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2,2′-(2,6-Pyridinediyl)diquinoline

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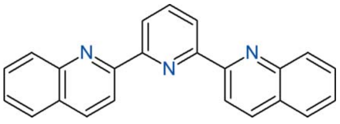
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.041; wR factor = 0.118; data-to-parameter ratio = 12.0.

The title molecule, $C_{23}H_{15}N_3$, is a terpyridine derivative resulting from the Friedländer annulation between 2,6-diacetylpyridine and N,N'-bis(2-aminobenzyl)ethylenediamine. The asymmetric unit contains one half-molecule, the complete molecule being generated by a mirror plane (one N atom and one C atom lie on the plane). The molecule, although aromatic, is deformed from planarity as a result of crystal packing forces: molecules are stacked along the short c axis, with a short separation of 3.605 (1) Å between the mean planes. The bent molecular shape is reflected in the dihedral angle of 16.10 (5)° between the essentially planar quinoline groups. In addition to $\pi\cdots\pi$ interactions, the crystal structure features weak inter-stack C—H$\cdots$N contacts involving atoms of the central pyridine rings which lie in a common crystallographic m plane.

Related literature

For the synthesis and the coordination behavior of the title molecule, see: Bertrand *et al.* (2009); Harris *et al.* (1969); Klassen *et al.* (1975). For a terpyridine derivative closely related to the title molecule, see: Sasaki *et al.* (1998). For the Friedländer condensation as a tool for the preparation of quinolines, see: Da Costa *et al.* (2009); Sridharan *et al.* (2009).



Experimental

Crystal data

$C_{23}H_{15}N_3$
M_r = 333.38
Orthorhombic, *Pnma*
a = 11.960 (2) Å
b = 34.509 (6) Å
c = 3.9509 (5) Å
V = 1630.7 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 K
0.40 × 0.20 × 0.10 mm

Data collection

Siemens P4 diffractometer
5603 measured reflections
1469 independent reflections
1032 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
2 standard reflections every 48 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.118
S = 1.02
1469 reflections
122 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.11 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
C1—H1$A$$\cdots$N1$^{\rm i}$	0.93	2.72	3.641 (3)	169

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

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus* and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2726).

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2,2′-(2,6-Pyridinediyl)diquinoline

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S1. Comment

Thirty years after cisplatin was approved by the FDA for its use as a chemotherapy drug, studies regarding interactions between platinum-based complexes and basic sites in DNA remain actives. Recently, Bertrand *et al.* (2009) showed that Pt^{II} cationic complexes bearing 2,2′:6′,2"-terpyridine or a terpyridine derivative as ligand have the ability to platinate the human telomeric G-quadruplex. Interestingly, both the binding affinity and the platination activity seem to be determined by the extension of the aromatic surface of the terpyridine derivative. One of the ligands used in that work was 2,2′-(2,6-pyridinediyl)bis-quinoline, synthesized through the Friedländer condensation (Da Costa *et al.*, 2009; Sridharan *et al.*, 2009) between 2,6-diacetylpyridine and 2-nitrobenzaldehyde. We now report the crystal structure of this aromatic ligand.

The title terpyridine derivative was obtained as a by-product during the preparation of a macrocyclic ligand (see *Experimental*). More suitable synthesis are however available in the literature (Harris *et al.*, 1969; Klassen *et al.*, 1975; Bertrand *et al.*, 2009). The molecule (Fig. 1) displays the crystallographic *m* symmetry, with atoms N1, C1 and H1A placed in the mirror planes normal to [010]. The molecular conformation observed in the solid-state is not suitable for coordination through the three N atoms: the quinoline N atoms are placed in a *trans* arrangement with respect to the central pyridine N atom, while a *cis*,*cis* conformation is required for the molecule to be a terdentate ligand. However, as invariably found in non-hindered terpyridine derivatives, aromatic fragments are free to rotate, for example about the C3—C4 bond in the case of the title molecule. Such a behavior has been reported, for example, for the coordination to Ru^{II} of a closely related terpyridine ligand, namely 2,6-bis(5,6,7,8-tetrahydroquinol-2-yl)pyridine (Sasaki *et al.*, 1998).

Molecules are stacked along the short axis *c*, at a distance of 3.605 Å (separation between two mean planes passing through two neighboring molecules in the [001] direction, see Fig.2, inset). This short separation, although larger than that observed in graphite (*ca.* 3.36 Å), results in strong $\pi\cdots\pi$ interactions in the stacks, which, in turn, deform the molecules from planarity. The dihedral angle between the central pyridine ring and the quinoline substituent is 8.13 (8)°. The bent shape is also reflected in the dihedral angle between quinoline systems, 16.10 (5)° (Fig. 2, inset). Finally, the crystal structure is completed by weak intermolecular C—H···N contacts (Table 1 and Fig. 2), linking the stacks in the [100] direction.

