

Interpenetrating supramolecular
lattices in 4,4'-bipyridine–2,3,5,6-
tetrahydroxy-1,4-benzoquinone (3/2)John A. Cowan,^{a*} Judith A. K. Howard^b and Michael A. Leech^b^aInstitut Laue Langevin, BP 156, 38042 Grenoble CEDEX 9, France, and ^bDepartment of Chemistry, University of Durham, Durham DH1 3LE, England
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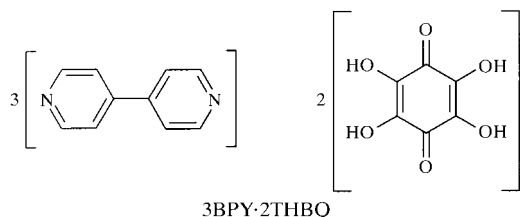
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4,4'-Bipyridine (BPY) and 2,3,5,6-tetrahydroxy-1,4-benzoquinone (THBQ) crystallize in a 3:2 ratio as a neutral molecular adduct, $3C_{10}H_8N_2 \cdot 2C_6H_4O_6$, in space group $P\bar{1}$. There are two independent and centrosymmetric THBQ molecules and two different BPY molecules in the asymmetric unit, one of which lies about an inversion centre. The molecules link together through $O-H \cdots O$ and $O-H \cdots N$ hydrogen bonds to form three interpenetrating networks which create a 'superlattice' of three times the volume of the primitive cell.

Comment

To investigate a variety of molecular interactions in the solid state, in particular $N-H \cdots O$ and $O-H \cdots N$ hydrogen bonds, we have produced new cocrystals of 4,4'-bipyridine (BPY) and tetrahydroxybenzoquinone (THBQ). Cocrystals of organic acids and bipyridines have been studied extensively and have been observed to form a wide variety of intermolecular hydrogen bonds (Reetz *et al.*, 1994; MacLean *et al.*, 1999; Lough *et al.*, 2000). We have reported recently the structure of BPY with 2,5-dihydroxy-1,4-benzoquinone (Cowan *et al.*, 2001), and as a natural progression of the series, we have investigated BPY with THBQ and present here the structure of 4,4'-bipyridine–2,3,5,6-tetrahydroxy-1,4-benzoquinone (3/2) (Fig. 1).



There are two independent centrosymmetric THBQ molecules in the structure. One THBQ molecule shows a spiral arrangement of the hydroxy H atoms similar to that observed by Klug (1965), while the other adopts a 'crab-like' conformation, with the $O-H$ bonds almost parallel to the quinone

$C=O$ groups. The geometry of the non-H atoms in both THBQ molecules is not significantly different from that observed by Klug (1965).

There are also two independent BPY molecules in the structure, one of which lies across an inversion centre; the other is complete within the asymmetric unit. In the complete BPY molecule, the pyridine rings are twisted at $19.9(1)^\circ$ with respect to each other, while the other BPY molecule is required to be planar by symmetry. The twist in the unique BPY molecule optimizes three weak $C-H \cdots O$ hydrogen bonds [$C14 \cdots O2^i$, $C16 \cdots O6$ and $C18 \cdots O4^{ii}$; symmetry codes: (i) $x, y-1, z$; (ii) $x-1, y-1, z$].

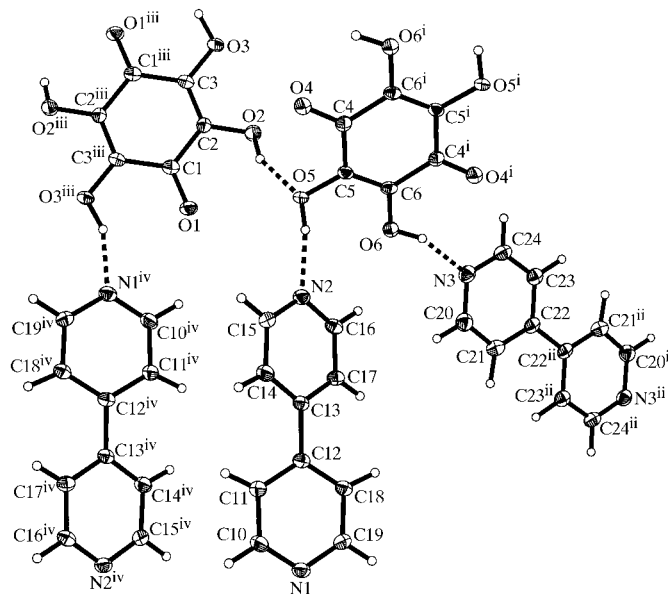


Figure 1

The molecules of the title adduct shown with 50% probability displacement ellipsoids. The dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $-1-x, -y, -z$; (iii) $2-x, 2-y, -z$; (iv) $1-x, -y, 1-z$.]

