

## Bis( $\beta$ -alaninium) biphenyl-4,4'-disulfonate

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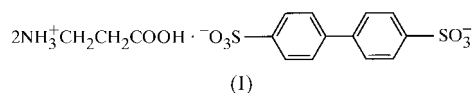
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In the crystal structure of the title compound,  $2\text{C}_3\text{H}_8\text{NO}_2^+ \cdot \text{C}_{12}\text{H}_8\text{O}_6\text{S}_2^{2-}$ , N—H $\cdots$ O hydrogen bonds formed between the amino H atoms and the sulfonate O atoms give rise to the assembly of cationic  $\beta$ -alaninium dimers and centrosymmetric biphenyl-4,4'-disulfonate anions into an extended two-dimensional layer. The resulting hydrogen-bonded ribbons can be described as  $C_2^2(6)R_4^4(12)$  according to graph-set notation. C—H $\cdots$ O hydrogen bonds between adjacent sheets further extend the structure into a three-dimensional arrangement.

### Comment

Sulfonate salts have been used to grow X-ray quality crystals of peptides which were otherwise difficult to obtain, and to study recognition patterns between the sulfonate and molecules of biological interest (Sudbeck *et al.*, 1994). Detailed hydrogen-bond graph-set analyses have been carried out for three arenesulfonate salts of amino acids (Sudbeck *et al.*, 1995). We present here an interesting extended two-dimensional network generated by the hydrogen-bonding interactions between the sulfonate O atoms of biphenyl-4,4'-disulfonate (BPDS) and the amino H atoms of the cationic  $\beta$ -alaninium dimer in the title compound, (I).



The BPDS anion is located on a crystallographic inversion centre. There is half a BPDS molecule and one  $\beta$ -alanine molecule in the asymmetric unit. The carboxylic acid group of the  $\beta$ -alanine forms hydrogen bonds with another such group to give a dimeric centrosymmetric  $R_2^2(8)$  ring (Etter, 1990). Each of the  $\text{NH}_3^+$  groups in the extended  $\beta$ -alanine dimers is hydrogen bonded to three O atoms belonging to three different sulfonate groups, and *vice versa* for the sulfonate groups, resulting in a puckered two-dimensional sheet, as

illustrated in Fig. 2. The hydrogen-bonded ribbons formed by the amino H atoms and the sulfonate O atoms can be described as  $C_2^2(6)R_4^4(12)$  (Etter, 1990). A similar 12-membered ring motif formed by N—H $\cdots$ O hydrogen bonds was observed in bis(glycine) 1,5-naphthalenedisulfonate dihydrate (Sudbeck *et al.*, 1995).

All the hydrogen-bond donors and acceptors in (I) are involved in strong hydrogen-bonding interactions, as shown in Table 1. Interestingly, the length of the extended  $\beta$ -alanine dimer, 11.34 Å, *i.e.* the distance between the two terminal N atoms, is compatible with the 10.63 Å length of BPDS. Also, the least-squares plane of the carboxylic acid group is almost coplanar with the biphenyl rings, as indicated by the dihedral angle of 5.9°. Finally, there is one further hydrogen bond formed between a C—H group of the phenyl ring and an alanine O atom, with a C2 $\cdots$ O5 distance of 3.36 Å and a C2—H1 $\cdots$ O5 angle of 158°. This weak hydrogen bond is formed between two adjacent sheets and extends the two-dimensional array into a three-dimensional framework.

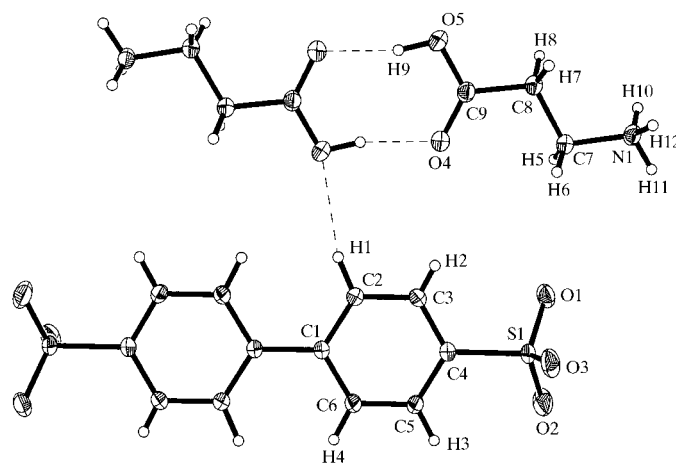
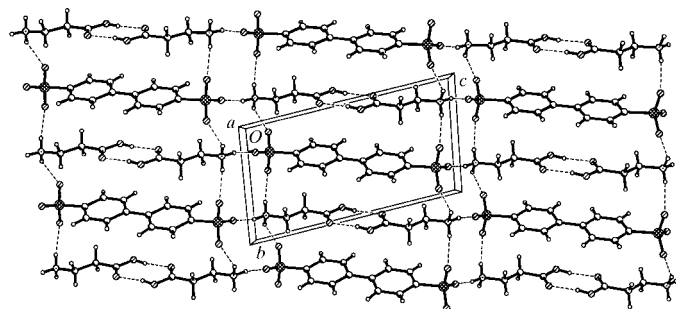


Figure 1

The molecular structure of (I) generated by inversion centres, showing 30% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii and hydrogen bonds are shown as dashed lines.

