

Monoalkylated 4'-aryl-substituted terpyridines

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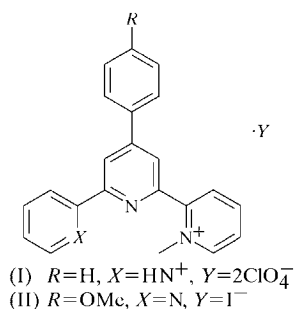
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1-Methyl-2-[4-phenyl-6-(pyridinium-2-yl)pyridin-2-yl]pyridinium diperchlorate, $C_{22}H_{19}N_3^{2+} \cdot 2ClO_4^-$, (I), and 2-[4-(methoxyphenyl)-2,2'-bipyridin-6-yl]-1-methylpyridinium iodide, $C_{23}H_{20}N_3O^+ \cdot I^-$, (II), both crystallize in the monoclinic space group $P2_1/c$. In contrast with the monocharged molecule of (II), the doubly charged molecule of (I) contains an additional protonated pyridine ring. One of the two perchlorate counteranions of (I) interacts with the cation of (I) via an N—H...O hydrogen bond. In (II), two molecules related by a centre of symmetry are connected by weak π – π interactions, forming dimers in the crystal structure.

Comment

Substituted terpyridines, which are common planar tridentate ligands for the complexation of a broad variety of heavy and transition metal ions, are frequently used as building blocks for supramolecular assemblies and composite fluorescent sensors (Cargill Thompson, 1997; Lainé *et al.*, 2002; Goodall *et al.*, 2002; Mutai *et al.*, 2001). Terpyridines can also be exploited for the construction of bifunctional fluorescent reporters, enabling the simultaneous and co-operative spectroscopic recognition of two different analytes, thereby meeting the



increasing interest in advanced sensory devices responding to two or more chemical inputs. A straightforward approach to such bifunctional molecules signalling protons and metal ions involves 4'-aryl-substituted 2,2':6',2''-terpyridines equipped

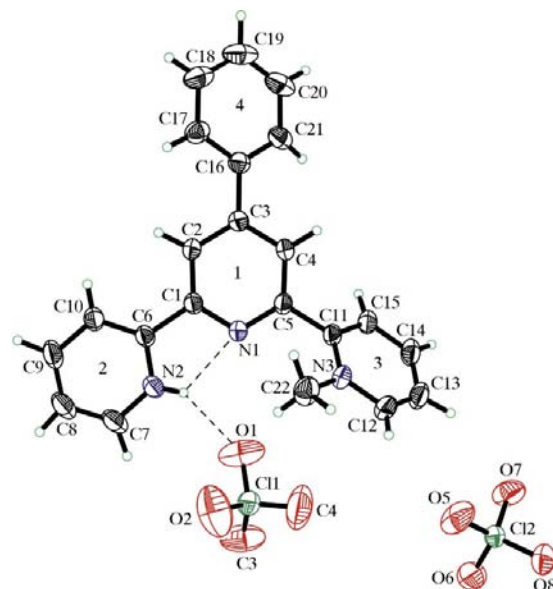


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids. High anisotropic displacement parameters indicate rotational disorder of the perchlorate anions.

with different donor substituents (Li *et al.*, 2004). The stepwise and unexpectedly strong protonation-induced spectroscopic effects observed for these molecules led us to synthesize the alkylated compounds (I) and (II) as model systems for the corresponding protonated ligands.

