Crystal structure of 2-amino-4-methylpyridininum 4-nitrobenzenesulfonate, $[C_6H_9N_2][C_6H_4NO_5S]$

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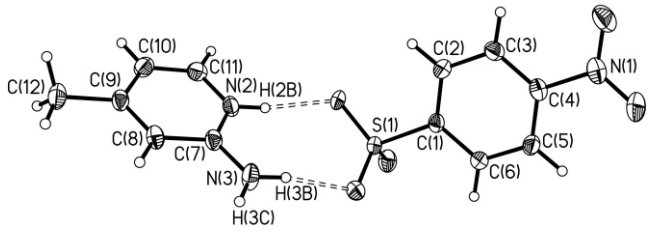

Abstract

$C_{12}H_{13}N_3O_5S$, monoclinic, $P2_1/n$ (no. 14), a = 8.769(2) Å, b = 11.090(2) Å, c = 14.119(3) Å, β = 102.35(3)°, V = 1341.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.158, T = 150 K.

Source of material

A solution of 2-amino-4-methylpyridine (0.540 g, 5 mmol) in CH_2Cl_2 (30 mL) was treated with 4-nitrobenzenesulfonyl chloride (1.11 g, 5 mmol) and the pH of the reaction mixture was adjusted to 8 with sodium carbonate solution (10 %). The reaction mixture was refluxed. The progress of reaction was monitored by thin layer chromatography (TLC), using ethyl acetate and *n*-hexane in 2:1 ratio as eluent. After completion of the reaction (4 h), the solid crude was filtered. The clear filtrate solution was kept at 4 °C to give the colorless single crystals of the title compound (yield 88 %).

Discussion

In continuation of our recent work on synthesis of new ligands with sulfur and nitrogen donor atoms [1-5], reactions of sulfonylchloride derivatives with heterocyclic amines in CH_2Cl_2 at room temperature and under reflux condition have been studied. Treatment of sulfonylchloride compounds with amines at room temperature led to the corresponding sulfonamides [6,7].

The title compound is a new proton transfer compound and it was formed due to hydrolysis of 4-nitrosulfonyl chloride to 4-nitrobenzenesulfonyl acid and H atom being transferred to the endocyclic imine nitrogen atom. Crystal field forces, static electronic, hydrogen-bonding and $\pi\cdots\pi$ stacking interactions cause the stabilization of the crystal structure. A salient feature in the crystal packing of the title compound is that the $[C_5H_9N_2]^+$ cations and $[C_6H_4NO_5S]^-$ anions are connected not only by static electronic and crystal field forces, but also by intermolecular hydrogen bonds. In the crystal, cations and anions are linked into chains parallel to [010] by intermolecular N–H···O hydrogen bonds and further stabilization is provided by weak C–H···O hydrogen bonds. A considerable feature of the compound is the presence of $\pi\cdots\pi$ stacking interactions between pyridine rings with a distance of 3.49(1) Å for Cg2···Cg2 (Cg2: N2/C7-C11).

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.30 × 0.40 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.68 cm^{-1}
Diffractometer, scan mode:	Stoe Stadi 4, rotation, ω
$2\theta_{max}$:	63.46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10519, 3189
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2411
$N(param)_{refined}$:	190
Programs:	SHELXS-97, SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2B)	4*e*	0.3347	0.5314	0.0968	0.027
H(3B)	4*e*	0.2286	0.5981	0.2218	0.035
H(3C)	4*e*	0.0770	0.6700	0.2013	0.035
H(2A)	4*e*	0.7475	0.6246	0.2557	0.028
H(3A)	4*e*	0.9478	0.7263	0.3630	0.029
H(5A)	4*e*	0.8262	0.5571	0.5910	0.028
H(6A)	4*e*	0.6305	0.4521	0.4833	0.027
H(8A)	4*e*	–0.0610	0.7135	0.0359	0.028
H(10A)	4*e*	0.1391	0.5834	–0.1765	0.032
H(11A)	4*e*	0.3373	0.5041	–0.0606	0.031
H(12A)	4*e*	–0.1880	0.7480	–0.1235	0.047
H(12B)	4*e*	–0.1665	0.6419	–0.1963	0.047
H(12C)	4*e*	–0.0717	0.7653	–0.1957	0.047

