Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(4-aminopyridinium) 2,5-dioxidobenzoquinone dihydrate

John A. Cowan,[a,b]* Judith A. K. Howard,[b] Michael A. Leech[b] and Ian D. Williams[c]

[a]Institut Laue Langevin, BP 156, 38042 Grenoble CEDEX 9, France, [b]Department of Chemistry, University of Durham, Durham DH1 3LE, England, and [c]Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

Correspondence e-mail: cowan@ill.fr

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.068
wR factor = 0.148
Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

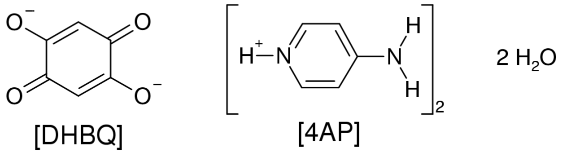
Received 15 May 2001
Accepted 31 May 2001
Online 15 June 2001

4–Aminopyridine (4AP) and 2,5-dihydroxybenzonquinone (DHBQ) crystallize in a 2:1 ratio as a molecular salt with two molecules of water, *i.e.* $2C_5H_7N_2^+\cdot C_6H_2O_4^{2-}\cdot 2H_2O$ in space group $P2_1/c$. The 4AP molecules and the DHBQ molecules pack to form infinite one-dimensional hydrogen-bonded chains mediated by the water molecules, which themselves act as tetrahedral centres and link the chains in three dimensions.

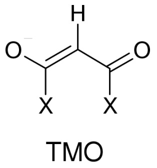
Comment

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 2,5-dihydoxybenzoquinone (DHBQ) and 4-aminopyridine (4AP).

DHBQ is a weak organic acid structurally and chemically very similar to squaric acid. This is reflected in the crystal structures it forms; the recently reported structure of DHBQ with 4,4′-bipyridine (Cowan *et al.*, 2001) is closely related to the squarate analogue reported by Reetz *et al.* (1994) and the present structure is very similar to that observed in 4AP and squarate (Karle *et al.*, 1996).



The DHBQ molecule has become deprotonated and consequently shows partial delocalization in the present structure. The conformation is similar to that reported by Kulpe (1974) for the potassium salt and discussed by Kulpe & Dähne (1978). They describe DHBQ as two coupled trimethineoxonol (TMO, see below) connected by two long Csp^2—Csp^2 bonds. The long Csp^2—Csp^2 bond is between C1 and C2 [C1—C2 1.542 (3) Å] and is even longer than the typical Csp^3—Csp^3 bond length (C—C = 1.53 Å; Allen *et al.*, 1992).



The pyridine group of the 4AP has become protonated and forms N—H···O hydrogen bonds to the DHBQ. In contrast to the squarate and 4AP system in which one strong N—H···O

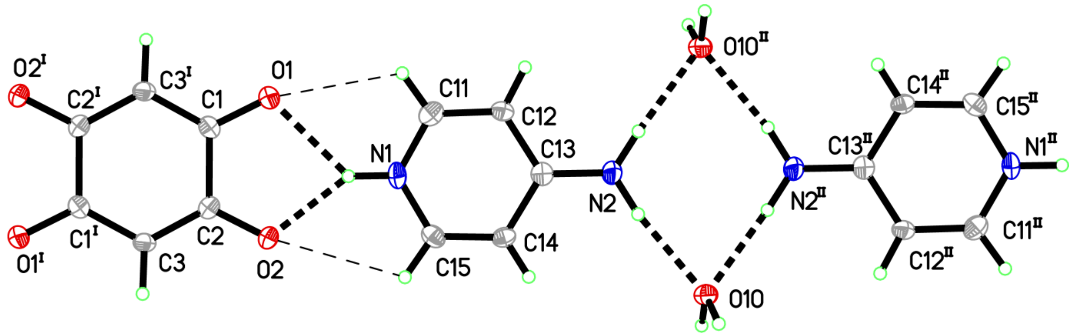


Figure 1
The moieties of the title compound shown with 50% probability displacement ellipsoids. The dashed lines indicate hydrogen bonds. [Symmetry codes: (I) $4 - x, -y, 2 - z$; (II) $1 - x, -y, 1 - z$.]

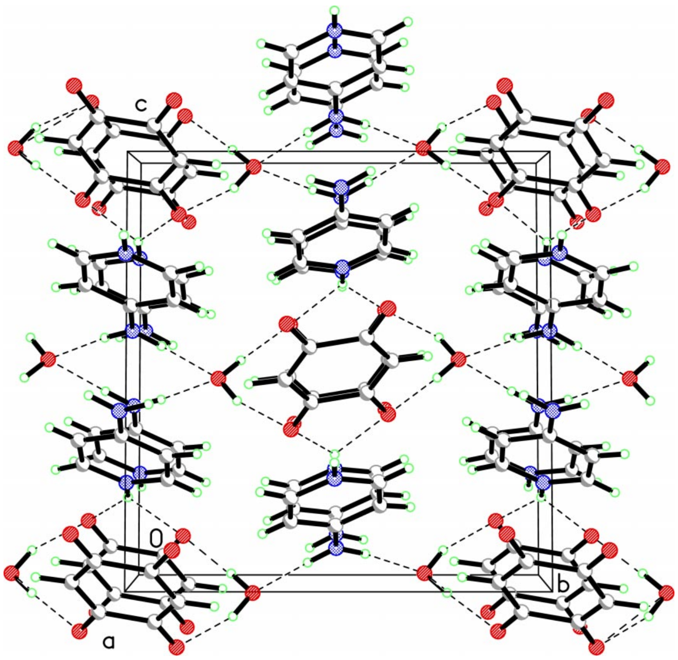


Figure 2
Packing diagram viewed along the *a* axis. The dashed lines indicate hydrogen bonds. It can be seen easily how the water molecules bind the structure together.