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. While the molecule of (II) carries only a single positive charge, protonation of the N atom in pyridine ring 2 gives rise to a second positive charge in the molecule of (I). The H atom at N2 in (I) was found in a difference Fourier map. Its existence also follows from the C6—N2—C7 bond angle of $123.6(3)^\circ$. The bond angles at the non-protonated

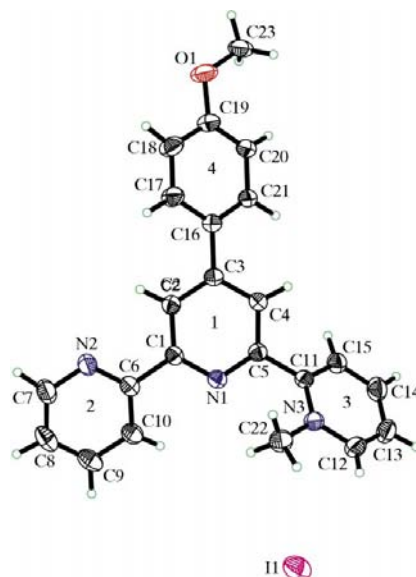


Figure 2

The molecular structure of (II), showing 30% probability displacement ellipsoids.

pyridine N atoms are significantly smaller than 120° , e.g. C1–N1–C5 = $117.3(2)^\circ$ in (I), and C1–N1–C5 = $117.2(2)^\circ$ and C6–N2–C7 = $117.2(3)^\circ$ in (II). In the crystal structure of (I), there are two perchlorate anions, one of which is connected to the molecular cation by an intermolecular N2–H···O1 hydrogen bond (Table 2). Furthermore, the protonated atom N2 acts as a donor for an intramolecular N2–H···N1 hydrogen bond. Despite the connection of one perchlorate anion to the cation, both anions show a high degree of rotational disorder, as indicated by the displacement ellipsoids (Fig. 1).

The molecular conformations of (I) and (II) can be described by the dihedral angles between the pyridine rings, which are very similar for (I) and (II). The dihedral angle between rings 1 and 2 is $11.3(2)^\circ$ in (I) and $16.5(1)^\circ$ in (II), that between rings 1 and 3 is $49.6(1)^\circ$ in (I) and $46.8(1)^\circ$ in (II), and that between rings 1 and 4 is $30.6(1)^\circ$ in (I) and $30.7(1)^\circ$ in (II). However, while in (I) atoms N1 and N2 are in *cis* positions, in (II) a *trans* arrangement is observed. This different orientation of pyridine ring 2 is indicated by the N1–C1–C6–N2 torsion angle, which is $-10.0(3)^\circ$ in (I) and $164.2(2)^\circ$ in (II).

π – π electron interactions between pyridine rings of neighbouring molecules are of special interest for the explanation of spectroscopic properties. These interactions are defined by the

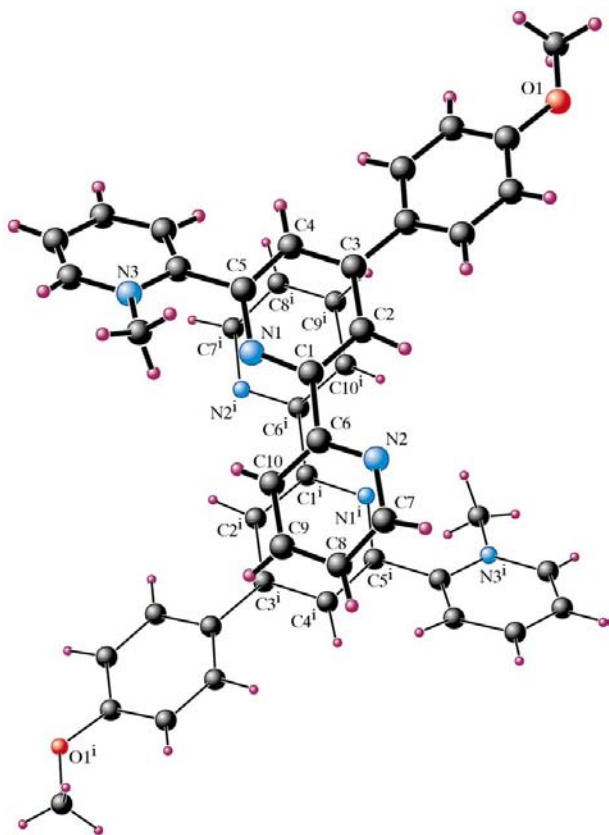


Figure 3
The arrangement of two symmetry-related molecular cations of (II) connected by π – π electron interactions [symmetry code: (i) $2 - x, -y, 1 - z$].