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.52003(6)	0.45028(5)	0.28242(4)	0.0183(3)	0.0254(3)	0.0157(3)	–0.0007(2)	0.0003(2)	0.0006(2)
N(1)	4*e*	1.0265(2)	0.7132(2)	0.5518(1)	0.0234(9)	0.0282(9)	0.031(1)	0.0016(8)	–0.0021(8)	–0.0031(8)
N(2)	4*e*	0.2567(2)	0.5621(2)	0.0538(1)	0.0171(9)	0.0253(9)	0.024(1)	0.0001(7)	–0.0010(7)	0.0020(7)
N(3)	4*e*	0.1506(2)	0.6310(2)	0.1802(1)	0.028(1)	0.037(1)	0.020(1)	0.0074(8)	–0.0033(8)	–0.0042(8)

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Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.6730(2)	0.5289(2)	0.3604(2)	0.017(1)	0.0213(9)	0.018(1)	0.0029(8)	0.0009(8)	0.0006(8)
C(2)	4*e*	0.7649(2)	0.6103(2)	0.3235(2)	0.024(1)	0.027(1)	0.018(1)	0.0000(8)	0.0030(8)	0.0025(8)
C(3)	4*e*	0.8825(2)	0.6707(2)	0.3867(2)	0.021(1)	0.024(1)	0.026(1)	–0.0031(8)	0.0038(9)	0.0028(8)
C(4)	4*e*	0.9030(2)	0.6486(2)	0.4847(2)	0.019(1)	0.0219(9)	0.024(1)	0.0013(8)	0.0004(8)	–0.0019(8)
C(5)	4*e*	0.8106(2)	0.5692(2)	0.5230(2)	0.022(1)	0.029(1)	0.018(1)	0.0024(8)	0.0015(8)	0.0015(8)
C(6)	4*e*	0.6950(2)	0.5082(2)	0.4594(2)	0.020(1)	0.027(1)	0.020(1)	–0.0026(8)	0.0035(8)	0.0018(8)
C(7)	4*e*	0.1439(2)	0.6218(2)	0.0855(2)	0.020(1)	0.0213(9)	0.021(1)	–0.0034(8)	–0.0010(8)	–0.0013(8)
C(8)	4*e*	0.0203(2)	0.6706(2)	0.0157(2)	0.021(1)	0.021(1)	0.025(1)	0.0001(8)	–0.0021(8)	–0.0025(8)
C(9)	4*e*	0.0166(2)	0.6567(2)	–0.0808(2)	0.021(1)	0.0209(9)	0.024(1)	–0.0049(8)	–0.0031(8)	0.0032(8)
C(10)	4*e*	0.1391(3)	0.5933(2)	–0.1097(2)	0.030(1)	0.028(1)	0.021(1)	–0.0029(9)	0.0038(9)	0.0017(9)
C(11)	4*e*	0.2553(3)	0.5474(2)	–0.0417(2)	0.023(1)	0.028(1)	0.027(1)	–0.0002(8)	0.0070(9)	0.0021(8)
C(12)	4*e*	–0.1135(3)	0.7073(2)	–0.1554(2)	0.029(1)	0.033(1)	0.026(1)	0.0010(9)	–0.0050(9)	0.003(1)
O(1)	4*e*	1.1128(2)	0.7790(2)	0.5176(1)	0.036(1)	0.041(1)	0.045(1)	–0.0172(8)	–0.0013(8)	0.0008(8)
O(2)	4*e*	1.0374(2)	0.6990(2)	0.6384(1)	0.041(1)	0.064(1)	0.026(1)	–0.0136(9)	–0.0030(8)	–0.0112(9)
O(3)	4*e*	0.3785(2)	0.4856(1)	0.3126(1)	0.0193(7)	0.0354(8)	0.0236(8)	0.0004(6)	0.0041(6)	0.0005(6)
O(4)	4*e*	0.5569(2)	0.3236(1)	0.2977(1)	0.0303(8)	0.0238(7)	0.0265(8)	–0.0005(6)	–0.0004(6)	–0.0019(6)
O(5)	4*e*	0.5215(2)	0.4901(1)	0.1846(1)	0.0234(8)	0.0421(9)	0.0131(8)	–0.0024(7)	–0.0007(6)	0.0028(7)

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