organic compounds

A zwitterionic viologen disulfonate–hydroquinone charge-transfer crystal: 2,2′-(4,4′-bipyridinium-1,1′-diyl)di(ethanesulfonate)–hydroquinone (1/2)[1]

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The structure of the title compound, $C_{14}H_{16}N_2O_6S_2 \cdot 2C_6H_6O_2$, consists of 2,2′-(4,4′-bipyridinium-1,1′-diyl)di(ethanesulfonate) molecules (with crystallographically imposed twofold symmetry) that are hydrogen bonded to each other, as well as to hydroquinone molecules, in a complex three-dimensional motif. The orange color of the crystals is indicative of the donor–acceptor interaction between the electron-rich hydroquinone π-donor and the electron-deficient bipyridinium π-acceptor. The dihedral angle between the bipyridyl planes is 38.31 (11)°. The distance from the centroid of one of the hydroquinone molecules to the center of the bipyridinium group is 3.653 (3) Å, which is within the range typically observed for molecular complexes exhibiting charge-transfer characteristics.

Comment

Electron-donor–acceptor interactions have been recognized as playing a key role in the development of unusual optical, electrical and magnetic properties of crystalline materials (Hubig & Kochi, 1995). Since the discovery of neutral–ionic transitions induced by temperature or pressure in mixed π-stacked organic charge-transfer crystals, extensive studies have been carried out on these types of systems (Aoki & Nakayama, 1997; Brocks, 1997). In particular, charge-transfer complexes incorporating viologen (N,N'-disubstituted-bipyridinium) as the electron-acceptor component have been the subject of much research, due to the potential use of viologen in photochemical energy conversion systems (Jones & Malba, 1985). In addition, the interaction of the viologen moiety with π-electron donors has been extensively exploited in the design of supramolecular assemblies, including rotaxanes, catenanes and molecular shuttles (Asakawa et al., 1996;

Simonsen et al., 1998; Hu et al., 1998; Loeb & Wisner, 2000; Willner et al., 1992). The intermolecular interactions of viologen derivatives with electron-rich aromatic systems are therefore of great interest.

We report here the crystal structure of the charge-transfer complex 2,2′-(4,4′-bipyridinium-1,1′-diyl)di(ethanesulfonate)–hydroquinone, (I). The orange color of these crystals is indicative of the interaction between the hydroquinone π-donor and the bipyridinium π-acceptor components of the complex, which gives rise to charge-transfer electronic transitions.
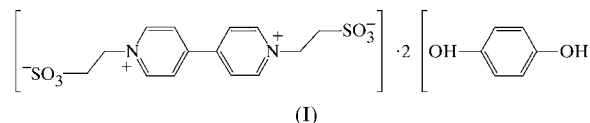

(I)

Fig. 1 shows the molecular structure of (I), along with the atom-numbering scheme. The two halves of the bipyridinium moiety are related by a twofold axis of symmetry. The dihedral angle between the bipyridyl planes is 38.31 (11)°. The two halves of the hydroquinone molecules are also related by symmetry, the first by an inversion center and the second by a twofold axis, as indicated in Fig. 1.

In previous reports, the packing of viologen crystals in the solid state has been described as a stacking of planar bipyridinium dications and anionic counter-ions. The anions exhibit close contacts between the N atoms and the C atoms of neighboring pyridyl rings, and are directed toward this cationic center rather than toward the centroid of the rings (Argay & Kálmán, 1995; Poojary et al., 1994; Russell & Wallwork, 1972). In the zwitterionic bipyridinium molecule described here, equivalent viologen disulfonate molecules pack in an end-to-end manner, as shown in Fig. 2. This packing allows the sulfonate anions to lie in between two cationic pyridinium units. The intramolecular distance from the N1/C1–C5 centroid to the O1/O2/O3 centroid is 3.964 (3) Å; the corresponding intermolecular distance is 5.146 (3) Å.

