

Packing effects in 4,4'-bis(4-hydroxybutyl)-2,2'-bipyridine and 4,4'-bis(4-bromobutyl)-2,2'-bipyridine

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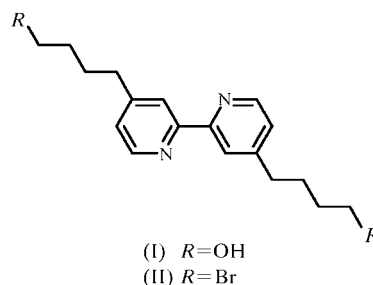
Structure analyses of 4,4'-bis(4-hydroxybutyl)-2,2'-bipyridine, C₁₈H₂₄N₂O₂, (I), and 4,4'-bis(4-bromobutyl)-2,2'-bipyridine, C₁₈H₂₂Br₂N₂, (II), reveal intermolecular hydrogen bonding in both compounds. For (I), O—H...N intermolecular hydrogen bonding leads to the formation of an infinite two-dimensional polymer, and π stacking interactions are also observed. For (II), C—H...N intermolecular hydrogen bonding leads to the formation of a zigzag polymer. The two compounds crystallize in different crystal systems, but both molecules possess C_i symmetry, with one half molecule in the asymmetric unit.

Comment

Compounds containing 2,2'-bipyridine (bpy) substituted at the 4,4'-positions with alkyl chains of different lengths are interesting precursors for functionalization with thiols, carboxylic acids, disulfides or other anchoring groups. Compounds with such terminating groups have displayed the potential to form a self-assembled monolayer on metallic or semiconducting surfaces (Bain, Troughton *et al.*, 1989; Haga *et al.*, 2000; Bain, Biebuyck & Whitesides, 1989; Vogelson *et al.*, 2003). Interestingly, bpy substituted with alkyl groups at the 4,4'-positions has been used as a covalent link in porphyrin–RuO₂ clusters, and the influence of the linking alkyl chain length on the photoinduced intramolecular electron transfer in such clusters has also been studied (Resch & Fox, 1991). Derivatives of [Ru(bpy)₃]²⁺ with different alkyl substituents (*e.g.* *tert*-butyl and nonyl) on the bipyridyl ligands have been prepared and, owing to their enhanced solubility, processed for the construction of electroluminescent devices (Rudmann *et al.*, 2002).

4,4'-Dialkyl-substituted 2,2'-bpy-based compounds have also been used to synthesize macrocyclic compounds (Chambron & Sauvage, 1986, 1987). Owing to the chelating nature of

bpy, metal complexes with alkyl-substituted bpy have been prepared and their behaviour as versatile solvatochromic probes that form metalloaggregates in water-rich media has been investigated (Gameiro *et al.*, 2001). Ruthenium(II) complexes of 2,2'-bpy derivatives, [Ru(Rbpy)₃]²⁺ [Rbpy is 4,4'-bis(alkylaminocarbonyl)-2,2'-bipyridine, where the alkyl is propyl, hexyl or adamantyl], have been synthesized and the kinetics of the photoinduced electron-transfer (ET) reaction between these complexes and methyl viologen (MV²⁺) has been investigated (Hamada *et al.*, 2003). Compounds derived from the alkylation of 4,4'-dimethyl-2,2'-bipyridine have also been screened for fungicidal activity against nine plant diseases (Kelly-Basetti *et al.*, 1995).



The different synthetic strategies used for the preparation of the 4,4'-substituted derivatives of 2,2'-bpy have been critically discussed and evaluated by Newkome *et al.* (2004). Our interest in alkyl-substituted bpy stems from the possibility of preparing prototype molecules with appropriate end groups that could form self-assembled monolayers when brought into contact with substrates such as gold, indium tin oxide (ITO), platinum or silver. We report here the crystal structure analyses of the important precursors 4,4'-bis(hydroxybutyl)-2,2'-bipyridine, (I), and 4,4'-bis(bromobutyl)-2,2'-bipyridine, (II), which will lead us to the final prototype compounds.

