

## 5,8-Dimethoxy-2,3-bis(2-pyridyl)- quinoxaline

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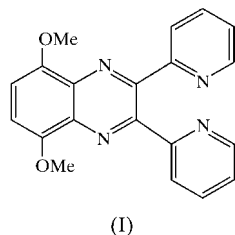
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In the crystal structure of the title compound,  $C_{20}H_{16}N_4O_2$ , the two pyridine rings subtend dihedral angles of  $39.0$  (1) and  $43.4$  (2)° with the mean quinoxaline plane and  $67.6$  (1)° with each other. The orientation of the pyridine rings is such that their N-donors face each other (*cis-cis* conformation) with a separation of  $3.169$  (2) Å. There exist significant  $\pi$ - $\pi$  interactions responsible for the formation of stacks along the crystallographic *a* axis of the crystal.

### Comment

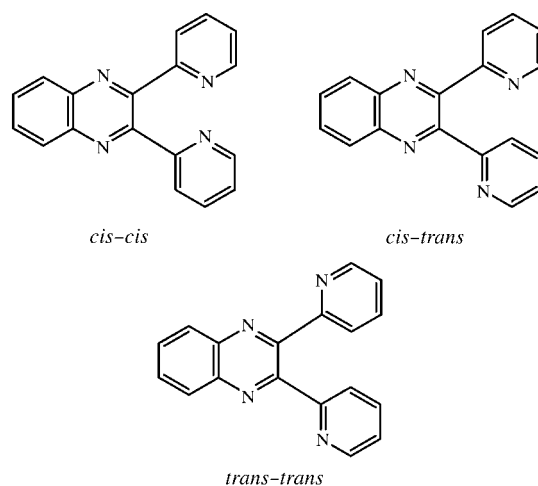
Polypyridyl bridging ligands have attracted considerable interest in recent years because of their potential as building blocks for supramolecular assemblies under complexation with transition metal ions (Leininger *et al.*, 2000; Bu *et al.*, 2001) and because the photophysical and redox properties of their functional complexes (Balzani *et al.*, 1996; Scott *et al.*, 1999; Veroni *et al.*, 2003) make them useful as light-harvesting and photonic molecular devices. Some of the polypyridyl compounds have been intensively 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 *et al.*, 1998). In our



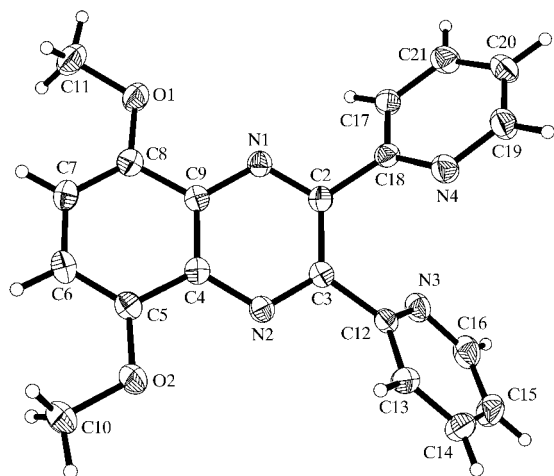
efforts to investigate systematically the syntheses, crystal structures and coordination chemistry of such compounds, we have reported the crystal structures of 5,6-bis(2-pyridyl)-2,3-pyrazinedicarbonitrile (Du *et al.*, 2001) and of the so-called

proton-sponge compounds 5,8-dimethoxy-2,3-bis(2-pyridinio)quinoxaline dinitrate (Liu *et al.*, 2001) and 5-nitro-2,3-bis(2-pyridinio)quinoxaline diperchlorate (Xu *et al.*, 2002). In the present paper, we report the crystal structure of the title compound, namely 5,8-dimethoxy-2,3-bis(2-pyridyl)quinoxaline, (I).

Compound (I) consists of a quinoxaline ring system substituted with two pyridyl rings and two methoxy groups. Selected bond distances and angles are given in Table 1. Such compounds have the potential to generate three possible configurations under appropriate conditions, *viz.* *cis-cis*, *cis-trans* and *trans-trans* (referring to the relations of the pyridyl N atoms to the quinoxaline system). The crystal structure of (I) exhibits the *cis-cis* conformational arrangement of the pyridyl rings (see *Scheme* below). A *cis-cis* conformation was also observed in the crystal structure of the N-protonated nitrate of the title compound, *viz.* 5,8-dimethoxy-2,3-bis(2-pyridinio)quinoxaline dinitrate (Liu *et al.*, 2001), and this conformation is also consistent with other related compounds (Woźniak, 1991; Kruger *et al.*, 2001). However, a variety of conformational arrangements of the pyridyl rings of (I) are observed in its transition metal complexes, namely *trans-trans* in the  $Zn^{II}$  complex  $[Zn(I)(H_2O)(NO_3)_2] \cdot 2CH_3CN$  (Bu *et al.*, 2002); *cis-trans* in the  $Ag^I$  complex  $[Ag(I)(CH_3CN)_2]_2(ClO_4)_2$  (Bu *et al.*, 2001), the  $Cu^I$  complex  $[Cu(I)(CH_3CN)_2](ClO_4)_2$ , the  $Ni^{II}$  complex  $[Ni(II)(NO_3)(H_2O)_2](NO_3) \cdot 2CH_3CN$  and the  $Co^{II}$  complex  $[Co(II)Cl_2(H_2O)]$  (Bu *et al.*, 2002); and *cis-cis* in the  $Cu^{II}$  complex  $[Cu(II)(NO_3)_2] \cdot CH_3CN$  (Bu *et al.*, 2002). These results indicate that the configuration of the title compound can spontaneously convert when coordinating to different metal centers.



