organic compounds

The 1:1 adduct of 2,5-dihydroxy-1,4-benzoquinone with 4,4'-bipyridine

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2,5-Dihydroxy-1,4-benzoquinone (DHBQ) and 4,4'-bipyridine (BPY) crystallize in a 1:1 ratio as a neutral molecular adduct, $C_6H_4O_4 \cdot C_{10}H_8N_2$, in space group $C2/c$, with half of each molecule in the asymmetric unit. The molecules are linked by a strong O—H···N hydrogen bond [O···N 2.6323 (15) Å] and a weak C—H···O hydrogen bond [C···O 3.2082 (17) Å] to form infinite stacks of parallel one-dimensional hydrogen-bonded ribbons. The two rings of the bipyridine are twisted at 28.3° with respect to each other, and the benzoquinone ring is inclined at an angle of 18.3° with respect to the plane of the neighbouring pyridine ring. The 4,4'-bipyridine molecule lies on a twofold axis and the benzoquinone molecule lies across an inversion centre.

Comment

To investigate a variety of molecular interactions in the solid state, in particular N—H···O and O—H···N hydrogen bonds, we have produced cocrystals of 4,4'-bipyridine (BPY) and 2,5-dihydroxy-1,4-benzoquinone (DHBQ). Cocrystals of organic acids and bipyridines have been studied extensively and have been observed to form a wide variety of hydrogen bonds. These two types of constituents have the ability to form cocrystals with different stoichiometries of the constituents and a variety have been observed by ourselves and by other workers, namely 1:1, 1:2 and 2:1 cocrystals of 4,4'-bipyridine and pyromellitic acid (Lough *et al.*, 2000; Williams *et al.*, 2001), and also 1:1 (Reetz *et al.*, 1994) and 2:3 ratios (MacLean *et al.*, 1999) for cocrystals of 4,4'-bipyridine and squaric acid. Surprisingly, we have found only one stoichiometry for cocrystals of DHBQ and BPY and present here the crystal structure of the 1:1 adduct, (I).

DHBQ is a weak organic acid with the possibility of single or double deprotonation, whereupon its shape and properties change significantly, as the charge becomes more delocalized. The neutral molecule was observed in the structure of the pure form by Semmingsen (1977), while the doubly deprotonated form was observed as the potassium salt by Kulpe (1974). In the neutral state, DHBQ can be a hydrogen-bond donor and/or acceptor, making it an excellent and novel tool for studying weak interactions in 'supramolecular' crystals.

BPY is a rather rigid weak bidentate base, popular in other crystal-engineering studies because of its bridging ability (Zaman *et al.*, 1999; Coupar *et al.*, 1996; Sharma & Zaworotko, 1996; MacLean *et al.*, 1999). The molecule can remain neutral or become singly or doubly protonated, its final state depending not only on the strength of the cocrystal acid, but also on its crystalline environment (Williams *et al.*, 2001).

DHBQ   BPY

(I)
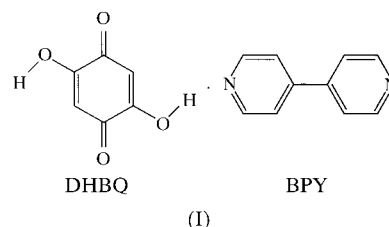
In the present structure, the molecular parameters of DHBQ agree closely with those of the neutral molecule (Semmingsen, 1977), and similarly for BPY, which in (I) is also typical of the neutral form. Both molecules are symmetrical, since the DHBQ lies across a crystallographic inversion centre and the BPY lies upon a twofold axis (Fig. 1). The angle subtended at the N atom of the bipyridine molecule [117.5 (1)°] compares well with the average of 116.5° for neutral bipyridine molecules in the Cambridge Structural Database (CSD; Allen & Kennard, 1993); the average CSD value for the recorded protonated form is 121.5°. This parameter also accords with H2 being bound to O2 and not to the bipyridine [O2—H2 0.96 (2) Å].

The dominant interaction for the packing is the strong O2—H2···N1 hydrogen bond [O···N 2.6323 (15) Å], which is assisted by the weaker C14—H14···O1 hydrogen bond [C···O 3.2082 (17) Å], thus linking the molecules together into one-dimensional chains. The chains lie in the *ac* plane and propagate in the [103] direction (Fig. 2).

