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Bis(DL-phenylalaninium) sulfate monohydrate

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Key indicators

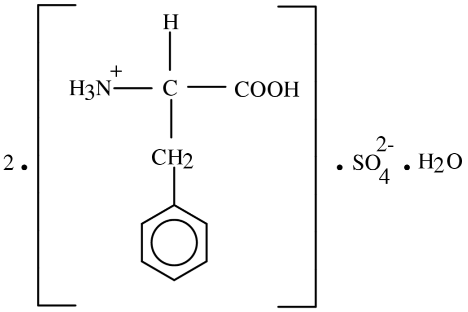
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.119
Data-to-parameter ratio = 13.1

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

The crystal structure of the title compound, $2C_9H_{12}NO_2^{+}\cdot SO_4^{2-}\cdot H_2O$, consists of two protonated phenylalaninium cations linked together by hydrogen bonding with the water molecule and the sulfate anion. The aggregation of the hydrophobic zone is along $(10\overline{1})$ and of the hydrophilic zone is along $(20\overline{2})$. The phenylalaninium molecules show sterically least favourable *g*+ or *g*− conformations.

Comment

The crystal structures of amino acids and their complexes have provided a wealth of interesting features pertaining to their patterns of aggregation and their ionic interactions (Vijayan, 1988; Prasad & Vijayan, 1993). The crystal structures of L-phenylalanine hydrochloride (Gurskaya & Vainshtein, 1963; Al-Karaghouli & Koetzle, 1975), L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992), bis(L-phenylalanine) nitrate (Srikrishnan *et al.*, 1984), bis(L-phenylalanine) sulfate monohydrate (Nagashima *et al.*, 1992), L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997) have been reported. In the present study, the structure of DL-phenylalaninium sulfate monohydrate, (I), has been investigated (Fig. 1 and Table 1).



(I)

The asymmetric unit of (I) contains two crystallographically independent protonated phenylalaninium units (molecules *A* and *B*), one sulfate ion and a water molecule. The two phenylalaninium molecules *A* and *B* adopt sterically least favourable *g*+ and *g*− conformations (Benedetti *et al.*, 1983; Suresh *et al.*, 1994) with χ^1 values of 56.2 (3) and −58.1 (3)°, respectively. There are striking similarities with L-phenylalnine L-phenylalaninium formate (Görbitz & Etter, 1992).

A chelated bifurcated hydrogen bond is observed in the case of (i) the amino N atom of molecule *A* with sulfate O atoms O1 and O4 and (ii) the amino N atom of molecule *B* with the sulfate O4 atom and the carboxyl O2*A* atom (Jeffrey

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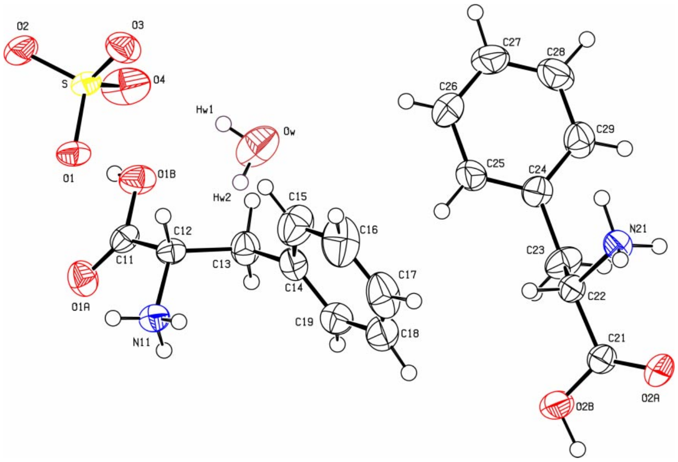

Figure 1
The molecular structure of (I) showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

& Saenger, 1991). The O4 atom of the sulfate anion acts as acceptor in hydrogen bonding with the water molecule and the amino N atom of molecules *A* and *B*. Interestingly, phenylalaninium molecule *A* forms a hydrogen bond with the sulfate anion only, while molecule *B* is hydrogen bonded to the sulfate anion, a carboxyl O atom and the water O atom. The sulfate anion links the phenylalaninium molecules into chains running along the *b* axis through hydrogen bonds with (i) the amino N atom of molecule *A* and (ii) the amino N and carboxyl O atoms of molecule *B*. The packing arrangement leads to the formation of a hydrophobic zone of phenyl rings along $(10\overline{1})$ and a hydrophilic zone along $(20\overline{2})$ (Fig. 2).

