

o-Phenylenediammonium bis(3-carboxy-4-hydroxybenzenesulfonate)

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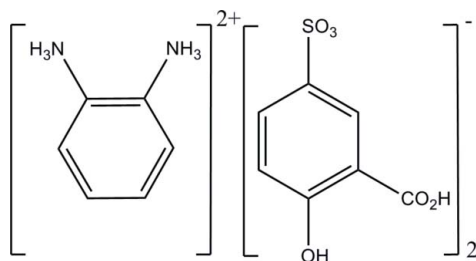
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Key indicators: single-crystal X-ray study; $T = 566$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.048; wR factor = 0.108; data-to-parameter ratio = 14.3.

In the title salt, $\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_5\text{O}_6\text{S}^-$, the negative charge of the anion resides on the sulfonate group. In the crystal, the cations and anions are linked by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a three-dimensional network. The complete dication is generated by crystallographic twofold symmetry.

Related literature

For related structures, see: Bakasova *et al.* (1991); Du *et al.* (2008); Meng *et al.* (2008); Raj *et al.* (2003); Smith (2005); Smith *et al.* (2004, 2005*a,b,c*, 2006); Wang & Wei (2007).



Experimental

Crystal data

 $\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_5\text{O}_6\text{S}^-$ $M_r = 544.50$ Monoclinic, $C2/c$ $a = 11.667$ (2) Å $b = 16.081$ (3) Å $c = 12.356$ (3) Å $\beta = 105.90$ (3)° $V = 2229.5$ (9) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.31$ mm⁻¹ $T = 566$ K $0.30 \times 0.28 \times 0.24$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)

 $T_{\min} = 0.902$, $T_{\max} = 0.923$

11440 measured reflections
2543 independent reflections
2019 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.108$ $S = 1.00$

2543 reflections

178 parameters

5 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1B} \cdots \text{O1}^{\text{i}}$	0.856 (10)	2.46 (2)	3.157 (3)	139 (2)
$\text{N1}-\text{H1B} \cdots \text{O4}^{\text{i}}$	0.856 (10)	2.424 (18)	3.176 (3)	147 (2)
$\text{N1}-\text{H1A} \cdots \text{O2}^{\text{ii}}$	0.860 (10)	1.939 (11)	2.795 (3)	174 (3)
$\text{N1}-\text{H1B} \cdots \text{O6}^{\text{iii}}$	0.856 (10)	2.46 (3)	2.836 (3)	107 (2)
$\text{N1}-\text{H1C} \cdots \text{O1}$	0.857 (10)	1.979 (17)	2.755 (3)	150 (3)
$\text{O3}-\text{H3A} \cdots \text{O6}$	0.86 (3)	1.82 (2)	2.600 (3)	151 (3)
$\text{O5}-\text{H5A} \cdots \text{O4}^{\text{iv}}$	0.849 (10)	1.819 (10)	2.668 (2)	178 (3)

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2658).

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supplementary materials

Acta Cryst. (2009). E65, o3173 [doi:10.1107/S1600536809049071]

***o*-Phenylenediammonium bis(3-carboxy-4-hydroxybenzenesulfonate)**

Y.-S. Ma and W.-W. Yang

Comment

A number of proton-transfer compounds of 3-carboxy-4-hydroxybenzenesulfonic acid with Lewis bases have been widely studied because of the good crystallinity of many of the compounds (Smith *et al.*, 2004; Wang & Wei, 2007; Meng *et al.*, 2008; Du *et al.*, 2008). The feature is the presence of hydrogen-bonding interactions, resulted from the aminium donor group and the sulfonate and carboxyl O-atom acceptors. There are some aniline-type proton-transfer compounds reported during the past several years. These include compounds with aniline (Bakasova *et al.*, 1991), the 4-X-substituted anilines (X = F, Cl, Br) (Smith *et al.*, 2005b), 3-aminobenzoic acid (Smith 2005), 4-aminobenzoic acid (Smith *et al.*, 2005c), benzylamine (Smith *et al.*, 2006), 1,4-phenylenediamine (Smith *et al.*, 2005a). The present paper is concerned with the crystal structure of a new proton-transfer compound of 3-carboxy-4-hydroxybenzenesulfonic acid with 1,2-phenylenediamine as Lewis base.