The molecular synthon of (I) is similar to one of the two which were observed in the two structures of 4,4'-bipyridine and squaric acid reported by Reetz *et al.* (1994), in which the bipyridine and squarate molecules form similar hydrogen-bonded chains. The other synthon, which has the same shape, occurs when the bipyridine has become protonated and an N—H···O hydrogen bond is supported by a weak C—H···O hydrogen bond.
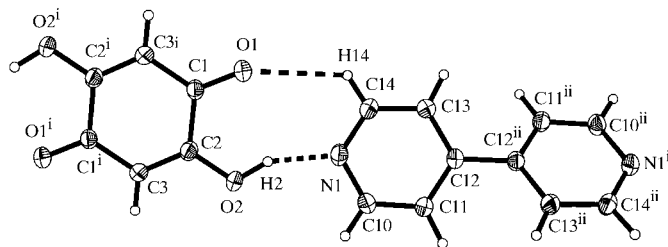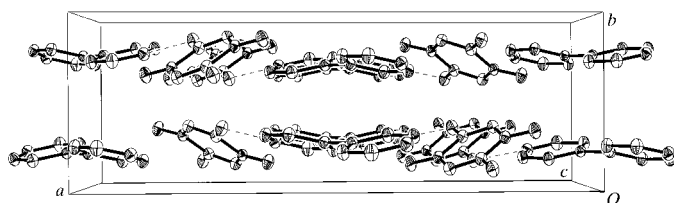

Figure 1
The molecules of (I) shown with 50% probability displacement ellipsoids. The dashed lines indicate hydrogen bonds and H atoms are drawn as small spheres of arbitrary radii [symmetry codes: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $2 - z$; (ii) $-x$, y, $\frac{1}{2} - z$].

In the closely related system combining 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid) and BPY to form crystals of the 1:1 adduct (Zaman *et al.*, 1999), the molecules also link together to form chains, but with a distinctly different synthon. The 4,4′-bipyridine in this adduct is the doubly protonated (BPY-2H)$^{2+}$, and the molecules are linked by bifurcated hydrogen bonds at each N atom, resulting in the planes of the quinone and the bipyridine lying mutually perpendicular and alternating their orientation along the molecular chain.

Figure 2
The packing of (I) viewed along the *c* axis. H atoms have been omitted for clarity.

The differences observed in the four structures discussed above can be attributed primarily to the relative strengths of the three acids, namely, squaric acid, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone and 2,5-dihydroxy-1,4-benzoquinone.

Experimental

Equimolar quantities of BPY and DHBQ were dissolved in methanol/water, producing an orange solution. Crystals of (I) suitable for X-ray structure determination were prepared by slow evaporation of the solvent at room temperature.

Crystal data

$C_6H_4O_4 \cdot C_{10}H_8N_2$	$D_x = 1.478$ Mg m^{-3}
$M_r = 296.28$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 932
$a = 20.8676$ (17) Å	reflections
$b = 7.0151$ (7) Å	$\theta = 13.70–29.49°$
$c = 9.1087$ (8) Å	$\mu = 0.108$ mm^{-1}
$\beta = 92.843$ (5)°	$T = 150$ (2) K
$V = 1331.8$ (2) Å^3	Needle, orange
$Z = 4$	$0.54 \times 0.20 \times 0.12$ mm

Data collection

Bruker SMART CCD diffractometer	$R_{int} = 0.060$
	$\theta_{max} = 27.48°$
ω scans	$h = -26 \rightarrow 27$
6874 measured reflections	$k = -9 \rightarrow 9$
1520 independent reflections	$l = -11 \rightarrow 11$
1286 reflections with $I > 2\sigma(I)$	

Table 1
Hydrogen-bonding geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O2—H2···N1	0.96 (2)	1.74 (3)	2.6323 (15)	154 (2)
C14—H14···O1	0.975 (19)	2.572 (19)	3.2082 (17)	122.9 (13)

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.6747P]$
$wR(F^2) = 0.113$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.062$	$(\Delta/\sigma)_{max} < 0.001$
1520 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
124 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
All H-atom parameters refined	

All H atoms were found in difference Fourier maps and were refined with isotropic displacement parameters. The C—H and O—H distances [C—H = 0.941 (17)–0.977 (17) Å] all refined to within standard ranges and there were no anomalous values of U_{iso}.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

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