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Zwitterionic 5-amino-2-naphthalenesulfonic acid

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.105
Data-to-parameter ratio = 10.8

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

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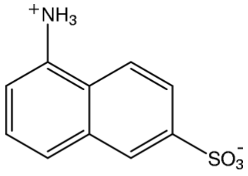
The crystal structure of 5-amino-2-naphthalenesulfonic acid (1,6-Cleve's acid), $C_{10}H_9NO_3S$, shows the presence of a sulfonate–aminium group zwitterion, *viz*. 5-ammonio-2-naphthalenesulfonate. All aminium H atoms are involved in head-to-tail intermolecular hydrogen-bonding interactions with separate sulfonate O-atom acceptors, giving a three-dimensional framework polymer structure.

Comment

Although the reported structures of benzenesulfonic acids are numerous in the literature, those of polycyclic aromatic sulfonic acids are rare. No amino-substituted naphthalenesulfonic acid structures have been reported [only the cell parameters of some compounds, including the title compound, have been published by Corbridge *et al.* (1966)], while only a limited number of substituted quinolinesulfonic acids are known, mainly those of the versatile bidentate complexing agent oxine (8-hydroxyquinoline): these are 8-hydroxyquinoline-5-sulfonic acid (a dihydrate) (Banerjee *et al.*, 1984), 8-hydroxy-2-methylquinoline-5-sulfonic acid (a monohydrate) (Merritt & Duffin, 1970), 8-hydroxy-7-nitroquinoline-5-sulfonic acid (Balasubramanian & Muthiah, 1996) and 8-hydroxy-7-iodoquinoline-5-sulfonic acid (Ferron) (Merritt & Duffin, 1970; Balasubramanian & Muthiah, 1996). With the sulfonic acids, the structures commonly incorporate water of solvation which is involved in intermolecular hydrogen bonding through the sulfonate O atoms. However, with acids having additional interactive secondary functional groups, the potential for structure expansion through hydrogen bonding is increased.



(I)

The title compound, 5-amino-2-naphthalenesulfonic acid (1,6-Cleve's acid, ANSA), (I), is an important compound having industrial chemical applications, not only in the manufacture of azo dyes (Stecher, 1968), but as an aniline polymer precursor for the synthesis of co-polymer materials with unusual ferromagnetic and antiferromagnetic properties (Yoshino *et al.*, 1994; Kawai *et al.*, 1994; Galaj *et al.*, 1995; Mizobuchi *et al.*, 1995; Atkinson *et al.*, 2000; Wei & Wan, 2003). These materials are covered by numerous patents, *e.g.* Galaj & Le Mehaute (1995) and Le Mehaute *et al.* (1995). More recent

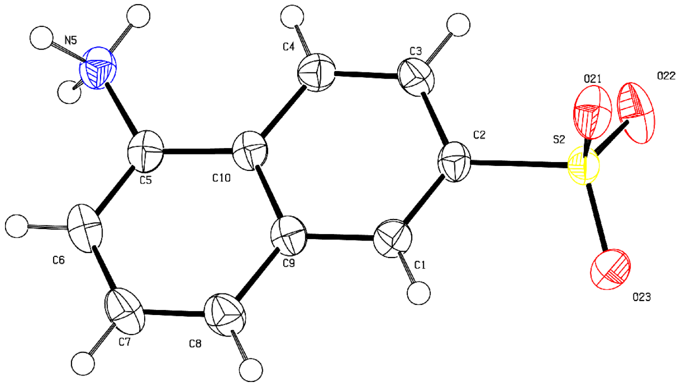


Figure 1
The molecular configuration and atom-numbering scheme for (I), with non-H atoms shown as 40% probability ellipsoids

