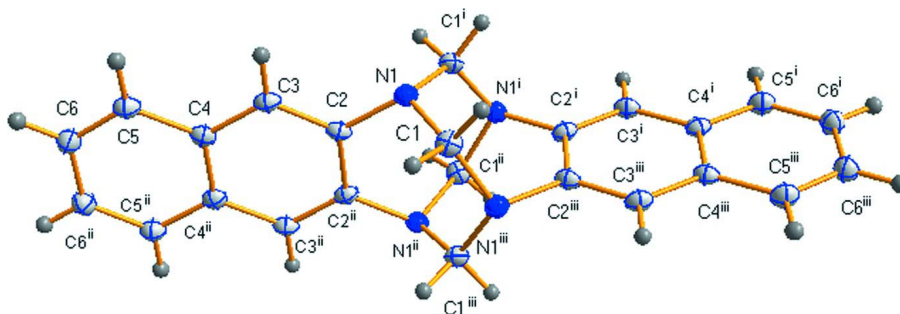
S2. Experimental

A solution of naphthalene-2,3-diamine (158 mg, 1 mmol) in methanol (10 ml) was added dropwise at 273 K to 5 ml of 37% aqueous formaldehyde. The reaction mixture was stirring at this temperature for 1 h and its completion was monitored by TLC. After completion, the contents were poured over cold water (10 ml). The resultant solid was isolated by filtration, washed with cold water, dried in vacuum and recrystallized from ethyl acetate to give the title compound with 28% yield. The melting point of the title structure is 484 K.

¹H NMR (δ , 400 MHz, CDCl₃): 4.55, 7.52, 7.74, 7.86. ¹³C NMR (δ , 100 MHz, CDCl₃): 70.2, 125.6, 126.2, 127.7, 133.0, 151.9.

S3. Refinement

The H atoms were found in difference Fourier maps and their coordinates were refined freely. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2 \times U_{eq}$ of the parent atom. As the structure contains only light atoms, the Friedel-pair reflections were merged and the Flack parameter has not been determined.

**Figure 1**

A view of (I) with the numbering scheme, displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $1 + y, 1 - x, -z$; (ii) $2 - x, -y, z$; (iii) $1 - y, -1 + x, -z$.

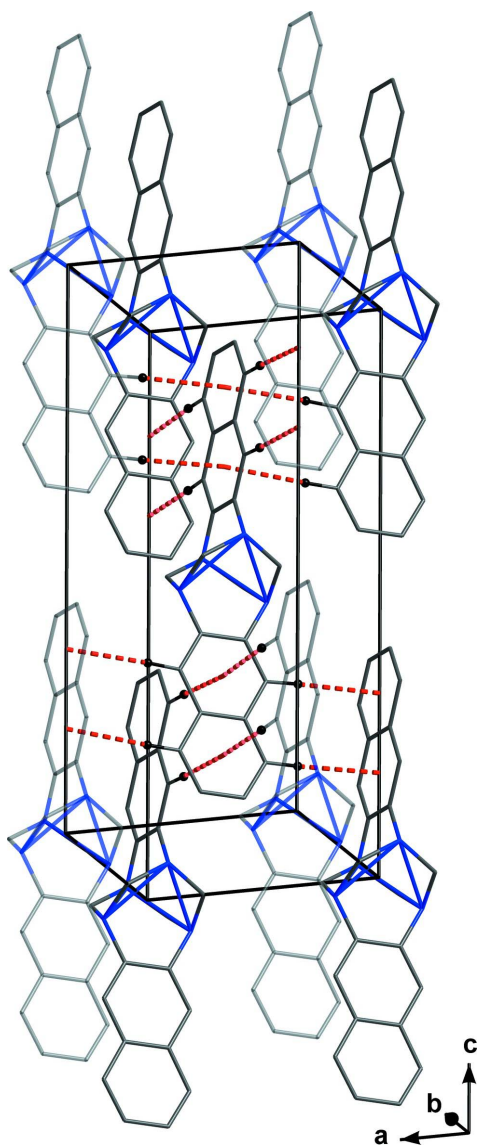


Figure 2

Packing of the molecules of the title compound view along *b* axis.