Experimental

The title compound, (I), was crystallized from an aqueous solution of DL-phenylalanine and sulfuric acid by slow evaporation.

Crystal data

$2C_9H_{12}NO_2^{+}\cdot O_4S^{2-}\cdot H_2O$
$M_r = 446.47$
Monoclinic, $P2_1/n$
$a = 14.560$ (2) Å
$b = 6.6000$ (12) Å
$c = 22.115$ (4) Å
$\beta = 90.70$ (2)°
$V = 2124.9$ (6) Å^3
$Z = 4$
$D_x = 1.396$ Mg m^{-3}
$D_m = 1.39$ Mg m^{-3}
D_m measured by flotation in a mixture of bromoform and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8.0$–15.8°
$\mu = 0.21$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.4 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.951$, $T_{max} = 0.980$
3825 measured reflections
3671 independent reflections
2806 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 7$
$l = -26 \rightarrow 26$
25 standard reflections every 3 reflections frequency: 60 min intensity decay: none

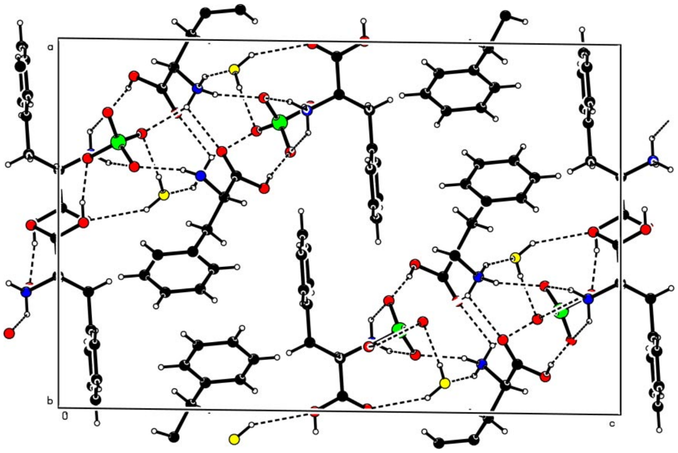

Figure 2
Packing of the molecules viewed down the *b* axis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.119$
$S = 1.05$
3671 reflections
281 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 1.5922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.201 (3)	O2*A*—C21	1.183 (3)
O1*B*—C11	1.307 (3)	O2*B*—C21	1.316 (3)
O1*A*—C11—C12—N11	0.8 (3)	O2A—C21—C22—N21	−18.5 (4)
N11—C12—C13—C14	56.2 (3)	N21—C22—C23—C24	−58.1 (3)
C11—C12—C13—C14	177.2 (2)	C21—C22—C23—C24	−176.9 (2)
C12—C13—C14—C15	60.9 (4)	C22—C23—C24—C25	−70.0 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1*B*—H1*B*···O1	0.82	1.80	2.614 (2)	170
O2*B*—H2*B*···O2^{i}	0.82	1.77	2.575 (3)	168
N11—H11*A*···O2^{ii}	0.89	2.49	2.992 (3)	116
N11—H11*B*···O3^{ii}	0.89	2.09	2.884 (3)	148
N11—H11*C*···O1^{iii}	0.89	1.97	2.831 (3)	163
N11—H11*C*···O4^{iii}	0.89	2.56	3.170 (3)	126
N21—H21*A*···O*W*^{iv}	0.89	2.01	2.836 (3)	154
N21—H21*C*···O4^{v}	0.89	2.05	2.843 (3)	147
N21—H21*C*···O2*A*^{vi}	0.89	2.33	2.826 (3)	115
N21—H21*B*···O3^{vii}	0.89	1.97	2.797 (3)	154
O*W*—H1···O4^{iii}	0.92 (2)	2.00 (2)	2.904 (3)	165 (4)
O*W*—H2···O1*A*	0.90 (2)	2.54 (3)	3.295 (3)	142 (3)

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

The H atoms of the water molecule were located and refined using *DFIX*. All other H atoms were fixed by *HFIX* and allowed to ride on the parent atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999).

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