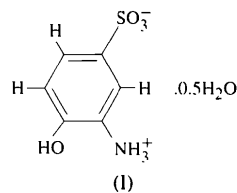


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3-Amino-4-hydroxybenzenesulfonic Acid Hemihydrate

BRIAN J. GUNDERMAN AND PHILIP J. SQUATTRITO*

Department of Chemistry, Central Michigan University,
Mount Pleasant, Michigan 48859, USA. E-mail:
3chwp5s@cmuvm.csv.cmich.edu

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Abstract

The title compound (3-ammonio-4-hydroxybenzenesulfonate hemihydrate, C₆H₇NO₄S · ½H₂O) crystallizes with two zwitterionic sulfonic acid molecules and one water molecule in the asymmetric unit. The acid molecules pack in layers in which the phenyl rings are nearly coplanar and the polar functional groups are directed towards adjacent layers. These layers stack so that the molecules of one slab are approximately orthogonal to those of the next. There is an extensive network of hydrogen bonds involving the water molecule and the ammonium, hydroxyl and sulfonate groups.

Comment

The present structure is part of a continuing study of the structural patterns in metal arenesulfonate salts (Gunderman & Squattrito, 1994) and sulfonic acids (Shubnell & Squattrito, 1994). These compounds typically form layered structures in which the phenyl rings are in the center of the layer and the sulfonate groups are on the exterior faces. Water molecules and metal ions are found between the layers associated with the sulfonate groups. The exact structure obtained is highly dependent on the nature of the metal ion, if one is present, and on the identity and location of other substituents on the rings. This is certainly true of 3-amino-4-hydroxybenzenesulfonic acid hemihydrate, (I), the first example we have examined to contain three polar substituents.

As shown in Fig. 1, there are two symmetry-independent molecules, both having the acidic proton on the N atom. The two molecules have nearly identical structural features. The ammonium H atoms are staggered relative to the adjacent hydroxyl group, with the shortest intramolecular H···O contacts being about 2.5 Å. Thus, there does not appear to be strong hydrogen bonding between the hydroxyl and ammonium groups on the same ring, though in both molecules, the C—C—O and C—C—N angles indicate that the two substituents are bent slightly towards one another (Table 2). The most significant difference between the two molecules is that the sulfonate group is rotated approximately 22° about the S—C bond in one relative to the other [torsion angles O(1)—S(1)—C(1)—C(2) 4.2(3) and O(5)—S(2)—C(7)—C(8) -18.1(3)°].

Compared to 2-aminotoluene-4-sulfonic acid (Shubnell & Squattrito, 1994), which differs only in having

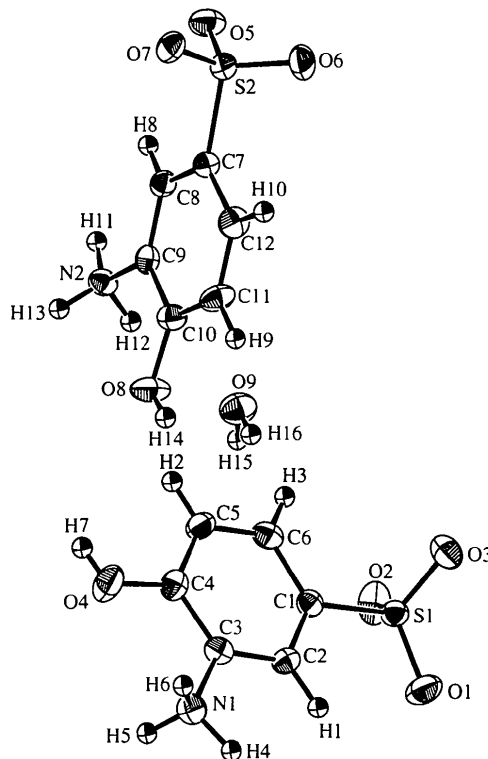


Fig. 1. ORTEP (Johnson, 1976) diagram of the two independent sulfonic acid molecules and the water molecule showing the atomic labeling scheme. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

