

5-Nitro-2,3-bis(2-pyridyl)quinoxaline

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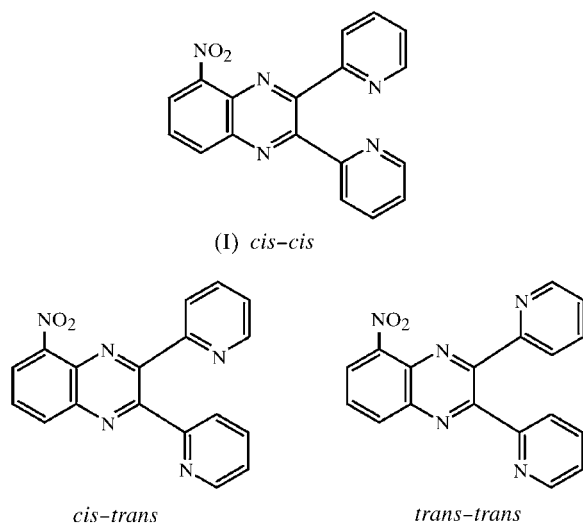
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In the crystal structure of the title compound, $C_{18}H_{11}N_5O_2$, two crystallographically independent molecules having the same composition and *cis-cis* conformation (arrangement of the pyridyl rings) are observed. A C—H...N hydrogen bond links the centrosymmetrically related molecules into a discrete pair [$C\cdots N = 3.462(4)$ Å], and the structure is stabilized further by π - π -stacking interactions between aromatic rings from two adjacent dimers.

Comment

Polypyridyl bridging ligands have attracted much attention as building blocks for supramolecular assemblies in recent years (Leininger *et al.*, 2000; Bu *et al.*, 2001). Some polypyridyl compounds have also been actively studied [such as 2,3-bis(2-pyridyl)quinoxaline and its derivatives, which represent an important class of chelating agents] because of the potential



functionality of their metal complexes as molecular devices and DNA probes (Holmlin & Barton, 1995; Balzani, Campagna *et al.*, 1998; Balzani, Gomez-Lopez & Stoddart, 1998). In efforts to investigate systematically the syntheses,

molecular structures and coordination chemistry of such compounds, we have reported the crystal structures of 5,6-bis(2-pyridyl)-2,3-pyrazinedicarbonitrile (Du *et al.*, 2001) and of the so-called proton-sponge compounds 2,3-bis(2-pyridinio)-5,8-dimethoxyquinoxaline dinitrate (Liu *et al.*, 2001) and 2,3-bis(2-pyridinio)-5-nitroquinoxaline diperchlorate (Xu *et al.*, 2002). In this contribution, we report the synthesis and crystal structure of 5-nitro-2,3-bis(2-pyridyl)quinoxaline, (I).

Compound (I) consists of a quinoxaline ring system substituted with two pyridyl (py) rings and a nitro group. Theoretically, such compounds have the potential to generate three possible configurations (referring to the relation of the pyridyl N atoms to the central ring) as depicted in the *Scheme* above, *viz.* *cis-cis*, *cis-trans* and *trans-trans*. The crystal structure of (I) contains two symmetry-independent molecules, *A* and *B*, that have the same composition. Note that both molecules have the unexpected *cis-cis* conformational arrangement of the pyridyl rings (Fig. 1); the favored orien-

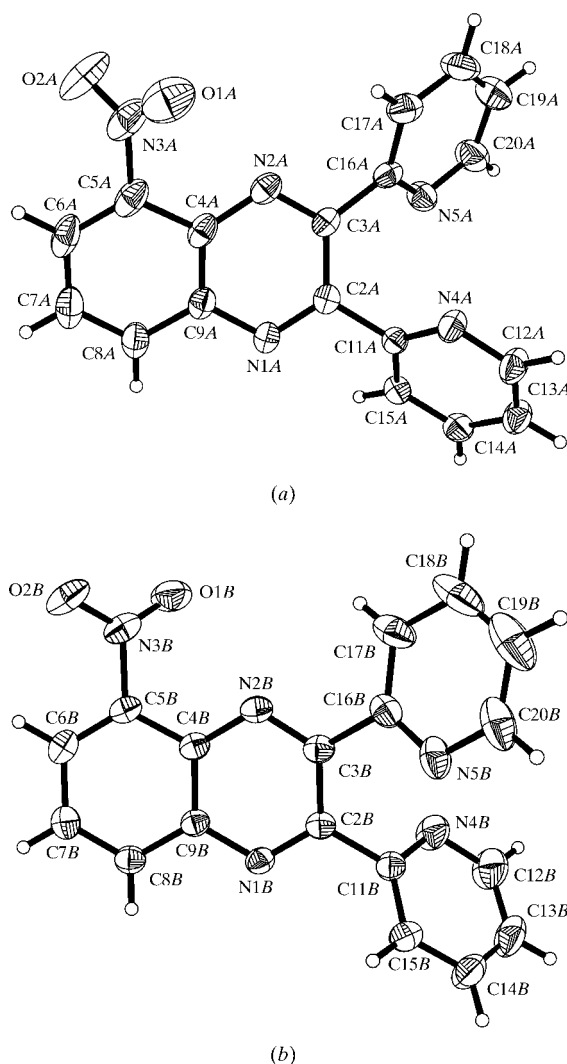


Figure 1
ORTEPII (Johnson, 1976) views of (a) molecule *A* and (b) molecule *B* of (I), with displacement ellipsoids shown at the 30% probability level.