hydrogen bond is formed (Karle *et al.*, 1996), a bifurcated N—H···O hydrogen bond is formed with similar N···O distances [N1···O1 2.875 (3) Å and N1···O2 2.757 (3) Å] (Fig. 1). The bifurcated N—H···O hydrogen bond is assisted by two almost equal-length weak C—H···O bonds [C11···O1 3.132 (4) Å and C11—H11—O1 115 (2)°, and C15···O2 3.177 (3) Å and C15—H15—O2 109 (2)°]. The aromatic rings of the DHBQ and the 4AP are inclined at an angle of 8.2° with respect to each other, but an imaginary torsion angle, O1···O2···C15···C11 of 0.4°, shows that most of this is a fold along an axis through O1 and O2. These C—H···O bonds are short and have large C—H···O angles compared with similar C—H···O bonds (Steiner, 1997), but they prevent rotation of the 4AP about an axis through N1 and N2 that would be allowed by the other hydrogen bonds in the chain.

The 4AP molecules pack with each other amino group to amino group. The unlikely close proximity of these two basic groups [N2···N2^{ii} 3.511 (5) Å and H2A···H2B^{ii} 2.52 (4) Å; symmetry code: (ii) $1 - x, -y, 1 - z$] is caused by hydrogen-bond formation to the lone pairs of the water molecule oxygen (Fig. 1) (N2—H2*A*···O10 and N2—H2*B*···O10^{ii}).

The molecules pack to form infinite hydrogen-bonded chains that propagate along the [301] direction. The chains form columns along the [$\overline{1}$03] direction. The water is an essential part of the supramolecular structure, it links the one-dimensional chains together by accepting hydrogen bonds from the amino groups of the 4AP molecules and also forms hydrogen bonds to the DHBQ molecules, which join adjacent chains together into a three-dimensional network (Fig. 2).

Experimental

Approximately 0.5 ml of a 0.2 *M* solution of 4-aminopyridine in methanol was poured slowly into a narrow test tube containing approximately 0.5 ml of a 0.2 *M* aqueous solution of 2,5-dihydroxybenzonquinone to produce a water/methanol interface. Thin red plate-like crystals suitable for X-ray analysis were produced by slow diffusion at the interface of the solutions.

Crystal data

$2C_5H_7N_2^+ \cdot C_6H_2O_4^{2-} \cdot 2H_2O$
$M_r = 364.36$
Monoclinic, $P2_1/c$
$a = 6.345\ (4)$ Å
$b = 11.353\ (8)$ Å
$c = 11.838\ (8)$ Å
$\beta = 95.684\ (16)°$
$V = 848.5\ (10)$ Å^3
$Z = 2$

$D_x = 1.426$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 980 reflections
$\theta = 5.0$–$23.9°$
$\mu = 0.11$ mm^{-1}
$T = 100\ (2)$ K
Plate, red
0.65 × 0.35 × 0.05 mm

Data collection

Bruker SMART–CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.804$, $T_{\max} = 1.000$
7323 measured reflections

1861 independent reflections
1475 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\max} = 27.1°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.148$
$S = 1.66$
1861 reflections
158 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

o564 John A. Cowan *et al.* • $2C_5H_7N_2^+ \cdot C_6H_2O_4^{2-} \cdot 2H_2O$ *Acta Cryst.* (2001). E**57**, o563–o565

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.95 (3)	2.14 (3)	2.875 (3)	133 (2)
N1—H1···O2	0.95 (3)	1.94 (3)	2.757 (3)	142 (2)
C11—H11···O1	0.96 (3)	2.60 (3)	3.132 (4)	115 (2)
C15—H15···O2	0.96 (3)	2.74 (3)	3.177 (3)	109 (2)
N2—H2*A*···O10	0.94 (3)	2.02 (3)	2.948 (3)	172 (2)
N2—H2*B*···O10$^{\rm i}$	0.94 (3)	2.02 (3)	2.963 (3)	174 (2)
O10—H10*A*···O1$^{\rm ii}$	0.95 (4)	1.83 (4)	2.770 (3)	168 (3)
O10—H10*B*···O2$^{\rm iii}$	0.91 (4)	1.90 (4)	2.779 (3)	161 (3)

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

All H atoms were found in the difference Fourier maps and were refined with isotropic displacement parameters; the C—H, N—H and O—H distances all refined to within standard ranges and there are no anomalous values of $U_{\rm iso}$. As we are interested in the behaviour of the H atoms with respect to any hydrogen-bonded networks, it would be artificial to add any constraints to this stable and converged refinement.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C, Table 9.5.1.1, pp. 685–706. Dordrecht: Kluwer.

Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cowan, J. A., Howard, J. A. K. & Leech, M. A. (2001). *Acta Cryst.* C**57**, 302–303.

Karle, I. L., Ranganathan, D. & Haridas, V. (1996). *J. Am. Chem. Soc.* **118**, 7128–7133.

Kulpe, S. (1974). *J. Prakt. Chem.* **316**, 353–362.

Kulpe, S. & Dähne, S. (1978). *Acta Cryst.* B**34**, 3616–3623.

Reetz, M. T., Höger, S. & Harms, K. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 181–183.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Steiner, T. (1997). *Chem. Commun.* pp. 727–734.

Acta Cryst. (2001). E**57**, o563–o565 John A. Cowan *et al.* • $2C_5H_7N_2^{+}\cdot C_6H_2O_4^{2-}\cdot 2H_2O$ **o565**