There are four conventional hydrogen bonds in the asymmetric unit. Each of the four hydroxy groups is a donor and each of the pyridine N atoms is an acceptor. The other acceptor is O5 which acts both as a donor and as an acceptor. The carbonyl groups could be regarded as acceptors for intramolecular hydrogen bonds, but the $O-H \cdots O$ angles are unacceptable ($O2-H2 \cdots O1 = 108^\circ$, $O3-H3 \cdots O1 = 105^\circ$ and $O6-H6 \cdots O4 = 106^\circ$), as is the case for a possible intramolecular hydrogen bond between H5 and O6 ($O5-H5 \cdots O6 = 102^\circ$).

Three different hydrogen-bonded chains are formed in the crystal; two arise from $O-H \cdots N$ hydrogen bonds and the third from $O-H \cdots O$ hydrogen bonds (Fig. 2). Chains of THBQ molecules propagate along the [111] direction, connected by $O-H \cdots O$ hydrogen bonds ($O2 \cdots O5$). Chains of BPY and THBQ molecules propagate along the [210] direction connected by $O-H \cdots N$ hydrogen bonds ($O6 \cdots N3$), and further $O-H \cdots N$ hydrogen-bonded chains of BPY and THBQ molecules are formed along the $[1\bar{3}1]$ direction [$O3 \cdots N1^{iii}$ and $O5 \cdots N2$; symmetry code: (iii) $x+1, y+2, z$].

When these three non-collinear chains intersect with one another, two-dimensional rings are created which connect together to form a three-dimensional supramolecular lattice. In the lattice, the THBQ molecules act as four-connecting (molecule containing C1) and six-connecting (molecule containing C4) nodes and the BPY molecules act only as links. The $[111]$ and $[1\bar{3}\bar{1}]$ chains link together into planar sheets incorporating both types of node. The $[210]$ chains connect the sheets *via* the six-connecting nodes after spanning two intervening planes.

The supramolecular structure can also be described by a supercell with axes of $a' = 16.798 \text{ \AA}$ $[210]$, $b' = 17.096 \text{ \AA}$ $[120]$,

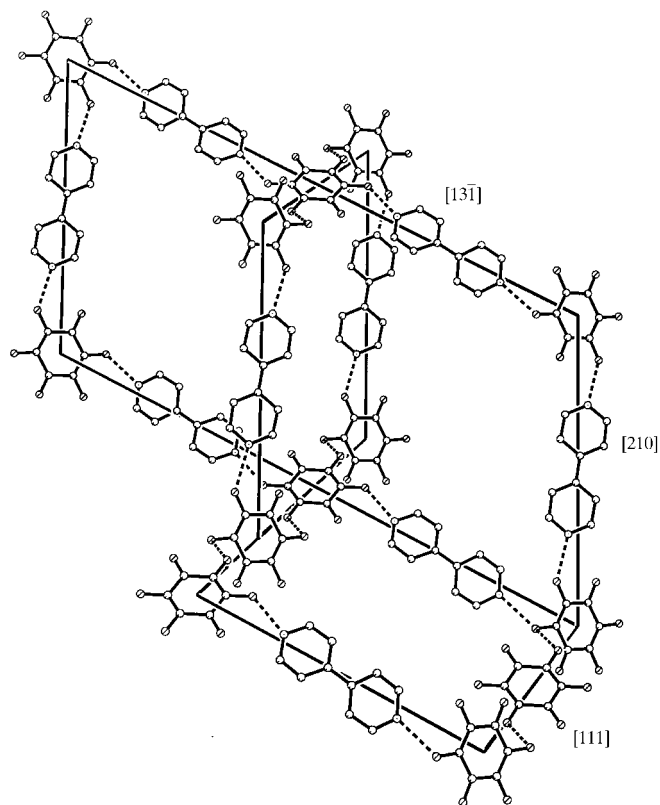


Figure 2

View of the molecular packing showing the formation of hydrogen-bonded chains, which link together to form a three-dimensional lattice. The dashed lines indicate hydrogen bonds and the parallelograms highlight the chains linked into rings. H atoms have been omitted for clarity.

$c' = 13.547 \text{ \AA}$ $[111]$, $\alpha' = 108.8^\circ$, $\beta' = 117.8^\circ$ and $\gamma' = 51.8^\circ$, and a volume of 2709 \AA^3 , three times that of the primitive unit cell.