The orientation of the nearly planar hydroquinone molecule toward the twisted bipyridinium group is also seen in Fig. 2. It has been suggested that the intermolecular interaction between aromatic systems is more accurately described as σ–π rather than π–π (Hunter & Sanders, 1990). This interaction is described primarily as an electrostatic one between the more positive σ framework of one molecule and the electron-rich π system of the other. In the case of (I), the nearly planar hydroquinone molecule is not parallel to the pyridinium rings. This geometry allows for a π–σ interaction between the electron-rich π system of the hydroquinone and the σ framework of each half of the bipyridinium group. The angle formed between the plane of the hydroquinone group and the plane of each bipyridyl ring is 19.16 (13)°. The distance from the centroid of the hydroquinone molecule to the center of the C3—C3′ bond is 3.653 (3) Å. Numerous charge-transfer complexes have been prepared, either as molecular crystals or as ion-pair salts, and, typically, a close approach of 3.5–3.7 Å of the electron-donor and -acceptor molecules is observed (Hubig & Kochi, 1995).
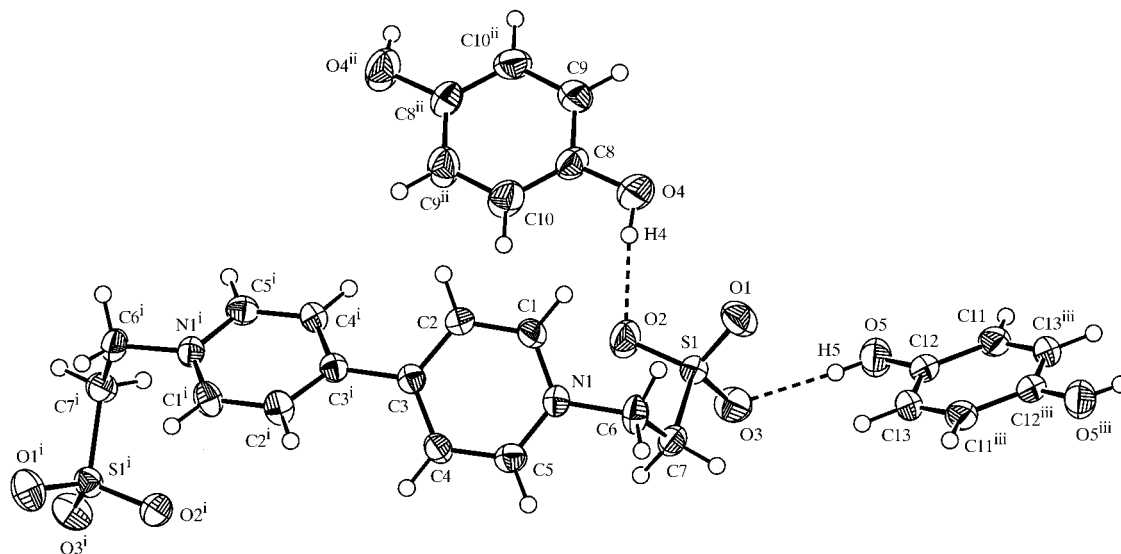
Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids at the 50% probability level [symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, y, \frac{3}{2} - z$; (iii) $-x, -y, 1 - z$].

As summarized in Table 1, hydrogen bonding is an important intermolecular interaction in the charge-transfer crystal of (I). All O atoms in this crystal act as hydrogen-bond acceptors. Further, the O atoms of the two hydroquinone molecules are also hydrogen-bond donors. Atoms O2 and O3 of the sulfonate group are hydrogen bonded to the acidic atoms H4 and H5 attached to the O atoms of the hydroquinone molecules. This interaction is indicated in Fig. 1. The

remaining sulfonate O atom (O1) is involved in the intermolecular C—H···O hydrogen bond, with the H atom located on atom C1 of the pyridinium ring (Fig. 2).

Two additional C—H···O interactions which fit the criteria of a hydrogen bond, as defined by Desiraju (1996), are observed in the crystal of (I). These are between the hydroquinone O atoms and two acidic C—H H atoms of the ethyl group, as illustrated in Fig. 3. These various hydrogen-bonding interactions result in the formation of the three-dimensional hydrogen-bonded network illustrated in the packing drawing (Fig. 4).
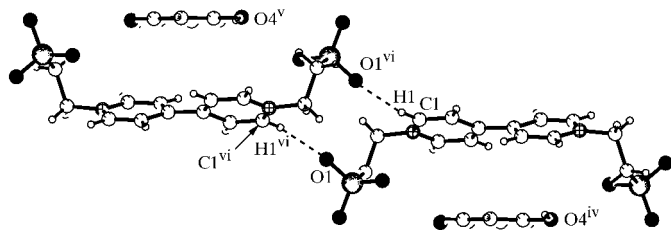

