organic compounds

4,4'-Bis(*N*,*N*-diethylamino)-2,2'-bi-pyridine

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The title compound, $C_{18}H_{26}N_4$, contains two almost identical independent molecules that lie about inversion centres. Each molecule has a planar bipyridine nucleus and two terminal diethylamine groups oriented at almost right angles to the core. These diethylamine branches act as spacers, producing a very open structure with one of the lowest densities reported among related compounds. The most important intermolecular interactions are of the $C-H\cdots\pi$ type, which connect non-equivalent moieties.

Comment

Bipyridine ligands have been used extensively to prepare coordination compounds with different metals. Ruthenium polypyridine complexes have been of particular interest because of their photophysical properties (Juris *et al.*, 1988; Kalyanasundaram, 1992). The systematic variation of substituents on different positions of the aromatic ring allows control over the redox and spin properties of these complexes. This possibility makes them attractive for use in applications such as molecular electronics, solar energy conversion and
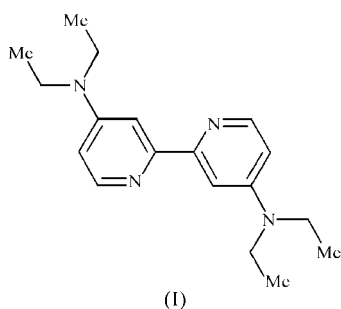
catalysis. In particular, the title compound, (I), has been used to increase the electron density on the metal, lowering its redox potential (Slattery *et al.*, 1994; Curtright & McCusker, 1999).

Compound (I) crystallizes in space group $P2_1/c$, with two independent almost identical molecules, *A* and *B* (Table 1), which lie about inversion centres (Fig. 1). In many free bipyridine ligands described in the literature [Cambridge Structural Database (CSD; Allen, 2002) refcodes EDOXAW, EDOXEA, KIDNAP, MILZUC, NAMKAN, NAMKAN01, NAMKAN02, NOFZUD, UHIBAO, VEXQAQ, VEXQAQ01 and VOLLAJ], the individual molecules appear to be bisected by a symmetry centre, a fact that defines their two most distinctive features, *viz.* the planarity of the aromatic kernel and the *transoid* arrangement of the substituents. The planar character of the bipyridyl $C_{10}N_2$ groups about the inversion centres in molecules *A* and *B* is almost perfect, with maximum deviations of 0.006 (1) and 0.004 (1) Å for the moieties in *A* and *B*, respectively; the bipyridine planes of molecules *A* and *B* are almost perpendicular to one another, subtending an interplanar angle of 89 (1)%. No pseudosymmetry relating the two moieties could be detected.

The terminal diethylamine groups deviate significantly from the mean plane of the molecular core; this departure is due in part to the slight rotation of the CNC_2 groups around the C—N bonds [by 7.1 (1) and 2.1 (1)° for *A* and *B*, respectively] and, more importantly, to the orientation of the terminal ethylene moieties almost at right angles out of the plane of the bipyridine nucleus. The appearance of the $CN(CH_2CH_3)_2$ groups suggests approximate twofold pseudosymmetry along the C—N bonds, with very similar C—N—C—C torsion angles for each branch [C4—N7—C8—C10 = −91.5 (1) and −89.5 (1)°, and C4—N7—C9—C11 = −88.4 (1) and −96.3 (1)° for molecules *A* and *B*, respectively]. As a result, the two independent molecules are almost superimposable, as
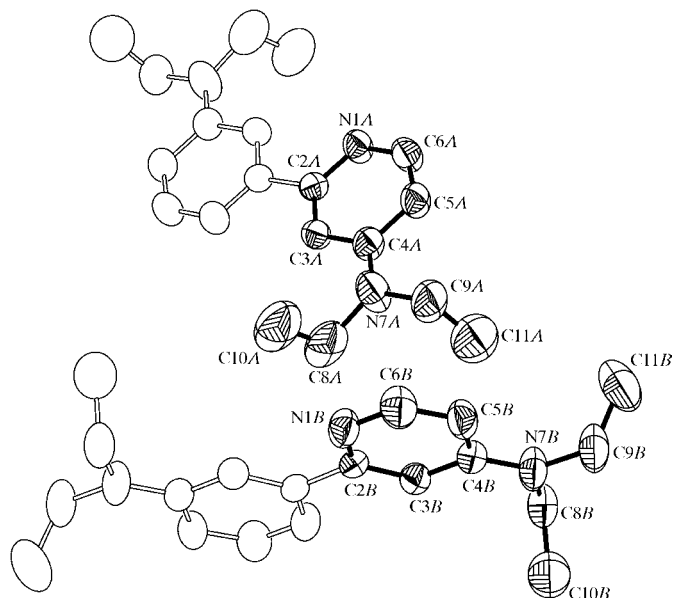

(I)

Figure 1
An *XP* (Sheldrick, 1994) view of (I). Displacement ellipsoids are drawn at the 40% probability level. The independent part of each molecule is shown in bold, with the atom-numbering scheme.

assessed by a least-squares fit of the two units, with a mean deviation of 0.10 (1) Å and a maximum deviation of 0.21 (1) Å for atom C10 (Fig. 2).