S2. Experimental

A mixture of 305 mg of 2,6-diacetylpyridine and 823 mg of $Ce(NO_3)_3.6H_2O$ in methanol (25 ml) was refluxed for 30 min, followed by slow addition of a dissolution of *N*,*N*′-bis(2-aminobenzyl)ethylenediamine (530 mg in 25 ml methanol). The mixture was kept under these conditions for 3.5 h, and then cooled to room temperature, giving a red precipitate. After 1.5 month, the resulting solid was filtered, washed with cold methanol, diethyl ether, and air dried. Suitable single crystals were picked off from the solid. m.p. 495–497 K (lit. 500–501 K: Klassen *et al.*, 1975).

S3. Refinement

All H atoms were placed in idealized positions, with C—H bond lengths fixed to 0.93 Å. Isotropic displacement parameters for H atoms were calculated from displacements of parent C atoms: $U_{iso}(H) = 1.2U_{eq}(C)$.

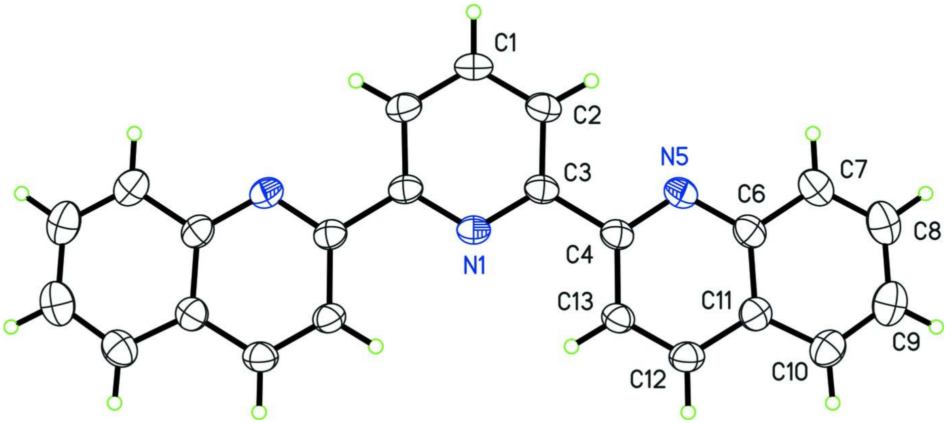

Figure 1

The structure of the title compound, with displacement ellipsoids at the 30% probability level for non-H atoms. Non-labeled atoms are generated by symmetry code *x*, 1/2-*y*, *z*.

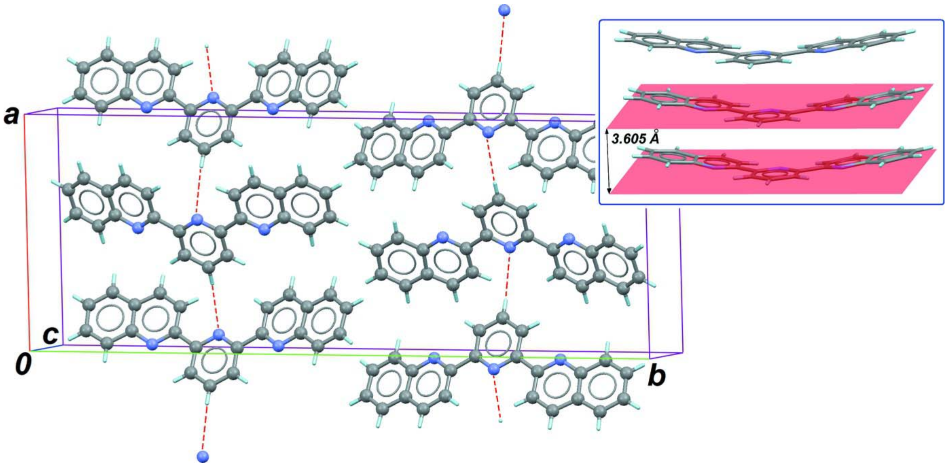

Figure 2

A part of the crystal structure, viewed down *c* axis. Dashed lines represent non-bonding intermolecular contacts. The inset shows a part of a stack along [001]. Two least-squares planes are represented (red), which were computed using all atoms in each selected molecule (Macrae *et al.*, 2008).