a methyl group in place of a hydroxyl group, the title compound adopts a more complicated packing scheme (Fig. 2). Both structures contain layers that stack in alternating 90° orientations along the *c* direction, however, the aminotoluenesulfonic acid molecules are all equivalent so that molecules within a layer are parallel to one another. In contrast, the 3-amino-4-hydroxybenzenesulfonic acid molecules in a given layer pack so that the planes of the phenyl rings of the two independent molecules are about 10.5° out of parallel. In addition, whereas one molecule has the sulfonate groups directed nearly along the *c* axis (*i.e.* perpendicular to the layer), the other molecule has them rotated about 120° so that the sulfonate groups are directed almost parallel to the layer. The net result, as in other sulfonates, is that the polar hydrophilic groups are on the surfaces of the layers, along with the water molecule, where they can interact *via* hydrogen bonds. Table 3 lists data for all hydrogen bonds in which the H...A distance is less than 2.2 Å. All of the ammonium and hydroxyl H atoms and one water H atom participate in short hydrogen bonds in which the sulfonate and water O atoms function as acceptors. The other water H atom is involved in a bifurcated set of hydrogen bonds to two sulfonate O atoms [H(15)...O(1) 2.27 (3) and H(15)...O(2) 2.33 (3) Å]. That this network is particularly strong is reflected in the rather small and regular displacement parameters of the non-H atoms, the large blocky habit and hardness of the crystals, and the rather high density of the material (1.65 Mg m⁻³ in comparison with 1.50 Mg m⁻³ for 2-aminotoluene-4-sulfonic acid, which actually contains an extra half mole of water per formula unit).

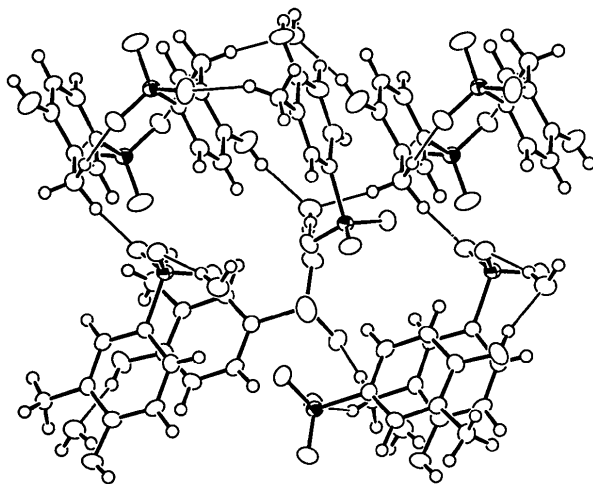


Fig. 2. ORTEP (Johnson, 1976) packing diagram showing parts of the two layers. The *c* axis is vertical in this view. The S atoms are shown with octant shading and hydrogen bonds are indicated by narrow lines. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

Experimental

The title compound crystallized from an aqueous solution of 3-amino-4-hydroxybenzenesulfonic acid monohydrate (Aldrich, 98%). Large block-shaped crystals grew from the warm brown solution on cooling and partial evaporation of the water.

Crystal data

C₆H₇NO₄S·½H₂O
M_r = 198.2
 Monoclinic
*P*2₁/*n*
a = 11.273 (3) Å
b = 10.410 (4) Å
c = 13.796 (3) Å
 β = 100.35 (2)°
V = 1592.7 (7) Å³
Z = 8
D_x = 1.65 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 24 reflections
 θ = 21.0–24.9°
 μ = 0.370 mm⁻¹
T = 296 K
 Block
 0.30 × 0.25 × 0.15 mm
 Red-brown

Data collection

Rigaku AFC-6S diffractometer
 ω scans
 Absorption correction: empirical *via* ψ scans of three reflections
 T_{\min} = 0.878, T_{\max} = 1.000
 3121 measured reflections
 2962 independent reflections

2185 observed reflections [*I* > 3σ(*I*)]
 R_{int} = 0.029
 θ_{\max} = 24.93°
 h = 0 → 13
 k = 0 → 12
 l = -16 → 16
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.3%

Refinement

Refinement on *F*
 R = 0.038
 wR = 0.040
 S = 2.65
 2185 reflections
 275 parameters
 Only coordinates of H atoms refined
 Weighting scheme based on measured e.s.d.'s
 $(\Delta/\sigma)_{\max}$ = 0.235