In the compound, the asymmetric unit consists of one half 1,2-phenylenediaminium dication and one 3-carboxy-4-hydroxy-benzenesulfonate anion. The hydrogen atom was transferred from the sulfonic group to the amino nitrogen atom, forming an 1:2 organic salt. In the anion (Fig. 1 and Table 1), the carboxyl group is nearly coplanar with the benzene ring [the dihedral angle is 3.9 °] and there is an intramolecular hydrogen bond O3—H···O6 2.600 (3) Å involving the hydroxy group and carboxyl atom. In addition, intermolecular hydrogen bonds between a sulfonate O atom and a carboxylate O atom [O5···O4 = 2.668 (2) Å; symmetry code: 1/2-x, 1/2+y, 1/2-z] connect the anions through head-to-tail into a one-dimensional chain (Fig. 2 and Table 2). The protonated N atoms form hydrogen bonds with three sulfonate O atoms and one carboxyl O atom [range 2.755 (3)—3.176 (3) Å] (Fig. 3 and Table 2), forming a three-dimensional network. The network are further consolidated by π — π stacking effects between the benzene rings of anions [the inter-ring centroid distance is 3.564 (1) Å].

Experimental

The title compound was synthesized by heating 3-carboxy-4-hydroxybenzenesulfonic acid (0.218 g, 1 mmol) and 1,2-phenylenediamine (0.108 g, 1 mmol) in water (20 mL) for 2 hours. After evaporation the solution, dark-blue block crystals formed in high yield.

Refinement

Carbon-bound H atoms were positioned geometrically (C—H = 0.93 Å), and were included in the refinement in the riding mode approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bound to O and N atoms were located in a difference Fourier map and refined with restraints [N—H and O—H = 0.85 (1) Å, with $U_{\text{iso}}(\text{H})$ values fixed at $1.5U_{\text{eq}}(\text{N})$ and $1.5U_{\text{eq}}(\text{O})$].

Figures

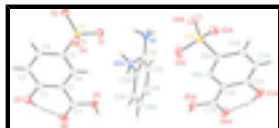


Fig. 1. A view of the compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level. [Symmetry code A = 1-x, y, 1/2-z]. The H-bonds are shown as dashed lines.



Fig. 2. View of the one-dimensional hydrogen bonded chain of 3-carboxylato-4-hydroxybenzenesulfonate shown with dashed lines, running along the *b* axis.

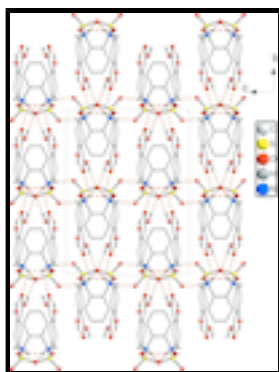
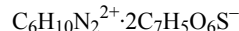


Fig. 3. The cell packing diagram indicating hydrogen bonds links with dashed lines, viewed down the *a* axis.

o-Phenylenediammonium bis(3-carboxy-4-hydroxybenzenesulfonate)

Crystal data



$M_r = 544.50$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 11.667 (2) \text{ \AA}$

$b = 16.081 (3) \text{ \AA}$

$c = 12.356 (3) \text{ \AA}$

$\beta = 105.90 (3)^\circ$

$V = 2229.5 (9) \text{ \AA}^3$

$Z = 4$

$F_{000} = 1128$

$D_x = 1.622 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6744 reflections

$\theta = 3.3\text{--}27.6^\circ$

$\mu = 0.31 \text{ mm}^{-1}$

$T = 566 \text{ K}$

Block, dark-blue

$0.30 \times 0.28 \times 0.24 \text{ mm}$

Data collection

Rigaku SCXmini
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $13.6612 \text{ pixels mm}^{-1}$

$T = 566 \text{ K}$

dtfind.ref scans

Absorption correction: Multi-scan
(CrystalClear; Rigaku, 2005)