Figure 2
A view of (I), showing the orientation of the planar hydroquinone with respect to the bipyridinium unit, as well as the C1—H1···O1 intermolecular hydrogen bonds [symmetry codes: (iv) $1 - x, -y, 1 - z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$].
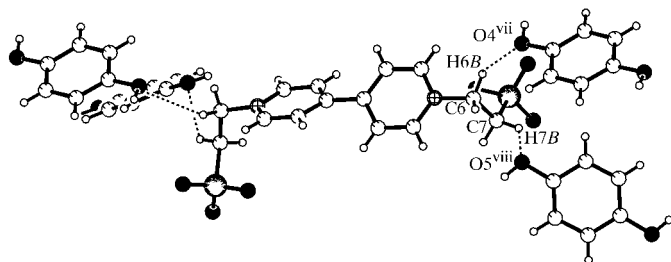

Figure 3
A view of (I), showing the hydroquinone O atoms as hydrogen-bond acceptors in C—H···O hydrogen bonds [symmetry codes: (vii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (viii) $x, -y, z - \frac{1}{2}$].
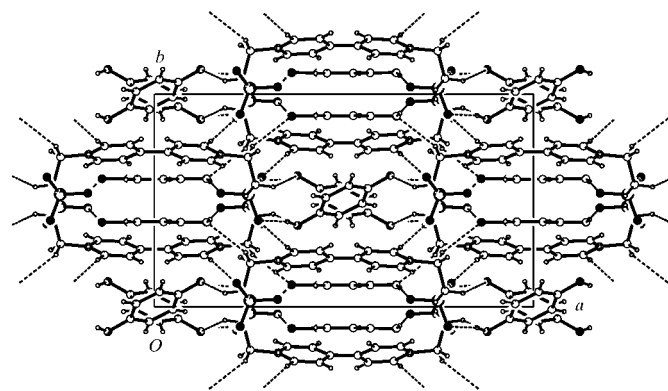

Figure 4
The molecular packing and hydrogen bonding in (I), viewed down the c axis. Black circles indicate O atoms, large shaded circles indicate S atoms and cross-hatched circles indicate N atoms.

Experimental

2,2'-(4,4'-Bipyridinium-1,1'-diyl)di(ethanesulfonate) was prepared as described previously by Vermeulen & Robinson (1996). Hydroquinone was purchased from Fisher. Crystals of (I) were obtained

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by dissolving 2,2'-(4,4'-bipyridinium-1,1'-diyl)di(ethanesulfonate) (0.192 g, 0.516 mol) and guanidinium hydrochloride (0.099 g, 1.03 mol) in deionized water (15 ml). Hydroquinone (0.050 g, 0.454 mol) was dissolved in warm methanol (15 ml). The methanol solution was added slowly to the aqueous solution with stirring. The mixture was aged at room temperature until orange crystals of (I) appeared.

Crystal data

$C_{14}H_{16}N_2O_6S_2 \cdot 2C_6H_6O_2$
$M_r = 592.62$
Monoclinic, $C2/c$
$a = 20.006 (5)$ Å
$b = 11.072 (3)$ Å
$c = 11.882 (3)$ Å
$\beta = 98.94 (2)°$
$V = 2600.2 (12)$ Å^3
$Z = 4$

$D_x = 1.514$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13.5–14.8°$
$\mu = 0.27$ mm^{-1}
$T = 296$ K
Prism, orange
$0.40 \times 0.24 \times 0.22$ mm

Data collection

Rigaku AFC-5S diffractometer
ω scans
Absorption correction: ψ scan (North et al., 1968)
$T_{min} = 0.921$, $T_{max} = 0.943$
2370 measured reflections
2301 independent reflections
1585 reflections with $I > 2\sigma(I)$

$R_{int} = 0.012$
$\theta_{max} = 25.1°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 13$
$l = -14 \rightarrow 13$
3 standard reflections
every 100 reflections
intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.098$
$S = 1.04$
2301 reflections
183 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 1.6343P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4···O2	0.82	1.93	2.740 (3)	171
O5—H5···O3	0.82	1.97	2.773 (3)	164
C1—H1···O1^i	0.93	2.26	3.120 (3)	154
C6—H6B···O4^i	0.97	2.59	3.292 (3)	129
C7—H7B···O5^{ii}	0.97	2.56	3.235 (3)	127

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

The rotational orientations of the hydroxyl groups were determined by the circular Fourier refinement method available in *SHELXL*97 (Sheldrick, 1997). All H atoms were treated as riding, with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.97 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965) and *PLATON* (Spek, 2000); software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON*.

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