$\Delta\rho_{\max}$ = 0.35 e Å⁻³
 $\Delta\rho_{\min}$ = -0.44 e Å⁻³
 Extinction correction: Zachariasen (1968) type II, Gaussian isotropic
 Extinction coefficient: 3.38 (14) × 10⁻⁶
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{eq}</i> |
|------|-------------|--------------|-------------|-----------------------|
| S(1) | 0.20617 (8) | 0.08093 (8) | 0.90684 (6) | 0.0236 (2) |
| S(2) | 0.68405 (8) | -0.01263 (8) | 1.69452 (6) | 0.0251 (2) |
| O(1) | 0.2269 (2) | 0.1161 (3) | 0.8096 (2) | 0.0404 (8) |
| O(2) | 0.0849 (2) | 0.0303 (2) | 0.9036 (2) | 0.0382 (8) |
| O(3) | 0.2286 (2) | 0.1849 (2) | 0.9785 (2) | 0.0331 (7) |
| O(4) | 0.5387 (2) | -0.3441 (3) | 1.0457 (2) | 0.0389 (8) |
| O(5) | 0.5772 (2) | -0.0468 (2) | 1.7346 (2) | 0.0347 (7) |
| O(6) | 0.7055 (2) | 0.1251 (2) | 1.6900 (2) | 0.0368 (7) |
| O(7) | 0.7918 (2) | -0.0803 (2) | 1.7447 (2) | 0.0322 (7) |
| O(8) | 0.6060 (2) | -0.2203 (3) | 1.2894 (2) | 0.0368 (8) |
| O(9) | 1.0067 (2) | -0.0138 (3) | 1.3153 (2) | 0.0367 (8) |

| | | | | |
|-------|------------|-------------|------------|-------------|
| N(1) | 0.5635 (3) | -0.2274 (3) | 0.8785 (2) | 0.0282 (9) |
| N(2) | 0.4598 (3) | -0.2989 (3) | 1.4089 (2) | 0.0250 (8) |
| C(1) | 0.3085 (3) | -0.0436 (3) | 0.9502 (2) | 0.0224 (9) |
| C(2) | 0.3941 (3) | -0.0836 (3) | 0.8955 (2) | 0.0233 (9) |
| C(3) | 0.4702 (3) | -0.1829 (3) | 0.9320 (2) | 0.0230 (9) |
| C(4) | 0.4624 (3) | -0.2449 (3) | 1.0203 (2) | 0.0254 (10) |
| C(5) | 0.3789 (3) | -0.2006 (3) | 1.0757 (2) | 0.0276 (10) |
| C(6) | 0.3025 (3) | -0.1011 (3) | 1.0405 (3) | 0.0268 (10) |
| C(7) | 0.6564 (3) | -0.0679 (3) | 1.5706 (2) | 0.0222 (9) |
| C(8) | 0.5680 (3) | -0.1586 (3) | 1.5399 (2) | 0.0223 (9) |
| C(9) | 0.5533 (3) | -0.2045 (3) | 1.4453 (2) | 0.0219 (9) |
| C(10) | 0.6260 (3) | -0.1644 (3) | 1.3797 (2) | 0.0249 (9) |
| C(11) | 0.7123 (3) | -0.0703 (4) | 1.4104 (3) | 0.031 (1) |
| C(12) | 0.7270 (3) | -0.0232 (3) | 1.5051 (3) | 0.029 (1) |

Table 2. Selected geometric parameters (Å, °)

| | | | |
|----------------|-----------|------------------|-----------|
| S(1)—O(1) | 1.449 (2) | S(2)—O(7) | 1.467 (2) |
| S(1)—O(2) | 1.458 (2) | S(2)—C(7) | 1.777 (3) |
| S(1)—O(3) | 1.457 (2) | O(4)—C(4) | 1.350 (4) |
| S(1)—C(1) | 1.767 (3) | O(8)—C(10) | 1.357 (4) |
| S(2)—O(5) | 1.457 (2) | N(1)—C(3) | 1.465 (4) |
| S(2)—O(6) | 1.457 (2) | N(2)—C(9) | 1.463 (4) |
| O(1)—S(1)—O(2) | 111.7 (2) | S(1)—C(1)—C(2) | 120.7 (2) |
| O(1)—S(1)—O(3) | 113.8 (2) | S(1)—C(1)—C(6) | 118.9 (2) |
| O(1)—S(1)—C(1) | 107.1 (1) | N(1)—C(3)—C(2) | 120.6 (3) |
| O(2)—S(1)—O(3) | 109.7 (1) | N(1)—C(3)—C(4) | 117.2 (3) |
| O(2)—S(1)—C(1) | 107.3 (1) | O(4)—C(4)—C(3) | 116.4 (3) |
| O(3)—S(1)—C(1) | 107.0 (1) | O(4)—C(4)—C(5) | 124.9 (3) |
| O(5)—S(2)—O(6) | 114.3 (1) | S(2)—C(7)—C(8) | 120.6 (2) |
| O(5)—S(2)—O(7) | 112.0 (1) | S(2)—C(7)—C(12) | 119.7 (3) |
| O(5)—S(2)—C(7) | 105.8 (1) | N(2)—C(9)—C(8) | 121.1 (3) |
| O(6)—S(2)—O(7) | 111.3 (1) | N(2)—C(9)—C(10) | 116.8 (3) |
| O(6)—S(2)—C(7) | 106.2 (1) | O(8)—C(10)—C(9) | 116.7 (3) |
| O(7)—S(2)—C(7) | 106.6 (1) | O(8)—C(10)—C(11) | 124.9 (3) |