A search of the Cambridge Structural Database (CSD, October 2000 Release; Allen & Kennard, 1993) shows that there are a total of three entries containing free  $\beta$ -alanine. Two are zwitterionic  $\beta$ -alanine [BALNIN (Jose & Pant, 1965) and BALNIN01 (Papavinasam *et al.*, 1986)] and one is cationic  $\beta$ -alanine [JAFHON; Averbuch-Pouchot *et al.*, 1988] crystallized as a phosphate salt. Compared with the three reported  $\beta$ -alanines, that in (I) has a different backbone conformation. The torsion angles of the C—C—C—N backbone are 84.0, 83.2, 60.2 and 174.3 (2)° in BALNIN, BALNIN01, JAFHON and (I), respectively. This can be understood as the result of self-tuning during the assembly process, for better intermolecular hydrogen-bonding interactions and a closer packing arrangement.

N—H···O hydrogen bonds formed between the amino H atoms of guanidinium and the sulfonate O atoms of BPDS have been used in organic crystal engineering to construct crystalline materials with inclusion properties (Swift *et al.*,



**Figure 2**  
The extended two-dimensional network formed by the complementary N—H···O hydrogen bonds.

1998; Russell *et al.*, 1997). During our studies of the coordination properties of sulfonate toward transition metals, we identified a novel hydrogen-bonding pattern, formed by the metal-coordinated amino H atoms and the sulfonate O atoms, acting as the supramolecular synthon which provides the directing forces for the assembly of one-dimensional Cd<sup>II</sup> arenedisulfonates (Cai *et al.*, 2001). The title compound provides another interesting example of how N—H···O hydrogen bonds can be utilized to direct the assembly process in crystal engineering with aminosulfonate compounds.

## Experimental

Biphenyl-4,4'-disulfonic acid (0.15 g, 0.5 mmol) was added to an aqueous solution of  $\beta$ -alanine (0.09 g, 1 mmol). The resulting solution was allowed to stand at room temperature. After 7 d, colourless plates of (I) were collected in 45% yield. Found: C 43.75, H 4.85, N 5.76, S 13.09%; calculated for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>: C 43.90, H 4.91, N 5.69, S 13.02%.

### Crystal data

2C<sub>3</sub>H<sub>8</sub>NO<sub>2</sub><sup>+</sup>·C<sub>12</sub>H<sub>8</sub>O<sub>6</sub>S<sub>2</sub><sup>2-</sup>  
*M<sub>r</sub>* = 492.51  
 Triclinic, *P*1  
*a* = 5.4565 (5) Å  
*b* = 7.3922 (7) Å  
*c* = 13.4798 (12) Å  
 $\alpha$  = 99.197 (2)°  
 $\beta$  = 90.039 (2)°  
 $\gamma$  = 101.465 (2)°  
*V* = 525.72 (8) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 1.556 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 945 reflections  
 $\theta$  = 4.3–29.7°  
 $\mu$  = 0.31 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Plate, colourless  
 0.27 × 0.15 × 0.05 mm

### Data collection

Bruker SMART1000 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Blessing, 1995)  
*T<sub>min</sub>* = 0.920, *T<sub>max</sub>* = 0.985  
 3197 measured reflections  
 2102 independent reflections  
 1906 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.021  
 $\theta_{max}$  = 26.4°  
*h* = -6 → 6  
*k* = -9 → 8  
*l* = -15 → 16

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.035  
*wR*(*F*<sup>2</sup>) = 0.114  
*S* = 1.09  
 2102 reflections  
 194 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.1603P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.44 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.32 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient: 0.056 (8)

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H10···O3	0.86 (3)	2.01 (3)	2.863 (2)	169 (2)
N1—H11···O2 <sup>i</sup>	0.89 (3)	1.89 (3)	2.756 (2)	166 (2)
N1—H12···O1 <sup>ii</sup>	0.90 (3)	2.13 (3)	2.958 (2)	151 (2)
O5—H9···O4 <sup>iii</sup>	0.87 (4)	1.83 (4)	2.690 (2)	171 (3)

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

All H atoms were located from the difference Fourier map. The refined C—H distances are in the range 0.84 (3)–0.99 (2) Å and *U<sub>iso</sub>* values for H atoms attached to C atoms are in the range 0.043 (6)–0.059 (7) Å<sup>2</sup>.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1608). Services for accessing these data are described at the back of the journal.

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