$T_{\min} = 0.902$, $T_{\max} = 0.923$

2543 independent reflections

2019 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 3.1^\circ$

$h = -15 \rightarrow 15$

$k = -20 \rightarrow 20$

$l = -15 \rightarrow 15$

11440 measured reflections

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.048$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.108$	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 3.7751P]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
2543 reflections	$(\Delta/\sigma)_{\max} < 0.001$
178 parameters	$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
5 restraints	$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1315 (2)	0.73023 (13)	0.37688 (17)	0.0286 (5)
C2	0.0224 (2)	0.71605 (15)	0.40005 (19)	0.0334 (5)
C3	-0.0144 (2)	0.63524 (16)	0.4130 (2)	0.0400 (6)
H3	-0.0870	0.6259	0.4285	0.048*
C4	0.0566 (2)	0.56927 (14)	0.40305 (19)	0.0338 (5)
H4	0.0314	0.5153	0.4108	0.041*
C5	0.16661 (19)	0.58267 (13)	0.38137 (17)	0.0255 (4)
C6	0.20342 (19)	0.66230 (13)	0.36823 (17)	0.0265 (4)
H6	0.2765	0.6711	0.3535	0.032*
C7	0.1671 (2)	0.81562 (14)	0.35783 (19)	0.0340 (5)
C8	0.5460 (2)	0.77864 (15)	0.2988 (2)	0.0463 (7)
H8	0.5770	0.8288	0.3315	0.056*
C9	0.5925 (2)	0.70459 (15)	0.3483 (2)	0.0379 (6)
H9	0.6545	0.7047	0.4142	0.046*
C10	0.54644 (18)	0.63079 (13)	0.29932 (17)	0.0258 (4)

supplementary materials

S1	0.25193 (5)	0.49616 (3)	0.36307 (5)	0.03052 (16)
O1	0.37475 (17)	0.52318 (12)	0.3896 (2)	0.0617 (6)
O2	0.23442 (14)	0.43243 (10)	0.43955 (14)	0.0367 (4)
O3	-0.05305 (18)	0.77829 (12)	0.40738 (17)	0.0513 (5)
H3A	-0.014 (3)	0.8226 (13)	0.403 (3)	0.077*
O4	0.2075 (2)	0.47241 (12)	0.24585 (15)	0.0656 (7)
O5	0.27040 (17)	0.82146 (10)	0.33577 (16)	0.0444 (5)
H5A	0.276 (3)	0.8699 (10)	0.310 (2)	0.067*
O6	0.10406 (17)	0.87634 (10)	0.36053 (16)	0.0498 (5)
N1	0.59386 (18)	0.55255 (12)	0.35330 (17)	0.0326 (4)
H1A	0.6474 (19)	0.5606 (17)	0.4158 (14)	0.049*
H1B	0.620 (2)	0.5226 (15)	0.3080 (19)	0.049*
H1C	0.5367 (18)	0.5255 (15)	0.368 (2)	0.049*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0364 (12)	0.0250 (11)	0.0238 (10)	0.0015 (9)	0.0075 (9)	0.0000 (8)
C2	0.0353 (12)	0.0369 (13)	0.0288 (11)	0.0079 (10)	0.0101 (10)	0.0001 (10)
C3	0.0319 (13)	0.0456 (15)	0.0469 (14)	0.0002 (11)	0.0184 (11)	0.0031 (12)
C4	0.0349 (12)	0.0316 (12)	0.0364 (13)	-0.0060 (10)	0.0121 (10)	0.0003 (10)
C5	0.0297 (11)	0.0241 (10)	0.0233 (10)	0.0008 (8)	0.0080 (9)	-0.0009 (8)
C6	0.0278 (11)	0.0261 (11)	0.0258 (11)	-0.0005 (9)	0.0079 (9)	-0.0008 (8)
C7	0.0448 (14)	0.0277 (12)	0.0280 (12)	0.0027 (10)	0.0073 (10)	-0.0003 (9)
C8	0.0600 (18)	0.0249 (12)	0.0618 (17)	-0.0104 (11)	0.0298 (13)	-0.0116 (11)
C9	0.0422 (14)	0.0343 (13)	0.0382 (13)	-0.0092 (11)	0.0126 (11)	-0.0088 (10)
C10	0.0263 (11)	0.0235 (10)	0.0288 (11)	-0.0002 (8)	0.0094 (9)	0.0011 (8)
S1	0.0387 (3)	0.0218 (3)	0.0332 (3)	0.0037 (2)	0.0134 (2)	0.0026 (2)
O1	0.0403 (11)	0.0380 (11)	0.1180 (19)	0.0047 (8)	0.0410 (12)	0.0108 (11)
O2	0.0404 (9)	0.0279 (8)	0.0394 (9)	-0.0004 (7)	0.0070 (7)	0.0091 (7)
O3	0.0508 (12)	0.0455 (11)	0.0653 (12)	0.0171 (9)	0.0291 (10)	0.0021 (10)
O4	0.1183 (19)	0.0432 (11)	0.0312 (10)	0.0353 (12)	0.0134 (11)	-0.0044 (8)
O5	0.0530 (11)	0.0263 (9)	0.0593 (12)	-0.0020 (8)	0.0246 (9)	0.0068 (8)
O6	0.0623 (12)	0.0272 (9)	0.0616 (12)	0.0110 (8)	0.0200 (10)	0.0001 (8)
N1	0.0339 (11)	0.0304 (11)	0.0322 (11)	0.0019 (9)	0.0070 (8)	0.0050 (9)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.398 (3)	C8—C9	1.380 (4)
C1—C6	1.399 (3)	C8—H8	0.9300
C1—C7	1.472 (3)	C9—C10	1.373 (3)
C2—O3	1.352 (3)	C9—H9	0.9300
C2—C3	1.391 (3)	C10—C10 ⁱ	1.391 (4)
C3—C4	1.372 (3)	C10—N1	1.460 (3)
C3—H3	0.9300	S1—O2	1.4459 (16)
C4—C5	1.398 (3)	S1—O1	1.447 (2)
C4—H4	0.9300	S1—O4	1.4495 (19)
C5—C6	1.374 (3)	O3—H3A	0.86 (3)