2,2′-(2,6-Pyridinediyl)diquinoline

Crystal data

$C_{23}H_{15}N_3$	$Z = 4$
$M_r = 333.38$	$F(000) = 696$
Orthorhombic, *Pnma*	$D_x = 1.358$ Mg m^{-3}
Hall symbol: -P 2ac 2n	Melting point = 495–497 K
$a = 11.960$ (2) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 34.509$ (6) Å	Cell parameters from 100 reflections
$c = 3.9509$ (5) Å	$\theta = 5.5–11.7°$
$V = 1630.7$ (5) Å^3	$\mu = 0.08$ mm^{-1}

T = 298 K
Plate, orange

0.40 × 0.20 × 0.10 mm

Data collection

Siemens P4 diffractometer
Radiation source: X-ray
Graphite monochromator
ω scans
5603 measured reflections
1469 independent reflections
1032 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.031
$\theta_{\rm max}$ = 25.1°, $\theta_{\rm min}$ = 2.4°
$h = -14 \rightarrow 14$
$k = -41 \rightarrow 41$
$l = -4 \rightarrow 4$
2 standard reflections every 48 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.118$
S = 1.02
1469 reflections
122 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.1644P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.11 e Å^{-3}
Extinction correction: *SHELXTL-Plus*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0069 (16)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
N1	0.05056 (13)	0.2500	0.0324 (4)	0.0465 (5)
C1	−0.15745 (18)	0.2500	−0.2714 (6)	0.0572 (6)
H1A	−0.2280	0.2500	−0.3703	0.069*
C2	−0.10509 (12)	0.28415 (5)	−0.1980 (4)	0.0539 (4)
H2A	−0.1388	0.3077	−0.2506	0.065*
C3	−0.00108 (11)	0.28327 (4)	−0.0443 (4)	0.0465 (4)
C4	0.05844 (12)	0.32017 (4)	0.0278 (4)	0.0468 (4)
N5	0.00977 (10)	0.35190 (4)	−0.0808 (3)	0.0522 (4)
C6	0.06408 (13)	0.38627 (4)	−0.0411 (4)	0.0522 (4)
C7	0.01369 (16)	0.42018 (5)	−0.1667 (5)	0.0667 (5)
H7A	−0.0563	0.4188	−0.2686	0.080*
C8	0.06583 (19)	0.45476 (5)	−0.1410 (5)	0.0752 (6)
H8A	0.0319	0.4769	−0.2279	0.090*
C9	0.17008 (19)	0.45757 (5)	0.0147 (5)	0.0762 (6)
H9A	0.2049	0.4816	0.0326	0.091*
C10	0.22110 (16)	0.42554 (5)	0.1402 (5)	0.0660 (5)
H10A	0.2907	0.4278	0.2437	0.079*
C11	0.16971 (13)	0.38897 (4)	0.1153 (4)	0.0528 (4)
C12	0.21698 (13)	0.35438 (4)	0.2379 (4)	0.0555 (4)
H12A	0.2859	0.3549	0.3468	0.067*
C13	0.16215 (12)	0.32044 (4)	0.1973 (4)	0.0511 (4)

H13A	0.1925	0.2975	0.2804	0.061*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0355 (9)	0.0555 (11)	0.0484 (10)	0.000	0.0022 (8)	0.000
C1	0.0364 (11)	0.0734 (16)	0.0619 (14)	0.000	−0.0071 (11)	0.000
C2	0.0404 (8)	0.0637 (10)	0.0576 (10)	0.0072 (7)	−0.0014 (7)	−0.0021 (8)
C3	0.0361 (7)	0.0586 (9)	0.0448 (8)	0.0043 (7)	0.0045 (6)	−0.0018 (7)
C4	0.0395 (8)	0.0554 (9)	0.0456 (8)	0.0054 (7)	0.0048 (7)	−0.0030 (7)
N5	0.0442 (7)	0.0569 (8)	0.0555 (8)	0.0078 (6)	0.0016 (6)	−0.0002 (7)
C6	0.0506 (9)	0.0563 (10)	0.0498 (9)	0.0089 (8)	0.0066 (7)	−0.0027 (8)
C7	0.0688 (11)	0.0654 (11)	0.0659 (11)	0.0147 (9)	0.0013 (9)	0.0016 (9)
C8	0.0985 (16)	0.0599 (12)	0.0672 (12)	0.0145 (11)	0.0066 (12)	0.0053 (10)
C9	0.0981 (16)	0.0617 (11)	0.0687 (13)	−0.0086 (11)	0.0121 (11)	−0.0025 (10)
C10	0.0672 (11)	0.0673 (11)	0.0635 (11)	−0.0064 (10)	0.0044 (9)	−0.0083 (9)
C11	0.0522 (9)	0.0561 (10)	0.0501 (9)	0.0020 (7)	0.0060 (8)	−0.0062 (8)
C12	0.0443 (8)	0.0648 (11)	0.0575 (10)	0.0031 (8)	−0.0032 (7)	−0.0078 (8)
C13	0.0426 (8)	0.0545 (9)	0.0561 (9)	0.0077 (7)	−0.0033 (7)	−0.0043 (7)