The centrosymmetric molecular structure of (I) is shown in Fig. 1. The bond distances and angles are normal, and the bpy moiety is planar. Atoms C5, C2, C2A and C5A are collinear, and the N1—C2—C2A—C3A torsion angle is -0.84 (16°) [symmetry code: (A) $-x, 1 - y, -z$].

Analysis of the crystal packing diagram (Fig. 2) reveals interesting features at the supramolecular level. Intermolecular hydrogen bonding occurs between the lone pairs on the N atoms of the bipyridine group and the H atoms of the hydroxy groups [O1—H1...N1ⁱ = 1.91 (2) Å; for details and

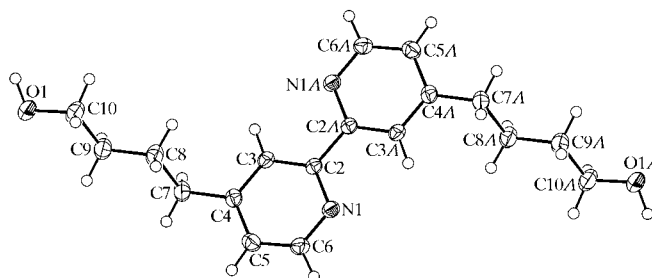


Figure 1
The molecular structure of (I), with displacement ellipsoids at the 50% probability level. [Symmetry code: (A) $-x, 1 - y, -z$.]

symmetry code, see Table 1]. As a result, the diol molecules lie one behind the other, as in a tandem arrangement, giving rise to well ordered double-stranded chains forming a two-dimensional polymeric sheet structure parallel to (10 $\bar{1}$). These chains are aligned parallel to one another in the *ac* plane. Another notable feature of the crystal structure is that the diol molecules lying in different planes are interconnected through π - π contacts established between the bpy moieties, with an interplanar distance of 3.296 (1) Å and a centroid-centroid offset (or ring slippage) of about 1.25 Å (Fig. 2).

Halogenation (Chambron & Sauvage, 1987) of (I) yielded an interesting precursor in the form of the corresponding dibromide, namely 4,4'-bis(bromobutyl)-2,2'-bipyridine, (II). The molecular structure of (II) is depicted in Fig. 3. Again the molecule is centrosymmetric, and the bond distances and angles are normal. Atoms C5, C2, C2A and C5A of the bpy moiety are collinear, and the N1-C2-C2A-N3A torsion angle is 1.1 (4)° [symmetry code: (A) 2 - *x*, 1 - *y*, 2 - *z*].

Part of the crystal structure of (II) is illustrated in Fig. 4. It can be seen that a zigzag polymeric chain is formed as a result of intermolecular hydrogen bonding between the lone pairs on the N atoms of the aromatic ring system and H atoms of the C atoms attached to the bromo groups in the alkyl chains (Table 2). The inherent fashion of hydrogen bonding in this molecule makes it nearly impossible to establish π - π interactions, as was observed in the case of the diol (I).

The dibromo derivative can, very efficiently, be complexed with different types of metal ions upon rotation of the pyridine

ring in order to obtain a *cis* conformation of the heteroaromatic rings. Furthermore, both the free ligand and the corresponding metal complex can undergo a very facile substitution of the bromo group with thioacetate (Gryko *et al.*, 1999, 2000; Zheng *et al.*, 1999). Such thioacetate functionalized molecules are extremely good candidates for immobilization on the surface of metals such as gold, silver and copper. The nanostructures thus created on such metallic surfaces can be characterized by a series of analytical techniques, for instance, scanning tunnelling microscopy (STM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), to elicit a great deal of information concerning the arrangement and packing of molecules on the surface, as well as their electrical and optical behaviour.

Experimental

Compound (I) was synthesized from 4,4'-dimethyl-2,2'-bipyridine in accordance with the procedure described by Chambron & Sauvage (1987). Suitable crystals of (I) were obtained as colourless rods by slow concentration of a solution in chloroform. Halogenation of (I) (Chambron & Sauvage, 1987) yielded the corresponding dibromide, (II). Crystals were grown from a solution in chloroform. ¹H NMR and elemental analyses for (I) and (II) have been reported previously (Chambron & Sauvage, 1987). For (I), δ_c (400 MHz, CD₃OD): 157.2, 154.9, 150.07, 125.5, 123.03, 62.58, 36.09, 33.12, 27.77; ESI-MS (MeOH): *m/z* 301 ([*M* + H]⁺, 100%). For (II), δ_c (400 MHz, CDCl₃): 155.10, 153.01, 148.74, 124.39, 121.94, 34.73, 33.33, 32.26, 28.83; ESI-MS (CHCl₃/MeOH): *m/z* 427 ([*M* + H]⁺, 100%).