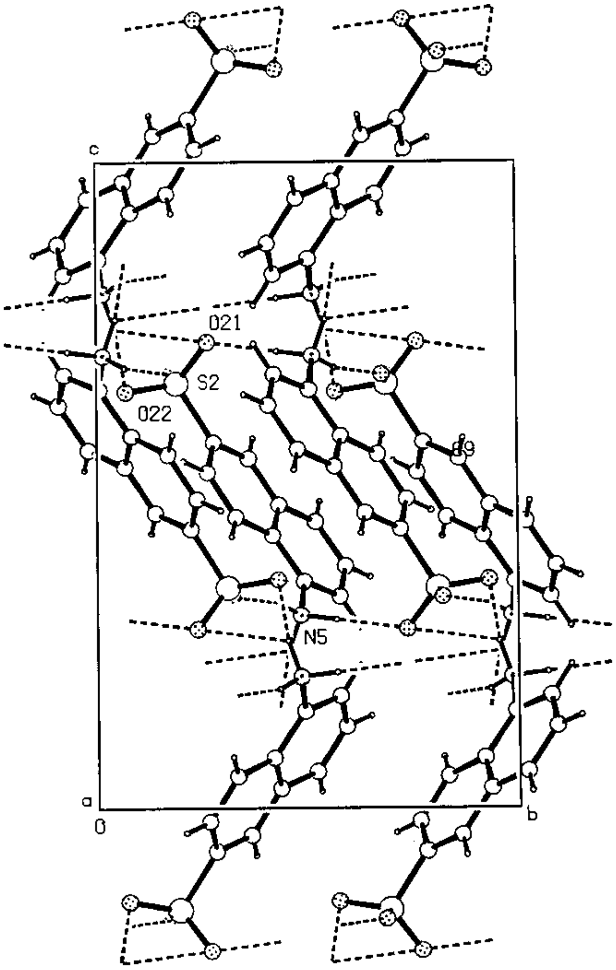


Figure 2
Perspective view of the packing in the unit cell, viewed down the *a* direction, showing hydrogen-bonding associations as broken lines.

applications include derivatives of (I) with enhanced anti-angiogenic activity, the crystal structure of an acidic fibroblast growth factor complexed to ANSA$^-$ being determined (Fernandez-Tornero *et al.*, 2003). Although (I) was obtained as a unintentional product in the attempted preparation of a proton-transfer compound, it provided a rare example of a naphthalenesulfonic acid which has, in addition, a secondary *trans*-related amino substituent with potential for longitudinal structure extension. Furthermore, (I) is not easily obtained as a crystalline material, having limited solubility in common solvents such as water, ethanol or ethers (Stecher, 1968). The structure of (I) was therefore completed and is reported here.

The individual molecules of (I) show, not surprisingly considering the presence of both sulfonic acid and amino groups, a zwitterionic form with the proton from the 2-sulfonic acid group residing on the 5-amino substituent group of the naphthalene molecule (Fig. 1). This is similar to what was found in orthanilic acid (Hall & Maslen, 1965), where the amino and acid groups are *ortho*-related. The substituted quinoline sulfonic acid ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) (Merritt & Duffin, 1970; Balasubramanian & Muthiah, 1996) is also zwitterionic, with the hetero N atom protonated. The aminium protons in (I) give structure extension *via* intermolecular head-to-tail hydrogen-bonding interactions with the sulfonate O-atom acceptors of three separate acid molecules, including an asymmetric three-centre $R_1^2(4)$ association with H5*C* [to O21$^{\rm iii}$ at 3.141 (3) Å and to O22$^{\rm iii}$ at 2.823 (3) Å; symmetry code: (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$]. These interactions (Table 1) give expansion of the structure in all axial directions, resulting in an extensive hydrogen-bonded framework polymer (Fig. 2).

Experimental

The title compound, (I), was isolated as violet-coloured crystals from the attempted preparation of a proton-transfer compound of 5-amino-2-naphthalenesulfonic acid with strychnine, by heating for 10 min under reflux 1 mmol quantities of the two reactants in 50% ethanol/water. The crystals formed as the major product after partial room-temperature evaporation of the hot-filtered solution.

Crystal data

$C_{10}H_9NO_3S$
$M_r = 223.24$
Orthorhombic, *Pbca*
$a = 11.120$ (2) Å
$b = 10.529$ (2) Å
$c = 16.253$ (3) Å
$V = 1902.9$ (6) Å^3
$Z = 8$
$D_x = 1.558$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 25 reflections
$\theta = 15$–20°
$\mu = 2.93$ mm^{-1}
$T = 295$ (2) K
Block, violet
0.30 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4F four-circle diffractometer
ω–2θ scans
2124 measured reflections
1725 independent reflections
1496 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 68°$
$h = -1 \rightarrow 13$
$k = -12 \rightarrow 1$
$l = -19 \rightarrow 1$
3 standard reflections
frequency: 160 min
intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 1.06$
1725 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 1.9163P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.47$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0030 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O23^{i}	0.90 (3)	1.97 (3)	2.852 (3)	165 (3)
N5—H5B···O21^{ii}	1.00 (3)	1.80 (3)	2.767 (3)	161 (3)
N5—H5C···O21^{iii}	1.00 (5)	2.51 (4)	3.141 (3)	120 (3)
N5—H5C···O22^{iii}	1.00 (5)	1.86 (4)	2.823 (3)	160 (3)
C1—H1···O23	0.93	2.59	2.937 (3)	103
C4—H4···O23^{i}	0.93	2.34	3.255 (3)	168
C7—H7···O21^{iv}	0.93	2.55	3.290 (3)	137

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

H atoms involved in hydrogen-bonding interactions (H5*A*, H5*B* and H5*C*) were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included at calculated positions in the refinement (C—H = 0.93 Å) as riding atoms, with U_{iso}(H) fixed at $1.2U_{eq}$(C).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) in *WinGX*; molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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