distance between the ring centroids (DC), the perpendicular distance of the centroid of one ring from the plane of the other (DP), and the interplanar angle. Surprisingly, only weak π – π electron interactions were observed in the crystal structure of (II). These interactions between two symmetry-related molecules form dimers, as depicted in Fig. 3. The parameters are as follows: for rings N1/C1–C5 and N2/C7–C11($2 - x, -y, 1 - z$), and for rings N2/C7–C11 and N1/C1–C5($2 - x, -y, 1 - z$), DC = $3.896(2) \text{ \AA}$, DP = 3.493 and 3.835 \AA , and the interplanar angle = 16.52° .

Experimental

For the preparation of (I), a mixture of 4'-phenyl-2,2',6',2''-terpyridine (0.3 g) and methyl *p*-toluenesulfonate (0.3 g, excess) was dissolved in toluene (5 ml) and refluxed for 12 h. The resulting oil was dissolved in acetonitrile (5 ml) and mixed with a hot solution of NaClO₄ (0.5 g) in acetonitrile (2 ml). The precipitate which formed was filtered off, washed with acetonitrile (2 ml) and ethanol (5 ml), and recrystallized twice from ethanol (yield 0.1 g; m.p. 571–573 K). Spectroscopic analysis, ¹H NMR (300 MHz, DMSO-*d*₆, δ): 4.43 (s, 3H, NCH₃), 7.58–7.70 (m, 5H, PyH, PhH), 8.01–8.04 (d, 2H, PhH), 8.14–8.20 (d, 1H, PyH), 8.25–8.28 (d, 1H, PyH), 8.51–8.60 (m, 2H, PyH), 8.76–8.83 (m, 2H, PyH), 8.91–8.95 (d, 1H, PyH), 9.23–9.26 (d, 1H, PyH). For the preparation of (II), CH₃I (0.5 g, excess) was added to a solution of 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine (0.3 g) in toluene (5 ml). After refluxing the reacting mixture for 8 h, the solvent was evaporated *in vacuo* and the solid product was recrystallized twice from methanol (yield 0.12 g; m.p. 478–481 K). Spectroscopic analysis, ¹H NMR (300 MHz, DMSO-*d*₆, δ): 3.85 (s, 3H, OCH₃), 4.42 (s, 3H, NCH₃), 7.14–7.17 (d, 2H, PhH), 7.53–7.57 (m, 1H, PyH), 7.96–8.06 (m, 4H, PyH, PhH), 8.24–8.28 (m, 2H, PyH), 8.42–8.52 (m, 2H, PyH), 8.78–8.84 (m, 2H, PyH), 9.21–9.24 (d, 1H, PyH).

Compound (I)

Crystal data

C₂₂H₁₉N₃²⁺·2ClO₄⁻
M_r = 524.30
Monoclinic, P2₁/c
a = 6.015 (2) Å
b = 13.073 (4) Å
c = 29.501 (10) Å
 β = 91.441 (7)°
V = 2319.1 (13) Å³
Z = 4

D_x = 1.502 Mg m⁻³
Mo K α radiation
Cell parameters from 13 428 reflections
 θ = 1.7–27.5°
 μ = 0.34 mm⁻¹
T = 293 (2) K
Needle, colourless
0.55 × 0.15 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1998)
 T_{\min} = 0.831, T_{\max} = 0.961
13 428 measured reflections

5216 independent reflections
3175 reflections with $I > 2\sigma(I)$
 R_{int} = 0.039
 θ_{\max} = 27.5°
 h = -7 → 7
 k = -16 → 14
 l = -38 → 33

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.054
 $wR(F^2)$ = 0.174
S = 0.99
5216 reflections
393 parameters
H atoms treated by a mixture of independent and restrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.108P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max}$ = 0.001
 $\Delta\rho_{\max}$ = 0.51 e Å⁻³
 $\Delta\rho_{\min}$ = -0.28 e Å⁻³
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.0035 (11)

Table 1
Selected interatomic distances (Å) for (I).