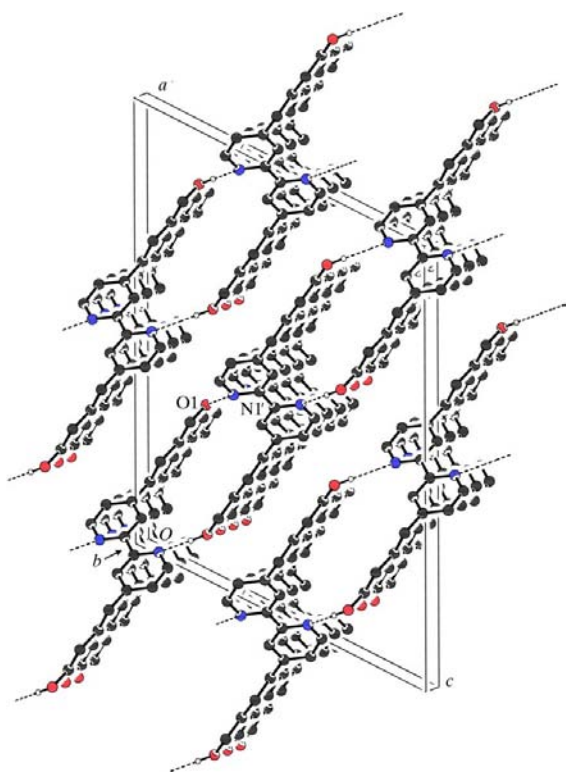


Figure 2
The crystal structure of (I), showing the formation of double-stranded hydrogen-bonded two-dimensional sheets parallel to (10 $\bar{1}$). Hydrogen bonds are represented by dashed lines. [Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

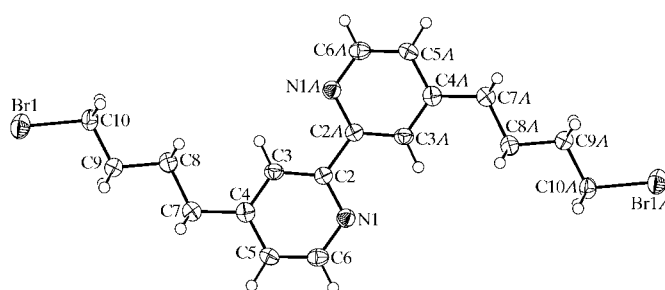


Figure 3
The molecular structure of (II), with displacement ellipsoids at the 50% probability level. [Symmetry code: (A) 2 - *x*, 1 - *y*, 2 - *z*.]

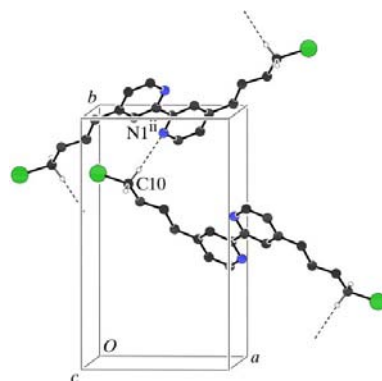


Figure 4
Part of the crystal structure of (II), showing the formation of the hydrogen-bonded C-H...N zigzag polymer chain. Hydrogen bonds are represented by dashed lines. [Symmetry code: (ii) $\frac{3}{2} - x, \frac{1}{2} + y, z$.]

