Crystal data

$C_{15}H_{13}N_3O_6$
$M_r = 331.28$
Monoclinic
$P2_1/c$
$a = 12.996\,(5)$ Å
$b = 10.106\,(5)$ Å
$c = 12.717\,(11)$ Å
$\beta = 110.35\,(6)°$
$V = 1566.0\,(16)$ Å^3
$Z = 4$
$D_x = 1.405$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10–11°$
$\mu = 0.111$ mm^{-1}
$T = 293\,(2)$ K
Square prism
0.50 × 0.25 × 0.25 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2878 measured reflections
2752 independent reflections
2051 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.038$
$\theta_{\rm max} = 24.97°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 12$
$l = -15 \rightarrow 14$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.131$
$S = 1.14$
2686 reflections
237 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.4754P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.019$

$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXTL/PC* (Sheldrick, 1994)
Extinction coefficient: 0.112 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N2—C2	1.457 (3)	C7—C8	1.462 (3)
N3—C4	1.447 (3)	C8—C9	1.356 (4)
O5—C1	1.330 (3)	C9—C10	1.411 (4)
O5—C6	1.410 (3)	C10—C11	1.349 (4)
C6—C12	1.359 (3)	C11—C12	1.434 (4)
C6—C7	1.454 (3)		
C1—O5—C6	117.9 (2)		

Atoms H3, H5, H9 and H11 were refined isotropically. All methyl-H atoms were located from a difference Fourier synthesis and thereafter allowed to refine as part of a rigid group which was allowed to rotate but not tip or distort. The high value of U_{11} for atom O1 is attributed to the considerable thermal motion in which this atom is involved, the data having been acquired at room temperature. However, there is no evidence for disorder in the relevant nitro group.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROFIT* (Strel'tsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1347). Services for accessing these data are described at the back of the journal.

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2,2′-Bipyridine-5-sulfonic acid

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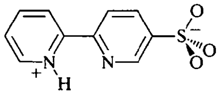
Abstract

The title compound, $C_{10}H_8N_2O_3S$, exists as a zwitterion, 6-(2-pyridinio)pyridine-3-sulfonate, following deprotonation of the sulfonic acid group and protonation of the N

atom of the unsubstituted pyridyl ring. The orientation of this N—H bond facilitates the formation of hydrogen-bonded dimers *via* two N—H···O hydrogen bonds.

Comment

X-ray diffraction studies on a single-crystal of 2,2′-bipyridine-5-sulfonic acid, (I), revealed that it exists as a zwitterion in which the sulfonic acid group is deprotonated and the N atom of the unsubstituted pyridyl ring is protonated. This zwitterionic form for the compound had been suggested previously on the basis of NMR studies (Herrmann, Thiel *et al.*, 1990).



(I)

The pyridyl rings in the title compound adopt a *cis* arrangement stabilized to some extent by a weak intramolecular N—H···N hydrogen bond [N1···N2 2.667 (2), N1···H2 2.31 Å and N2—H2···N1 105°; Fig. 1]. Other monoprotonated 2,2′-bipyridyl (bipyH$^+$) species have also been shown to exhibit this conformation in the solid state (Figgis *et al.*, 1978; Khan *et al.*, 1984), though in contrast, the crystal structures of 2,2′-bipyridyl (Merritt & Schroeder, 1956) and of diprotonated 2,2′-bipyridyl (bipyH$_2^{2+}$; Nakatsu *et al.*, 1972) have shown that these both adopt *trans* orientations.

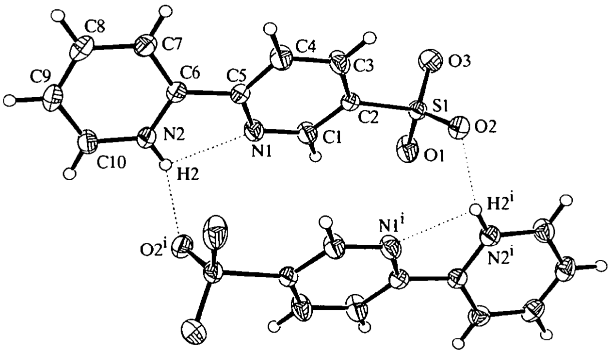


Fig. 1. *ORTEX* plot (McArdle, 1995) of (I) showing the labelling scheme and the hydrogen bonding [symmetry code: (i) $-x$, $-y$, $-z$]. Ellipsoids are represented at the 40% probability level.

The N1—C5—C6—N2 torsion angle in (I) [19.8 (2)°] demonstrates a twisting of the two pyridyl rings from coplanarity. This is the largest torsion angle so far observed for a bipyH$^+$ derivative, previous examples having been observed between 0 and 18° (Milani *et al.*, 1997; Allen *et al.*, 1991).