N1—C1	1.336 (3)	N3—C12	1.365 (4)
N1—C5	1.340 (3)	N3—C22	1.470 (4)
N2—C7	1.336 (4)	C1—C6	1.483 (3)
N2—C6	1.340 (3)	C3—C16	1.484 (3)
N3—C11	1.353 (3)	C5—C11	1.486 (3)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2N...O1	0.80 (3)	2.25 (3)	2.942 (5)	146 (3)
N2—H2N...N1	0.80 (3)	2.18 (3)	2.616 (3)	115 (3)
C13—H13...O7	0.98 (4)	2.53 (4)	3.401 (4)	148 (3)
C2—H2...O2 ⁱ	0.95 (3)	2.51 (3)	3.452 (4)	169 (2)
C4—H4...O8 ⁱⁱ	0.94 (2)	2.48 (2)	3.393 (4)	163.7 (19)
C22—H22...O6 ⁱⁱⁱ	0.95 (2)	2.41 (2)	3.341 (4)	167 (3)
C19—H19...O6 ^{iv}	0.98 (3)	2.53 (3)	3.400 (5)	148 (2)

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$; (iii) $x - 1, y, z$; (iv) $x - 2, y - 1, z$.

Compound (II)

Crystal data

$C_{23}H_{20}N_3O^+I^-$
 $M_r = 481.32$
 Monoclinic, $P2_1/c$
 $a = 13.854 (4) \text{ \AA}$
 $b = 13.448 (4) \text{ \AA}$
 $c = 12.141 (4) \text{ \AA}$
 $\beta = 111.146 (5)^\circ$
 $V = 2109.7 (11) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.515 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 11 870 reflections
 $\theta = 2.2\text{--}27.5^\circ$
 $\mu = 1.54 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Prism, colourless
 $0.48 \times 0.45 \times 0.35 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.483, T_{\max} = 0.584$
 11 870 measured reflections

4729 independent reflections
 4104 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -17 \rightarrow 16$
 $k = -9 \rightarrow 17$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.124$
 $S = 1.16$
 4729 reflections
 334 parameters
 H atoms treated by a mixture of independent and restrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.3488P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.77 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.08 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0072 (8)

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C5	1.336 (3)	N2—C7	1.337 (4)
N1—C1	1.345 (3)	C3—C16	1.482 (3)
C1—C6	1.485 (3)	N3—C12	1.351 (4)
O1—C19	1.370 (3)	N3—C11	1.352 (3)
O1—C23	1.413 (4)	N3—C22	1.481 (4)
N2—C6	1.335 (4)	C5—C11	1.483 (3)
C19—O1—C23	118.0 (3)	C12—N3—C11	120.5 (3)
C6—N2—C7	117.2 (3)	C12—N3—C22	117.2 (3)

All H-atom positions of (I) and (II) were determined by difference Fourier syntheses and refined isotropically using restraints for the H atoms on C8, C17 and C22; the C—H range is 0.89 (3)–1.00 (3) Å in (I) and 0.88 (4)–1.07 (4) Å in (II).

For both compounds, data collection: SMART-NT (Bruker, 1999); cell refinement: SAINT-NT (Bruker, 1999); data reduction: SAINT-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). For compound (I), molecular graphics: SHELXTL-NT (Sheldrick, 1999). For compound (II), molecular graphics: SHELXTL-NT (Sheldrick, 1999) and CELLGRAF (Reck et al., 1996). For both compounds, software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1654). Services for accessing these data are described at the back of the journal.

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