The three separate 'lattices' which create an interpenetrating mesh within the supercell are shown in Fig. 3. Examination of the structure with *PLATON* (Spek, 1990) showed that there are no cavities of significant size within this structure. A similar structural motif occurs in cocrystals of a 3:2 ratio of BPY and trimesic acid (Sharma & Zaworotko, 1996), in which three two-dimensional interpenetrating hydrogen-bonded grids are formed, but unlike the present structure, large voids are formed in the crystal.

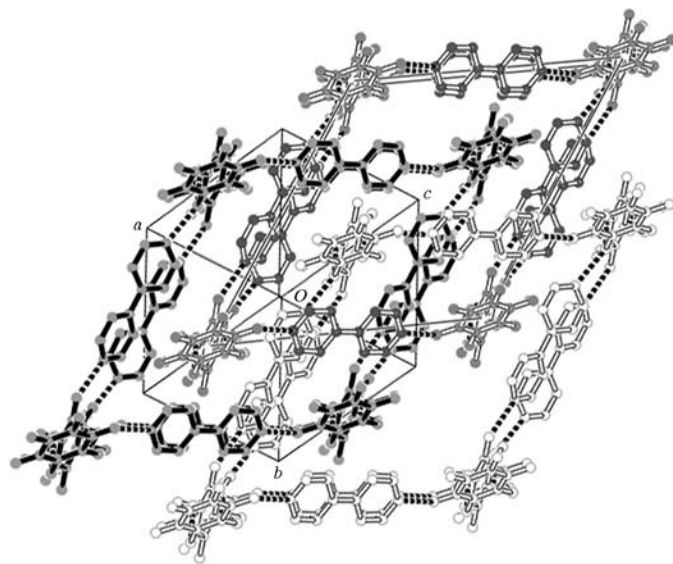


Figure 3

Packing diagram viewed close to the $[111]$ direction. The primitive unit cell and the supercell based on $[111]$, $[210]$ and $[120]$ have been indicated. The separate interpenetrating lattices are coloured differently. H atoms and some molecules have been omitted for clarity.

Experimental

4,4'-Bipyridine (156 mg, 1 mmol) and 2,3,5,6-tetrahydroxy-1,4-benzoquinone dihydrate (156 mg, 1 mmol) were dissolved in methanol and water producing a deep-red solution. Crystals suitable for X-ray structure determination were obtained by slow evaporation of the solvent at room temperature.

Crystal data

$3\text{C}_{10}\text{H}_8\text{N}_2 \cdot 2\text{C}_6\text{H}_4\text{O}_6$
 $M_r = 812.74$
 Triclinic, $P\bar{1}$
 $a = 8.8856 (8) \text{ \AA}$
 $b = 9.0728 (9) \text{ \AA}$
 $c = 12.9288 (11) \text{ \AA}$
 $\alpha = 109.164 (5)^\circ$
 $\beta = 92.476 (5)^\circ$
 $\gamma = 111.074 (5)^\circ$
 $V = 903.17 (14) \text{ \AA}^3$

$Z = 1$
 $D_x = 1.492 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 910 reflections
 $\theta = 9.3\text{--}22.1^\circ$
 $\mu = 0.11 \text{ mm}^{-1}$
 $T = 100 (2) \text{ K}$
 Irregular, brown
 $0.6 \times 0.4 \times 0.3 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.754$, $T_{\max} = 1.000$
 9859 measured reflections

4127 independent reflections
 2628 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\max} = 27.5^\circ$
 $h = -10 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.067$
 $S = 1.07$
 4127 reflections
 319 parameters

Only coordinates of H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O2—H2...O5 | 0.84 (2) | 1.91 (2) | 2.692 (2) | 153 (2) |
| O3—H3...N1 ⁱ | 0.97 (2) | 1.74 (2) | 2.651 (2) | 155 (1) |
| O5—H5...N2 | 0.88 (2) | 1.79 (2) | 2.635 (2) | 161 (1) |
| O6—H6...N3 | 0.94 (2) | 1.82 (2) | 2.707 (2) | 157 (1) |
| C14—H14...O2 ⁱⁱ | 0.96 (2) | 2.36 (2) | 3.268 (2) | 158 (1) |
| C16—H16...O6 | 0.96 (1) | 2.40 (1) | 3.066 (2) | 126 (1) |
| C18—H18...O4 ⁱⁱⁱ | 0.97 (1) | 2.34 (2) | 3.274 (2) | 162 (1) |

 Symmetry codes: (i) $1+x, 2+y, z$; (ii) $x, y-1, z$; (iii) $x-1, y-1, z$.

All H atoms were found in the difference Fourier maps and were refined with isotropic displacement parameters fixed to their parent atoms; the C—H [0.95 (2)–1.04 (1) Å] and O—H distances all refined to within standard ranges.

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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1161). Services for accessing these data are described at the back of the journal.

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