In addition to forming an intramolecular hydrogen bond, the acidic proton bonded to N2 also hydrogen bonds to an O atom on the sulfonate group of a neighbouring molecule [N2···O2^i 2.817 (2), H2···O2^i 2.04 Å and N2—H2···O2^i 149°; symmetry code: (i) $-x$, $-y$, $-z$]. The H atom lies slightly above the plane composed of atoms N2, N1 and O2, with the sum of the three X···H2···Y angles being 354.9°. Hydrogen bonding to a neighbouring molecule facilitates dimerization of (I) through two N—H···O hydrogen bonds and the formation of 18-membered rings which straddle crystallographic inversion centres in the lattice array. Hydrogen bonds from the N—H bond in bipyH$^+$ have been observed previously to nitrate (Khan *et al.*, 1984) and perrhenate anions (Herrmann, Kuchler *et al.*, 1990), as well as to carboxylic acids (Mvros-Sermek *et al.*, 1996) and coordinated oxalate (Decurtins *et al.*, 1993). However, according to the results of a search of the Cambridge Structural Database (Allen *et al.*, 1991), this structure represents the first instance in which the substituents on the bipyridyl molecule allow hydrogen bonding which leads to dimerization.

Experimental

Crystals of (I) were obtained by slow evaporation of an aqueous solution at room temperature.

Crystal data

$C_{10}H_8N_2O_3S$
$M_r = 236.24$
Triclinic
$P\bar{1}$
$a = 6.108\,(1)$ Å
$b = 7.026\,(2)$ Å
$c = 11.492\,(2)$ Å
$\alpha = 97.21\,(2)°$
$\beta = 99.23\,(2)°$
$\gamma = 96.39\,(2)°$
$V = 478.6\,(2)$ Å^3
$Z = 2$
$D_x = 1.639$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.0–17.7°$
$\mu = 0.330$ mm^{-1}
$T = 293\,(2)$ K
Block
0.30 × 0.30 × 0.27 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1913 measured reflections
1685 independent reflections
1540 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.006$

$\theta_{\max} = 24.97°$
$h = 0 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -13 \rightarrow 13$
3 standard reflections every 80 reflections frequency: 150 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.082$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.413$ e Å^{-3}
$\Delta\rho_{\min} = -0.324$ e Å^{-3}

$S = 1.075$
1681 reflections
147 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.2614P]$
where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.040 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

S1—O3	1.4383 (15)	N1—C1	1.333 (2)
S1—O1	1.4460 (14)	N1—C5	1.335 (2)
S1—O2	1.4564 (14)	N2—C10	1.337 (2)
S1—C2	1.781 (2)	N2—C6	1.345 (2)
O3—S1—O1	115.02 (10)	C1—C2—S1	119.58 (13)
O3—S1—O2	112.42 (9)	C3—C2—S1	122.39 (13)
O1—S1—O2	112.51 (9)	N1—C5—C4	122.8 (2)
O3—S1—C2	105.89 (8)	N1—C5—C6	114.87 (15)
O1—S1—C2	104.44 (8)	N2—C6—C7	118.34 (15)
O2—S1—C2	105.51 (8)	N2—C6—C5	116.19 (14)
C1—N1—C5	116.97 (15)	C10—C9—C8	118.8 (2)
C10—N2—C6	123.35 (15)	N2—C10—C9	119.8 (2)
N1—C1—C2	124.4 (2)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{i}	0.86	2.04	2.817 (2)	149

Symmetry code: (i) $-x, -y, -z$.

All H atoms were located from difference Fourier synthesis and were allowed to refine riding on their parent atoms. It was possible to positionally refine the proton attached to N2, however, as 'free' refinement yielded a position which was close (within experimental error) to that calculated, it was ultimately refined riding on its parent atom.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *CELDIM* in *CAD*-4-*PC Software*. Data reduction: *XCAD* (McArdle & Higgins, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1080). Services for accessing these data are described at the back of the journal.

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1:1 Complexes of chloranilic acid with pyrazine and morpholine: one- and two-dimensional hydrogen-bond networks

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Abstract

The hydrogen-bonded 1:1 complexes of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone) with pyrazine (1,4-diazine), pyrazine–chloranilic acid (1/1), $C_4H_4N_2\cdot C_6H_2Cl_2O_4$, (1), and with morpholine, morpholinium chloranilate, $C_4H_{10}NO^+\cdot C_6HCl_2O_4^-$, (2), were prepared and their crystal structures were determined at room temperature. The two components in (1) are linked by O—H···N hydrogen bonds to form a one-dimensional chain. In (2), molecules of chloranilic acid form an O—H···O hydrogen-bond chain and that of morpholine links the two chains with N—H···O hydrogen bonds, forming the two-dimensional hydrogen-bond network in the crystal.

Comment

1:1 Complexes of chloranilic acid with pyrazine and morpholine in the solid state were studied using IR data. For both complexes it was reported that a charge transfer accompanied by a proton transfer occurs between the two components, resulting in $C_4H_5N_2^+\cdot C_6HCl_2O_4^-$ (Issa *et al.*, 1991) and $C_4H_{10}NO^+\cdot C_6HCl_2O_4^-$ (Habeeb *et al.*, 1995), the anion and the cation of which are held by N—H(N)···O hydrogen bonds. In the present study, we prepared the 1:1 complexes and determined their crystal structures at room temperature to investigate the hydrogen bonds.