C5—S1	1.761 (2)	O5—H5A	0.849 (10)
C6—H6	0.9300	N1—H1A	0.860 (10)
C7—O6	1.228 (3)	N1—H1B	0.856 (10)
C7—O5	1.310 (3)	N1—H1C	0.857 (10)
C8—C8 ⁱ	1.378 (6)		
C2—C1—C6	119.2 (2)	C8 ⁱ —C8—H8	119.8
C2—C1—C7	119.8 (2)	C9—C8—H8	119.8
C6—C1—C7	121.0 (2)	C10—C9—C8	119.5 (2)
O3—C2—C3	117.2 (2)	C10—C9—H9	120.3
O3—C2—C1	122.6 (2)	C8—C9—H9	120.3
C3—C2—C1	120.2 (2)	C9—C10—C10 ⁱ	120.17 (14)
C4—C3—C2	119.9 (2)	C9—C10—N1	119.4 (2)
C4—C3—H3	120.0	C10 ⁱ —C10—N1	120.45 (11)
C2—C3—H3	120.0	O2—S1—O1	111.92 (12)
C3—C4—C5	120.4 (2)	O2—S1—O4	112.98 (12)
C3—C4—H4	119.8	O1—S1—O4	111.50 (15)
C5—C4—H4	119.8	O2—S1—C5	106.86 (10)
C6—C5—C4	120.0 (2)	O1—S1—C5	107.06 (11)
C6—C5—S1	121.00 (17)	O4—S1—C5	106.05 (11)
C4—C5—S1	118.93 (16)	C2—O3—H3A	104 (2)
C5—C6—C1	120.3 (2)	C7—O5—H5A	108 (2)
C5—C6—H6	119.8	C10—N1—H1A	111.8 (19)
C1—C6—H6	119.8	C10—N1—H1B	110.2 (19)
O6—C7—O5	122.7 (2)	H1A—N1—H1B	112 (3)
O6—C7—C1	122.7 (2)	C10—N1—H1C	108.4 (19)
O5—C7—C1	114.6 (2)	H1A—N1—H1C	107 (3)
C8 ⁱ —C8—C9	120.33 (15)	H1B—N1—H1C	107 (3)
C6—C1—C2—O3	-178.6 (2)	C2—C1—C7—O6	-0.5 (3)
C7—C1—C2—O3	-0.9 (3)	C6—C1—C7—O6	177.2 (2)
C6—C1—C2—C3	-0.7 (3)	C2—C1—C7—O5	-179.4 (2)
C7—C1—C2—C3	177.0 (2)	C6—C1—C7—O5	-1.7 (3)
O3—C2—C3—C4	178.0 (2)	C8 ⁱ —C8—C9—C10	0.1 (5)
C1—C2—C3—C4	0.0 (4)	C8—C9—C10—C10 ⁱ	-0.1 (4)
C2—C3—C4—C5	0.9 (4)	C8—C9—C10—N1	-178.5 (2)
C3—C4—C5—C6	-1.0 (3)	C6—C5—S1—O2	147.63 (18)
C3—C4—C5—S1	-177.25 (19)	C4—C5—S1—O2	-36.1 (2)
C4—C5—C6—C1	0.2 (3)	C6—C5—S1—O1	27.6 (2)
S1—C5—C6—C1	176.44 (16)	C4—C5—S1—O1	-156.21 (19)
C2—C1—C6—C5	0.6 (3)	C6—C5—S1—O4	-91.6 (2)
C7—C1—C6—C5	-177.1 (2)	C4—C5—S1—O4	84.6 (2)