1,12,14,25-tetraazaheptacyclo[12.12.1.1^{12,25}.0^{2,11}.0^{4,9}.0^{15,24}.0^{17,22}]octacos-2,4(9),5,7,10,15,17 (22),18,20,23-decaene

Crystal data

$C_{24}H_{20}N_4$	$D_x = 1.338 \text{ Mg m}^{-3}$
$M_r = 364.5$	Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$
Tetragonal, $I\bar{4}2m$	Cell parameters from 3581 reflections
Hall symbol: I -4 2	$\theta = 5.1\text{--}67.0^\circ$
$a = 7.1996 (2) \text{ \AA}$	$\mu = 0.63 \text{ mm}^{-1}$
$c = 17.4511 (5) \text{ \AA}$	$T = 120 \text{ K}$
$V = 904.56 (6) \text{ \AA}^3$	Irregular shape, yellow
$Z = 2$	$0.45 \times 0.22 \times 0.15 \text{ mm}$
$F(000) = 384$	

Data collection

Agilent Xcalibur	$T_{\min} = 0.50, T_{\max} = 0.90$
diffractometer with an Atlas (Gemini ultra Cu)	4873 measured reflections
detector	273 independent reflections
Radiation source: Enhance Ultra (Cu) X-ray	268 reflections with $I > 3\sigma(I)$
Source	$R_{\text{int}} = 0.025$
Mirror monochromator	$\theta_{\max} = 67.1^\circ, \theta_{\min} = 5.1^\circ$
Detector resolution: 10.3784 pixels mm^{-1}	$h = -8 \rightarrow 8$
Rotation method, ω scans	$k = -8 \rightarrow 8$
Absorption correction: multi-scan	$l = -20 \rightarrow 20$
(<i>CrysAlis PRO</i> ; Agilent, 2010)	

Refinement

Refinement on F^2	4 constraints
$R[F > 3\sigma(F)] = 0.027$	Only H-atom coordinates refined
$wR(F) = 0.077$	Weighting scheme based on measured s.u.'s $w =$
$S = 1.85$	$1/(\sigma^2(I) + 0.0016I^2)$
273 reflections	$(\Delta/\sigma)_{\max} = 0.003$
51 parameters	$\Delta\rho_{\max} = 0.08 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$

Special details

Refinement. The refinement was carried out against all reflections. The conventional *R*-factor is always based on *F*. The goodness of fit as well as the weighted *R*-factor are based on *F* and F^2 for refinement carried out on *F* and F^2 , respectively. The threshold expression is used only for calculating *R*-factors *etc.* and it is not relevant to the choice of reflections for refinement.

The program used for refinement, Jana2006, uses the weighting scheme based on the experimental expectations, see `_refine_ls_weighting_details`, that does not force *S* to be one. Therefore the values of *S* are usually larger than the ones from the *SHELX* program.

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	0.86029 (13)	0.13971 (13)	0.04360 (8)	0.0180 (4)
C1	0.7560 (2)	0	0	0.0187 (4)
C2	0.92982 (16)	0.07018 (16)	0.11529 (9)	0.0175 (4)