Table 3. Hydrogen-bonding geometry (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|------------------------------------|----------|----------|-----------|---------|
| N(1)—H(4)...O(5 ⁱ) | 1.01 (3) | 1.75 (3) | 2.758 (4) | 171 (3) |
| N(1)—H(5)...O(9 ⁱⁱ) | 0.94 (3) | 1.93 (3) | 2.869 (4) | 173 (3) |
| N(1)—H(6)...O(3 ⁱⁱⁱ) | 0.91 (3) | 1.92 (3) | 2.814 (4) | 166 (3) |
| O(4)—H(7)...O(9 ^{iv}) | 0.80 (3) | 1.95 (4) | 2.723 (4) | 165 (4) |
| N(2)—H(11)...O(3 ^v) | 0.92 (3) | 1.94 (3) | 2.852 (4) | 167 (3) |
| N(2)—H(12)...O(6 ^{vi}) | 0.97 (3) | 2.01 (3) | 2.774 (4) | 134 (3) |
| N(2)—H(13)...O(2 ^{vii}) | 0.93 (3) | 1.93 (3) | 2.800 (4) | 156 (3) |
| O(8)—H(14)...O(1 ^{viii}) | 0.77 (3) | 1.97 (3) | 2.741 (3) | 176 (4) |
| O(9)—H(16)...O(7 ^{ix}) | 0.81 (3) | 1.93 (4) | 2.734 (4) | 169 (4) |

Symmetry codes: (i) $x, y, z - 1$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, -y, 2 - z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{5}{2} - z$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) $1 - x, -y, 3 - z$; (vii) $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$; (viii) $2 - x, -y, 3 - z$.

All H atoms were located on difference electron density maps and their positions refined with fixed isotropic B values equal to 1.2 times those of the attached atoms at the time of their inclusion, with bond distances O—H 0.77 (3)–0.85 (3), N—H 0.91 (3)–1.01 (3) and C—H 0.90 (3)–0.98 (3) Å.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data, torsion angles and intermolecular distances involving both H and non-H atoms have been deposited with the IUCr (Reference: BK1189). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Photoproduct Derived from 9-Benzyl-Substituted Dibenzobarrelene†

THOMAS MATHEW,^a S. AJAYA KUMAR,^a SURESH DAS,^a NIGAM P. RATH^{b*} AND M. V. GEORGE^{c‡}

^aPhotochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India, ^bDepartment of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121, USA, and ^cRadiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

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Abstract

Photolysis of 11,12-dibenzoyl-9-benzyl-9,10-ethenoanthracene in the absence of oxygen, gives 9a,10-dibenzoyl-9-benzylidene-4b,9,9a,10-tetrahydroindeno[1,2-a]indene, C₃₇H₂₆O₂, (3). The structure of (3) has been unambiguously established through X-ray crystallographic analysis.

Comment

We reported earlier that the partial photolysis of 11,12-dibenzoyl-9-benzyl-9,10-ethenoanthracene, (1), in the absence of air, gives exclusively the 9-benzylidene-dibenzopentalene (3), derived from the dibenzosemibullvalene precursor (2) (Pratapan, Ashok, Cyr, Das & George, 1987).

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‡ Also at the Regional Research Laboratory (CSIR), Trivandrum 695 019, India.