tation of the pyridyl rings is such that their N atoms face one another. We have reported recently a novel box-like dinuclear Ag^{I} complex of (I), in which (I) takes the *cis-trans* configuration (Liu & Du, 2002), that is, the configuration of (I) is spontaneously converted when coordinated to an Ag^{I} center. In addition, in the crystal structure of the N-protonated perchlorate of the title compound (Xu *et al.*, 2002), the unexpected *trans-trans* configuration is observed.

In the structure of (I), two pyridyl rings in the same molecule are not coplanar with either one another or with the quinoxaline ring system because of steric hindrance between the pyridyl ring H atoms. The dihedral angles between the planes of the pyridyl rings are $60.3(4)$ and $110.1(4)^\circ$ in molecules *A* and *B*, respectively. The $\text{N}_{\text{py}} \cdots \text{N}_{\text{py}}$ separation is $3.048(3)$ Å for molecule *A* and $3.191(5)$ Å for molecule *B*. In fact, the existence of the adjacent pyridine substituents causes a substantial out-of-plane twist, even in the quinoxaline system [$\text{C}11\text{A}-\text{C}2\text{A}-\text{C}3\text{A}-\text{C}16\text{A} = 21.5(3)^\circ$ and $\text{C}11\text{B}-\text{C}2\text{B}-\text{C}3\text{B}-\text{C}16\text{B} = -19.9(3)^\circ$]. In the quinoxaline systems, the mean deviations from the best-fit planes describing the rings are $0.0697(3)$ and $0.0572(4)$ Å for molecules *A* and *B*, respectively. The quinoxaline systems make dihedral angles with the two pyridyl rings of $36.8(2)$ and $39.8(4)^\circ$ in molecule *A*, and $146.1(4)$ and $54.3(3)^\circ$ in molecule *B*. The $\text{N}2\text{A}-\text{C}3\text{A}$, $\text{N}1\text{A}-\text{C}2\text{A}$, $\text{N}2\text{B}-\text{C}3\text{B}$ and $\text{N}1\text{B}-\text{C}2\text{B}$ bond distances (mean 1.316 Å; Table 1) are noticeably shorter than the $\text{N}2\text{A}-\text{C}4\text{A}$, $\text{N}1\text{A}-\text{C}9\text{A}$, $\text{N}2\text{B}-\text{C}4\text{B}$ and $\text{N}1\text{B}-\text{C}9\text{B}$

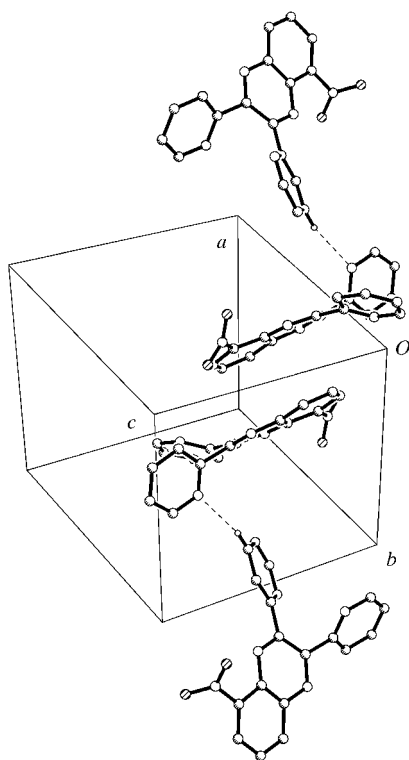


Figure 2

A view of the hydrogen-bonding and π - π -stacking interactions in the unit cell of (I).

distances (mean 1.369 Å), which is typical for the structural geometry of the quinoxaline system (Rasmussen *et al.*, 1990). All N—C bond lengths are well within the range of values normally considered standard for C—N single (1.47 Å) and C=N double bonds (1.28 Å).