Symmetry codes: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1B \cdots O1 ⁱ	0.856 (10)	2.46 (2)	3.157 (3)	139 (2)
N1—H1B \cdots O4 ⁱ	0.856 (10)	2.424 (18)	3.176 (3)	147 (2)

supplementary materials

N1—H1A···O2 ⁱⁱ	0.860 (10)	1.939 (11)	2.795 (3)	174 (3)
N1—H1B···O6 ⁱⁱⁱ	0.856 (10)	2.46 (3)	2.836 (3)	107 (2)
N1—H1C···O1	0.857 (10)	1.979 (17)	2.755 (3)	150 (3)
O3—H3A···O6	0.86 (3)	1.82 (2)	2.600 (3)	151 (3)
O5—H5A···O4 ^{iv}	0.849 (10)	1.819 (10)	2.668 (2)	178 (3)

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

Fig. 1

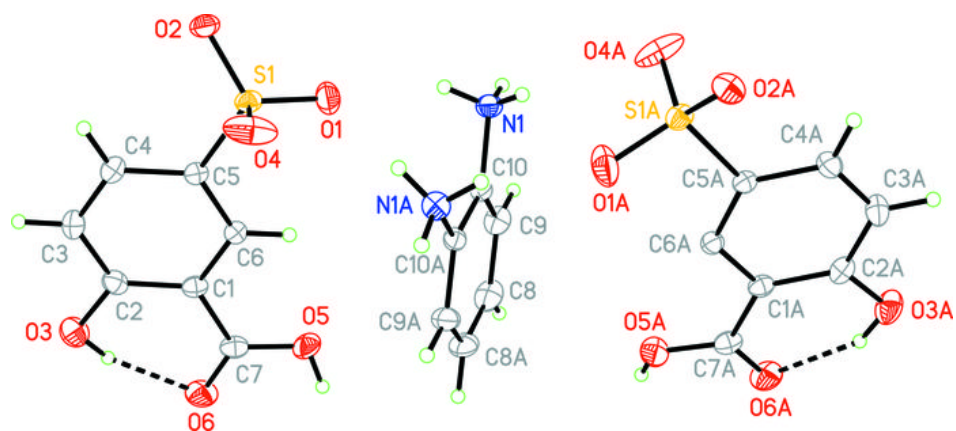


Fig. 2

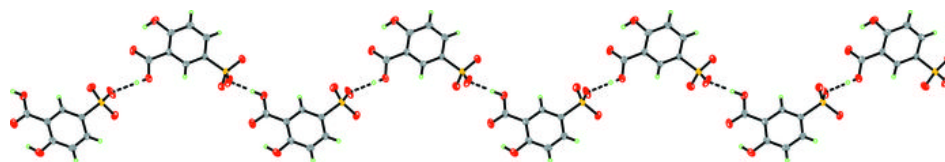


Fig. 3