As a result of their out-of-plane orientation, the terminal methyl arms act as effective spacers between molecules, precluding any approach between planar groups and consequently any π–π contact, perhaps the most common interaction among unsubstituted aromatic ligands. There are instead C—H$\cdots\pi$ close contacts connecting molecules A and B almost at right angles to one another (Table 2 and Fig. 3). However, these interactions do not seem to provide strong cohesion, as they result in loose packing and an extremely light structure with a calculated density of 1.143 Mg m^{-3}, lower than that of any of the similarly substituted bipyridyl molecules so far reported; the average density of the 12 comparable compounds found in the CSD is 1.26 (8) Mg m^{-3}, with a range of 1.175–1.426 Mg m^{-3}.

Distances and angles in the molecule are unexceptional and match those found in similar ligands.
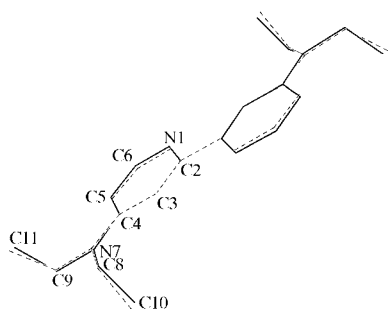

Figure 2
A schematic superimposition diagram (*XP*; Sheldrick, 1994) of molecules A and B.
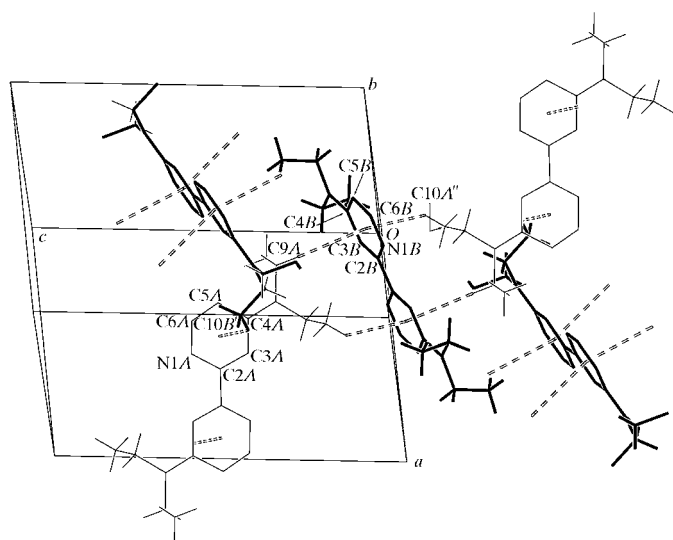

Figure 3
A view of the intermolecular interactions, showing the C—H$\cdots\pi$ contacts. Light lines: molecules A; heavy lines: molecules B. Aromatic H atoms not involved in intermolecular interactions have been omitted for clarity. [Symmetry codes: (') $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; ('') $1 - x, 1 - y, -z$.]

Experimental

The title compound was prepared according to reported procedures (Maerker & Case, 1958; Slattery *et al.*, 1994).

Crystal data

C$_{18}$H$_{26}$N$_4$	$D_x = 1.143$ Mg m^{-3}
$M_r = 298.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 274
$a = 11.0642$ (12) Å	reflections
$b = 11.0554$ (12) Å	$\theta = 3.1$–23.4°
$c = 14.3447$ (15) Å	$\mu = 0.07$ mm^{-1}
$\beta = 98.754$ (2)°	$T = 293$ (2) K
$V = 1734.2$ (3) Å^3	Block, colourless
$Z = 4$	$0.22 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	$R_{int} = 0.072$
	$\theta_{max} = 25.0°$
φ and ω scans	$h = -13 \rightarrow 13$
3053 measured reflections	$k = 0 \rightarrow 13$
3053 independent reflections	$l = 0 \rightarrow 17$
1646 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.068$	$+ 1.468P]$
$wR(F^2) = 0.173$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	$(\Delta/\sigma)_{max} = 0.002$
3053 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
209 parameters	$\Delta\rho_{min} = -0.10$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N7A—C9A	1.483 (5)	N7B—C9B	1.467 (4)
N7A—C8A	1.501 (5)	N7B—C8B	1.483 (4)
C8A—C10A	1.421 (6)	C8B—C10B	1.457 (5)
C9A—C11A	1.441 (6)	C9B—C11B	1.469 (5)
C9A—N7A—C8A	116.5 (3)	C9B—N7B—C8B	115.1 (3)

Table 2
C—H$\cdots\pi$ contacts for (I).

hpd is the H-atom-to-ring-plane distance, hcd is the H-atom-to-ring-centre distance and sa is the slippage angle (angle subtended by the hcd vector to the plane normal).

Group 1/Group 2	hpd (Å)	hcd (Å)	sa (°)
C9A—H9AB/N1A–C6A	3.04 (1)	3.05 (1)	5.2 (2)
C10A''—H10A''/N1B–C6B	2.93 (1)	3.18 (1)	23.0 (2)
C10B'—H10E'/N1A–C6A	2.88 (1)	2.92 (1)	9.5 (2)

Symmetry codes: (') $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; ('') $1 - x, 1 - y, -z$.

In spite of having a good external appearance, the crystals were of extremely poorly diffracting power, as assessed by the low N_{obs}/N_{uniq} ratio. All H atoms were included at idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93–0.97 Å and U_{iso}(H) values of 1.2–1.5 times U_{eq}(C). The H atoms of the terminal methyl groups were allowed to rotate about the C—C bonds.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1772). Services for accessing these data are described at the back of the journal.

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