Geometric parameters (Å, º)

N1—C3^{i}	1.3383 (16)	C7—C8	1.350 (2)
N1—C3	1.3383 (16)	C7—H7A	0.9300
C1—C2	1.3658 (18)	C8—C9	1.394 (3)
C1—C2^{i}	1.3658 (18)	C8—H8A	0.9300
C1—H1A	0.9300	C9—C10	1.357 (2)
C2—C3	1.385 (2)	C9—H9A	0.9300
C2—H2A	0.9300	C10—C11	1.407 (2)
C3—C4	1.486 (2)	C10—H10A	0.9300
C4—N5	1.3123 (18)	C11—C12	1.407 (2)
C4—C13	1.410 (2)	C12—C13	1.352 (2)
N5—C6	1.3615 (19)	C12—H12A	0.9300
C6—C7	1.407 (2)	C13—H13A	0.9300
C6—C11	1.410 (2)		
C3^{i}—N1—C3	118.13 (17)	C6—C7—H7A	119.6
C2—C1—C2^{i}	119.3 (2)	C7—C8—C9	120.52 (18)
C2—C1—H1A	120.3	C7—C8—H8A	119.7
C2^{i}—C1—H1A	120.3	C9—C8—H8A	119.7
C1—C2—C3	119.07 (15)	C10—C9—C8	120.48 (18)
C1—C2—H2A	120.5	C10—C9—H9A	119.8
C3—C2—H2A	120.5	C8—C9—H9A	119.8
N1—C3—C2	122.20 (14)	C9—C10—C11	120.57 (18)
N1—C3—C4	118.07 (13)	C9—C10—H10A	119.7
C2—C3—C4	119.69 (13)	C11—C10—H10A	119.7
N5—C4—C13	122.69 (14)	C12—C11—C10	124.15 (16)
N5—C4—C3	116.09 (13)	C12—C11—C6	117.07 (14)

C13—C4—C3	121.21 (13)	C10—C11—C6	118.78 (15)
C4—N5—C6	118.54 (13)	C13—C12—C11	119.96 (14)
N5—C6—C7	118.67 (15)	C13—C12—H12A	120.0
N5—C6—C11	122.39 (14)	C11—C12—H12A	120.0
C7—C6—C11	118.92 (15)	C12—C13—C4	119.27 (14)
C8—C7—C6	120.72 (18)	C12—C13—H13A	120.4
C8—C7—H7A	119.6	C4—C13—H13A	120.4

C2^{i}—C1—C2—C3	−1.4 (3)	C6—C7—C8—C9	−0.8 (3)
C3^{i}—N1—C3—C2	0.1 (3)	C7—C8—C9—C10	0.5 (3)
C3^{i}—N1—C3—C4	−177.46 (10)	C8—C9—C10—C11	0.0 (3)
C1—C2—C3—N1	0.6 (3)	C9—C10—C11—C12	179.83 (16)
C1—C2—C3—C4	178.17 (16)	C9—C10—C11—C6	−0.3 (3)
N1—C3—C4—N5	173.63 (14)	N5—C6—C11—C12	−1.3 (2)
C2—C3—C4—N5	−4.0 (2)	C7—C6—C11—C12	179.88 (15)
N1—C3—C4—C13	−5.2 (2)	N5—C6—C11—C10	178.75 (14)
C2—C3—C4—C13	177.17 (14)	C7—C6—C11—C10	0.0 (2)
C13—C4—N5—C6	3.0 (2)	C10—C11—C12—C13	−178.88 (16)
C3—C4—N5—C6	−175.81 (13)	C6—C11—C12—C13	1.2 (2)
C4—N5—C6—C7	178.05 (14)	C11—C12—C13—C4	0.8 (2)
C4—N5—C6—C11	−0.7 (2)	N5—C4—C13—C12	−3.1 (2)
N5—C6—C7—C8	−178.24 (16)	C3—C4—C13—C12	175.65 (14)
C11—C6—C7—C8	0.6 (2)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···N1^{ii}	0.93	2.72	3.641 (3)	169

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