C3	0.86239 (18)	0.13761 (18)	0.18326 (11)	0.0194 (4)
C4	0.9299 (2)	0.0701 (2)	0.25428 (9)	0.0181 (4)
C5	0.86279 (18)	0.13721 (18)	0.32562 (11)	0.0221 (4)
C6	0.93073 (18)	0.06927 (18)	0.39302 (9)	0.0222 (4)
H1	0.677 (2)	0.0686 (18)	-0.0400 (7)	0.0225*
H3	0.760 (2)	0.240 (2)	0.1798 (11)	0.0233*
H5	0.760 (2)	0.240 (2)	0.3243 (12)	0.0265*
H6	0.886 (2)	0.114 (2)	0.4421 (13)	0.0266*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0174 (5)	0.0174 (5)	0.0191 (8)	0.0016 (7)	0.0002 (4)	-0.0002 (4)
C1	0.0152 (8)	0.0201 (8)	0.0210 (7)	0	0	0.0003 (7)
C2	0.0158 (5)	0.0158 (5)	0.0208 (9)	0.0001 (7)	-0.0016 (5)	0.0016 (5)
C3	0.0174 (6)	0.0174 (6)	0.0235 (10)	0.0026 (7)	0.0007 (5)	-0.0007 (5)
C4	0.0168 (6)	0.0168 (6)	0.0208 (8)	-0.0015 (7)	-0.0008 (5)	0.0008 (5)
C5	0.0211 (6)	0.0211 (6)	0.0240 (10)	0.0031 (8)	0.0002 (4)	-0.0002 (4)
C6	0.0234 (6)	0.0234 (6)	0.0196 (7)	0.0012 (8)	0.0007 (5)	-0.0007 (5)

Geometric parameters (Å, °)

N1—C1	1.4680 (13)	C3—H3	1.042 (18)
N1—C1 ⁱ	1.4680 (13)	C4—C4 ⁱⁱⁱ	1.428 (2)
N1—C2	1.437 (2)	C4—C5	1.420 (2)
C1—H1	1.027 (13)	C5—C6	1.365 (2)
C1—H1 ⁱⁱ	1.027 (13)	C5—H5	1.047 (18)
C2—C2 ⁱⁱⁱ	1.4292 (17)	C6—C6 ⁱⁱⁱ	1.4106 (18)
C2—C3	1.370 (2)	C6—H6	0.97 (2)
C3—C4	1.417 (2)		
C1—N1—C1 ⁱ	115.64 (9)	C2—C3—C4	120.94 (12)
C1—N1—C2	113.00 (8)	C2—C3—H3	116.7 (11)
C1 ⁱ —N1—C2	113.00 (8)	C4—C3—H3	122.3 (11)
N1—C1—N1 ^{iv}	118.44 (11)	C3—C4—C4 ⁱⁱⁱ	118.99 (14)
N1—C1—H1	107.8 (7)	C3—C4—C5	122.26 (13)
N1—C1—H1 ⁱⁱ	105.1 (7)	C4 ⁱⁱⁱ —C4—C5	118.74 (14)
N1 ^{iv} —C1—H1	105.1 (7)	C4—C5—C6	120.80 (13)
N1 ^{iv} —C1—H1 ⁱⁱ	107.8 (7)	C4—C5—H5	117.5 (11)
H1—C1—H1 ⁱⁱ	112.7 (11)	C6—C5—H5	121.7 (11)
N1—C2—C2 ⁱⁱⁱ	119.50 (13)	C5—C6—C6 ⁱⁱⁱ	120.46 (14)
N1—C2—C3	120.43 (11)	C5—C6—H6	121.7 (10)
C2 ⁱⁱⁱ —C2—C3	120.06 (14)	C6 ⁱⁱⁱ —C6—H6	117.8 (10)

Symmetry codes: (i) $y+1, -x+1, -z$; (ii) $x, -y, -z$; (iii) $-x+2, -y, z$; (iv) $-y+1, x-1, -z$.

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

Cg1 and Cg2 are the centroids of the C2–C4/C2'–C4' and C4–C6/C4'–C6' rings, respectively.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C3—H3 \cdots Cg2 ^v	1.042 (18)	2.648 (14)	3.6921 (14)	178.2 (15)
C5—H5 \cdots Cg1 ^v	1.047 (18)	2.652 (14)	3.6979 (14)	178.0 (16)

Symmetry code: (v) $-y+1/2, x-1/2, -z+1/2$.