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A Photochromic Zwitterionic Viologen: 4,4′-Bipyridinium-1,1′-bis(2-ethylsulfonate) Monohydrate

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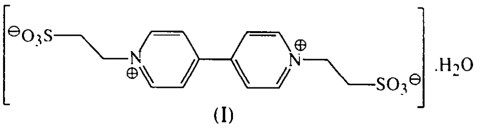
Abstract

The structural analysis of the title compound, $C_{14}H_{16}N_2O_6S_2.H_2O$, shows that the packing of the zwitterionic molecule in the crystal is such that the anionic sulfonate groups are located between the dicationic bipyridinium groups of adjacent molecules. Hydrogen bonds between a water molecule and the sulfonate groups link adjacent molecules into infinite molecular chains. The bipyridinium portions of adjacent molecules are not parallel, but form an angle of 58.0 (1)° with respect to one another, forming a wedge within which the anionic groups are located.

Comment

The viologens (1,1′-dialkylbipyridinium compounds) have been well studied because of their herbicidal properties (Summers, 1980) and their potential use as electron acceptors in photochemical redox systems (*e.g.* Meyer, 1989; Turro & Kavarnos, 1986). In addition, some of these compounds have photochromic properties in the solid state (Vermeulen & Thompson, 1992; Nakato, Kuroda & Kato, 1992; Kamogawa & Suzuki, 1987; Nagamura & Sakai, 1986). There is great interest, therefore, in their use in electrochromic display or photoelectrochromic memory systems (Kamogawa & Ono, 1991; Nagamura, Isoda, Sakai & Ogawa, 1990). Their molecular orientation in such a system is an important property to be controlled. Directional dependence of optical response is an important factor to be considered and has not yet been studied to any great extent. We have grown large single crystals (average 5 × 5 × 2 mm) of the title compound, (I). These crystals are photochromic and exhibit a directional dependence in their optical response. The crystal structure of (I) is reported here. The photochemistry will be presented in a subsequent paper.



(I)

In previous reports, the packing of viologen crystals in the solid state has been described as a stacking of planar bipyridinium dications and anionic counterions. In some cases, adjacent bipyridinium planes are parallel and the anions are located precisely between adjacent groups (Argay & Kálmán, 1995; Poojary, Vermeulen, Vicenzi, Clearfield & Thompson, 1994). In other cases, adjacent bipyridinium planes are not parallel but form a wedge that encompasses the counterion (Russell & Wallwork, 1972). The anions have close contacts between the N and neighboring C atoms of the pyridyl rings and are directed towards this cationic center rather than towards the centroid of the rings. In the bipridinium halides, this interaction is described as charge transfer in nature and is responsible for the colors of the halide salts. In all cases, there are no close contacts between adjacent bipyridinium groups because of charge–charge repulsion of the cationic centers.

Fig. 1 shows the molecular structure of (I) along with the atom-numbering scheme, while Fig. 2 shows the packing of the molecules in the crystal. Note that the zwitterion lies on an inversion center and the water molecule on a twofold axis. Adjacent molecules are connected *via* a hydrogen-bonding interaction between a water molecule and the sulfonate anions. The resulting molecular chains propagate infinitely in the [001] direction. The hydrogen-bond geometry is given in Table 2. Bipyridinium planes of adjacent

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molecules within the molecular chains form angles of 58.0 (1)° with respect to one another, giving the chain a corrugated conformation. The sulfonate anions are located between two adjacent bipyridinium groups; however, the intramolecular contacts are closer than the intermolecular ones. The intramolecular N1–C1–C5 centroid to O1–O2–O3 centroid distance is 3.669 (6) Å, compared with the equivalent intermolecular centroid–centroid distance of 3.882 (6) Å.

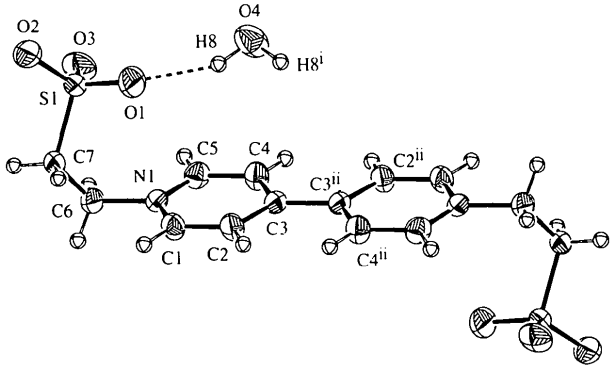

Fig. 1. The conformation and atom-numbering scheme of (I), with displacement ellipsoids at the 50% probability level. H atoms are shown as unlabeled isotropic spheres of arbitrary radii. Atom H8 is related to atom H8^{i} by a twofold rotation axis which passes through atom O4. The two halves of the molecule are related by an inversion center located at the midpoint of the C3—C3^{ii} vector. [Symmetry code: (ii) $1 - x, 1 - y, 1 - z$.]

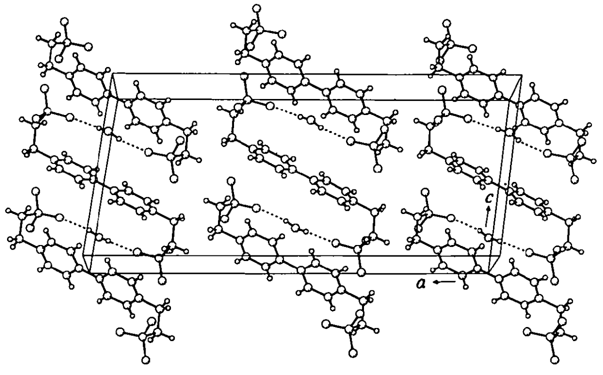

Fig. 2. The molecular packing and hydrogen bonding of (I). The hydrogen-bonding scheme produces infinite molecular chains parallel to the [001] direction.