There exists a single directed intermolecular $\text{C}18\text{A}-\text{H}18\text{A} \cdots \text{N}4\text{B}(-x+1, -y+1, -z+1)$ weak interaction [$\text{C} \cdots \text{N} = 3.462(4)$ Å and $\text{C}-\text{H} \cdots \text{N} = 167^\circ$], which links molecule *A* and an adjacent centrosymmetrically related molecule *B'* to form a dimer (Table 2). Furthermore, neighboring *B* molecules in the structure show a substantial π - π -stacking interaction (as depicted in Fig. 2), which further stabilizes the crystal structure. The closest approach between the quinoxaline systems is 3.4 Å, with the molecular stack stretching along the *a* direction. Examination of the structure with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids in the crystal lattice of (I).

Experimental

The title compound was synthesized and purified according to the method described by Xu *et al.* (2002), by the reaction of 1-nitro-2,3-phenylenediamine and 2,2'-pyridil (yield 80%). The spectral and elemental analysis data are satisfactory. ^1H NMR (400 MHz, CDCl_3): $7.24-7.30$ (*m*, 2H), $7.85-7.90$ (*m*, 3H), 8.00 (*d*, 1H, $J = 8.0$ Hz), 8.22 (*t*, 2H, $J = 6.8$ Hz), 8.28 (*d*, 1H, $J = 8.0$ Hz), 8.39 (*d*, 1H, $J = 4.0$ Hz), 8.43 (*d*, 1H, $J = 8.8$ Hz). Analysis calculated for $\text{C}_{36}\text{H}_{22}\text{N}_{10}\text{O}_4$: C 65.64, H 3.37, N 18.23%; found: C 65.55, H 3.64, N 18.26%. Light-yellow cubic single crystals of (I) suitable for X-ray diffraction were obtained by recrystallization from a hot ethanol solution.

Crystal data

$\text{C}_{36}\text{H}_{22}\text{N}_{10}\text{O}_4$
 $M_r = 329.22$
 Triclinic, $P1$
 $a = 10.942(4)$ Å
 $b = 11.630(4)$ Å
 $c = 12.906(4)$ Å
 $\alpha = 104.615(6)^\circ$
 $\beta = 93.419(6)^\circ$
 $\gamma = 93.292(6)^\circ$
 $V = 1581.9(9)$ Å³
 $Z = 4$

$D_x = 1.383$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 6571 reflections
 $\theta = 1.6-25.0^\circ$
 $\mu = 0.10$ mm⁻¹
 $T = 293(2)$ K
 Block, light yellow
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan [SAINT (Bruker, 1998) and SADABS (Sheldrick, 1997)]
 $T_{\text{min}} = 0.972$, $T_{\text{max}} = 0.981$
 6614 measured reflections

5555 independent reflections
 3032 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -13 \rightarrow 10$
 $k = -13 \rightarrow 13$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R(F) = 0.046$
 $wR(F^2) = 0.108$
 $S = 1.04$
 5555 reflections
 451 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.04008P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.16$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1A—N3A	1.221 (3)	O1B—N3B	1.222 (2)
O2A—N3A	1.224 (3)	O2B—N3B	1.220 (2)
N1A—C2A	1.317 (3)	N1B—C2B	1.314 (3)
N1A—C9A	1.373 (3)	N1B—C9B	1.371 (3)
N2A—C3A	1.314 (3)	N2B—C3B	1.318 (3)
N2A—C4A	1.368 (3)	N2B—C4B	1.362 (3)
N3A—C5A	1.463 (4)	N3B—C5B	1.466 (3)
N4A—C11A	1.336 (2)	N4B—C11B	1.324 (3)
N4A—C12A	1.336 (3)	N4B—C12B	1.340 (3)
N5A—C16A	1.336 (3)	N5B—C16B	1.338 (3)
N5A—C20A	1.332 (3)	N5B—C20B	1.328 (3)
O1A—N3A—O2A	123.8 (3)	O1B—N3B—O2B	124.1 (2)
C2A—N1A—C9A	117.2 (2)	C2B—N1B—C9B	117.69 (19)
C3A—N2A—C4A	116.7 (2)	C3B—N2B—C4B	117.38 (19)
C11A—N4A—C12A	116.4 (2)	C11B—N4B—C12B	115.5 (2)
C16A—N5A—C20A	116.9 (2)	C16B—N5B—C20B	117.0 (3)
C3A—C2A—C11A—N4A	41.9 (3)	C3B—C2B—C11B—N4B	−56.3 (3)
O1A—N3A—C5A—C4A	−48.9 (4)	O1B—N3B—C5B—C4B	43.2 (3)
O1A—N3A—C5A—C6A	131.2 (3)	O1B—N3B—C5B—C6B	−135.8 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C18A—H18A ⁱ ⋯N4B ⁱ	0.93	2.55	3.462 (4)	167

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

H atoms were placed in calculated positions and included in the final refinement in a riding-model approximation, with displacement parameters derived from the parent C atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1166). Services for accessing these data are described at the back of the journal.

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