The two planar pyridyl rings are not coplanar with each other or with the quinoxaline system because of steric clashes between the H atoms of the pyridyl rings. For the N4-pyridine ring, the maximum deviation of any atoms from the best-fit plane is  $0.008$  (2) Å, the average deviation being  $0.005$  (1) Å. For the N3-containing ring, the corresponding values are  $0.010$  (1) and  $0.006$  (2) Å. The dihedral angle subtended by the two pyridyl rings is  $67.6$  (1)° and the intramolecular  $N_{py} \cdots N_{py}$  separation is  $3.169$  (2) Å, which are comparable to the values



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

in 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline [59.3 (1)° and 2.891 (2) Å; Woźniak, 1991]. The existence of the adjacent pyridine substituents causes substantial out-of-plane twist in the quinoxaline ring system so that the C2–C3–C12–C18 torsion angle [–22.2 (2)°] is similar to that observed in the metal complexes [between 7.8 (3) and –20.3 (5)°; Bu *et al.*, 2002].

In the quinoxaline system, the mean deviation of any atom from the best-fit plane describing it is 0.054 (2) Å, with a maximum deviation of 0.096 (1) Å. The system can be better described as two rings; one is planar [C4–C9, the mean and maximum deviations being 0.009 (2) and 0.018 (2) Å, respectively], while the other (N1/C2/C3/N2/C4/C9) adopts a twist-boat conformation, albeit with only a small distortion [the mean and maximum deviations are 0.035 (2) and 0.054 (2) Å, respectively]. The planes of the two rings in the quinoxaline system subtend a dihedral angle of 5.3 (2)°, and the mean plane of the quinoxaline system makes dihedral angles of 39.0 (1) and 43.4 (2)° with the planes of the two pyridyl rings. It is concluded that the non-planarity of the quinoxaline system is caused by the intramolecular non-bonding contacts of the pyridyl rings, as this conformation is not observed in monopyridine-substituted quinoxaline compounds (Veroni *et al.*, 2003). The C2–N1 and C3–N2 bond distances [mean 1.317 (2) Å] are noticeably shorter than the N1–C9 and N2–C4 distances [mean 1.362 (2) Å], which is a typical geometry for the quinoxaline system (Rasmussen *et al.*, 1990). All N–C bond lengths are well within the range of values normally considered standard for single C–N (1.47 Å) and double C=N (1.28 Å) bonds.

Analysis of the crystal packing of (I) showed no weak hydrogen-bonding interactions of the C–H···N or C–H···O types. However, the neighboring parallel molecules in the unit cell show substantial  $\pi$ – $\pi$ -stacking interactions; the closest approach between the quinoxaline systems is ~3.4 Å, with the molecular stacks stretching along the *a* direction. In addition,

three weak C–H··· $\pi$  interactions were also observed, involving both the pyridyl rings and the quinoxaline systems. The H···C<sub>g</sub> (C<sub>g</sub> is the centroid of the aromatic ring) and H···Perp (Perp is the normal distance of the H atom to the aromatic ring) distances are in the ranges 3.10–3.19 and 2.89–3.10 Å, respectively, and are thus slightly longer than those found previously (Desiraju & Steiner, 1999). Examination of the structure with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids.

## Experimental

Compound (I) was synthesized and purified according to the method described by Bu *et al.* (2001). Light-yellow cubic single crystals of the title compound suitable for X-ray diffraction were obtained by recrystallization from a CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> solution.

### Crystal data

C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub>	$D_x = 1.372 \text{ Mg m}^{-3}$
$M_r = 344.37$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6907 reflections
$a = 7.0626 (11) \text{ \AA}$	$\theta = 1.9\text{--}25.0^\circ$
$b = 17.355 (3) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 13.674 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 95.958 (4)^\circ$	Block, light yellow
$V = 1667.0 (5) \text{ \AA}^3$	$0.40 \times 0.30 \times 0.15 \text{ mm}$
$Z = 4$	

### Data collection

Bruker SMART 1000 diffractometer	2954 independent reflections
$\omega$ scans	1225 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan [SAINT (Bruker 1998) and SADABS (Sheldrick, 1997)]	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.967$ , $T_{\text{max}} = 0.986$	$\theta_{\text{max}} = 25.0^\circ$
6907 measured reflections	$h = -5 \rightarrow 8$
	$k = -20 \rightarrow 20$
	$l = -16 \rightarrow 15$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$
$R(F) = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
2954 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
236 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0213 (19)

**Table 1**

Selected geometric parameters (Å, °).

O1–C8	1.3696 (19)	N3–C12	1.3447 (19)
O2–C5	1.3667 (19)	N1–C2	1.3178 (19)
N4–C19	1.344 (2)	N1–C9	1.3617 (18)
N4–C18	1.346 (2)	N2–C3	1.3155 (18)
N3–C16	1.340 (2)	N2–C4	1.3628 (18)
C19–N4–C18	116.68 (15)	C2–N1–C9	118.06 (13)
C16–N3–C12	116.47 (15)	C3–N2–C4	117.86 (13)

All H atoms were found in a difference electron-density map but were then placed in calculated positions (C–H = 0.93 and 0.96 Å for aromatic and methoxy H atoms, respectively) and included in the final refinement using the riding-model approximation, with displace-

ment parameters derived from the C atoms to which they were bonded [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and  $1.5U_{\text{eq}}(\text{C})$  for aromatic and methoxy H atoms, respectively].

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: GA1023). Services for accessing these data are described at the back of the journal.

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