Experimental

The title compound, (I), was prepared from the reaction of 4,4′-bipyridyl and the sodium salt of 2-bromoethanesulfonic acid. Crystals were obtained by slow evaporation of an aqueous solution at room temperature.

Crystal data

$C_{14}H_{16}N_2O_6S_2.H_2O$
$M_r = 390.43$
Monoclinic
$C2/c$
$a = 25.016\ (6)$ Å
$b = 5.881\ (8)$ Å
$c = 11.299\ (8)$ Å
$\beta = 98.17\ (3)°$
$V = 1645\ (2)$ Å^3
$Z = 4$
$D_x = 1.576$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 23 reflections
$\theta = 19.6–19.8°$
$\mu = 0.37$ mm^{-1}
$T = 296$ K
Prism
0.38 × 0.28 × 0.21 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 6° min^{-1} in ω, max. 3 repetitions)
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.95$, $T_{\max} = 1.00$
4170 measured reflections
2087 independent reflections

1551 observed reflections $[I > \sigma(I)]$
$R_{\rm int} = 0.068$
$\theta_{\max} = 27.5°$
$h = -32 \rightarrow 32$
$k = 0 \rightarrow 7$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.044$
$wR = 0.052$
$S = 1.48$
1551 reflections
114 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = 0.0003$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.33701 (2)	0.16440 (9)	0.12123 (5)	0.0305 (2)
O1	0.39465 (6)	0.1998 (4)	0.1512 (2)	0.0577 (7)
O2	0.32019 (7)	0.1449 (3)	−0.00680 (16)	0.0462 (6)
O3	0.31750 (7)	−0.0183 (3)	0.18876 (18)	0.0501 (7)
N1	0.36655 (7)	0.4563 (3)	0.35974 (17)	0.0298 (5)
C1	0.39609 (8)	0.6373 (4)	0.3384 (2)	0.0376 (7)
C2	0.44883 (8)	0.6554 (4)	0.3913 (2)	0.0360 (7)
C3	0.47161 (7)	0.4910 (4)	0.46978 (19)	0.0274 (6)
C4	0.43941 (8)	0.3049 (4)	0.4906 (2)	0.0362 (7)
C5	0.38714 (8)	0.2915 (4)	0.4330 (2)	0.0357 (7)
C6	0.30953 (8)	0.4418 (4)	0.2997 (2)	0.0371 (7)
C7	0.30544 (8)	0.4144 (4)	0.1663 (2)	0.0304 (6)
O4	1/2	0.0588 (5)	1/4	0.0627 (12)

Table 2. *Selected geometric parameters (Å, °)*

S1—O1	1.448 (2)	S1—C7	1.777 (3)
S1—O2	1.453 (2)	N1—C6	1.493 (3)
S1—O3	1.443 (2)	C6—C7	1.504 (3)
O1—S1—O2	112.44 (12)	C1—N1—C6	118.72 (18)
O1—S1—O3	112.58 (12)	C5—N1—C6	120.13 (18)
O1—S1—C7	106.40 (11)	N1—C6—C7	112.70 (17)
O2—S1—O3	113.33 (11)	S1—C7—C6	113.94 (16)
O2—S1—C7	105.84 (11)	H8—O4—H8^{i}	102.4
O3—S1—C7	105.49 (11)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H8···O1	0.91	2.02	2.836 (4)	148

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

The H8 atom was fixed at its difference Fourier map position. The remaining H atoms were placed at assumed positions (C—H 0.95 Å, $U = 1.2U_{eq}$ of the associated atom) and fixed.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*. Software used to prepare material for publication: *TEXSAN FINISH*; *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Methoxybenzaldehyde Nicotinoylhydrazone Dihydrate

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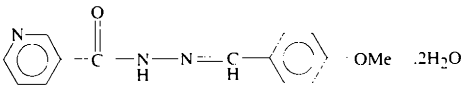
Abstract

The nearly planar aroylhydrazone molecule of the title compound, $C_{14}H_{13}N_3O_2.2H_2O$, exists as the keto tautomer in the solid state with an *E* configuration across the C═N bond. The crystal structure is stabilized by extensive hydrogen bonding involving the water and the hydrazone molecules.

Comment

In recent years there has been considerable interest in the chemistry of aroylhydrazone compounds because of their ability to chelate transition and lanthanide metal ions (Dutta & Hossain, 1985; Sergienko, Abramenko, Minacheva, Porai-Koshits & Sakharova, 1993; Rao & Gopal, 1991) and their medical properties (Constable & Holmes, 1987; Girges, Hanna, Berghot & Rassala, 1992). As part of our studies on the synthesis and characterization of these compounds, we determined the structure of the title compound, (I).



(I)

The C6—O1 [1.224 (2) Å] and N2—N3 [1.382 (2) Å] bond lengths in (I) (Fig. 1) indicate bond orders of two and one, respectively, confirming that the crystal contains the keto tautomer. The hydrazone moiety has an *E* configuration at the N3═C7 double bond. The dihedral angle between the planes of the pyridine and methoxyphenyl rings is 9.04 (6)° and these two planes make angles of 12.15 (6) and 3.10 (6)° with the plane of the central hydrazone moiety; the methoxy group C

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