Compound (I)
Crystal data

| | |
|--------------------------------|---|
| $C_{18}H_{24}N_2O_2$ | $D_x = 1.221 \text{ Mg m}^{-3}$ |
| $M_r = 300.39$ | Mo $K\alpha$ radiation |
| Monoclinic, $C2/c$ | Cell parameters from 4949 reflections |
| $a = 22.878 (3) \text{ \AA}$ | $\theta = 2.0\text{--}29.5^\circ$ |
| $b = 4.7657 (5) \text{ \AA}$ | $\mu = 0.08 \text{ mm}^{-1}$ |
| $c = 16.789 (2) \text{ \AA}$ | $T = 173 (2) \text{ K}$ |
| $\beta = 116.759 (9)^\circ$ | Rod, colourless |
| $V = 1634.5 (4) \text{ \AA}^3$ | $0.50 \times 0.17 \times 0.10 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|--|------------------------------------|
| Stoe IPDS diffractometer | $R_{\text{int}} = 0.048$ |
| φ oscillation scans | $\theta_{\text{max}} = 29.2^\circ$ |
| 11 138 measured reflections | $h = -30 \rightarrow 30$ |
| 2210 independent reflections | $k = -6 \rightarrow 6$ |
| 1733 reflections with $I > 2\sigma(I)$ | $l = -23 \rightarrow 22$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 0.3603P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.118$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 1.05$ | $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$ |
| 2210 reflections | $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$ |
| 148 parameters | |
| All H-atom parameters refined | |

Table 1

 Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

| $D\text{--}H\cdots A$ | $D\text{--}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{--}H\cdots A$ |
|----------------------------|---------------|-------------|-------------|-----------------------|
| $O1\text{--}H1\cdots N1^i$ | 0.95 (2) | 1.91 (2) | 2.8495 (14) | 172.5 (18) |

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

Compound (II)
Crystal data

| | |
|---------------------------------|---|
| $C_{18}H_{22}Br_2N_2$ | Mo $K\alpha$ radiation |
| $M_r = 426.20$ | Cell parameters from 4377 reflections |
| Orthorhombic, $Pbca$ | $\theta = 1.4\text{--}25.6^\circ$ |
| $a = 8.3566 (12) \text{ \AA}$ | $\mu = 4.61 \text{ mm}^{-1}$ |
| $b = 14.246 (2) \text{ \AA}$ | $T = 173 (2) \text{ K}$ |
| $c = 14.779 (2) \text{ \AA}$ | Plate, colourless |
| $V = 1759.4 (4) \text{ \AA}^3$ | $0.30 \times 0.20 \times 0.10 \text{ mm}$ |
| $Z = 4$ | |
| $D_x = 1.609 \text{ Mg m}^{-3}$ | |

Data collection

| | |
|--|--|
| Stoe IPDS-II diffractometer | 1560 independent reflections |
| ω scans | 1064 reflections with $I > 2\sigma(I)$ |
| Absorption correction: refinement of ΔF (DELTAABS in PLATON; Spek, 2003) | $R_{\text{int}} = 0.055$ |
| $T_{\text{min}} = 0.267, T_{\text{max}} = 0.631$ | $\theta_{\text{max}} = 25.1^\circ$ |
| 7834 measured reflections | $h = -9 \rightarrow 9$ |
| | $k = -16 \rightarrow 16$ |
| | $l = -17 \rightarrow 14$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | $w = 1/[\sigma^2(F_o^2) + (0.0503P)^2]$ |
| $wR(F^2) = 0.091$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.96$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 1560 reflections | $\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$ |
| 100 parameters | $\Delta\rho_{\text{min}} = -0.65 \text{ e \AA}^{-3}$ |

Table 2

 Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

| $D\text{--}H\cdots A$ | $D\text{--}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{--}H\cdots A$ |
|--------------------------------|---------------|-------------|-------------|-----------------------|
| $C10\text{--}H10A\cdots N1^ii$ | 0.99 | 2.52 | 3.506 (4) | 173 |

 Symmetry code: (ii) $\frac{3}{2} - x, \frac{1}{2} + y, z$.

For (I), H atoms were located in difference Fourier maps and refined isotropically [$C\text{--}H = 0.944 (16)\text{--}1.025 (18) \text{ \AA}$]. For (II), H atoms were included in calculated positions and treated as riding atoms [$C\text{--}H = 0.95\text{--}0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2004); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1818). Services for accessing these data are described at the back of the journal.

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