group bonded to C(5) about the C(5)—C(7) bond, the torsion angle N—C(7)—C(5)—C(6) being −8·5°. While the C(5)—C(7) bond distance is in good agreement with that calculated for a C(sp^3)—C(sp^2) bond (Bastiansen & Skancke, 1961), the C(7)—N bond length of 1·311 Å indicates about 35% double-bond character (Hahn, 1957) and, as would be expected, the atoms S, C(7), N, H(1N) and H(2N) are coplanar within the possible experimental error.

An intermolecular hydrogen bond is formed between the NH_2 group of one molecule and the S atom of the molecule related by a center of symmetry, forming a dimer as shown in Fig. 3. The distance H(2N)···S′ is 2·46 Å, N to S′ is 3·378 Å and the angle N—H···S′ is 170°. These values indicate stronger hydrogen bonding than do those reported by Brown (1978) who found an H···S distance of 2·62 Å and an angle N—H···S of 152°.

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Thienyl-DL-serine Monohydrate

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Abstract. $C_7H_9NO_3S.H_2O$, $M_r = 205·2$, orthorhombic, *Pbca*, $a = 28·038$ (8), $b = 9·817$ (6), $c = 6·536$ (4) Å, $Z = 8$, $D_x = 1·516$ Mg m^{-3}, Cu $K\alpha$ radiation ($\lambda = 1·54178$ Å, $\mu = 3·021$ mm^{-1}). Final $R = 0·078$. The thienyl ring is essentially planar and is nearly perpendicular to the plane defined by C^α, C^β and C^γ. The molecule exists as a zwitterion. The structure is stabilized by a network of strong N—H···O and O—H···O hydrogen bonds.

Introduction. Antimetabolites of amino acids and other biologically important molecules owe their action to a close similarity to normal metabolites and hence could easily be mistaken for normal metabolites in biological systems. In this context the structures of the hydrochlorides of *p*-nitrophenylalanine (Chacko, Swaminathan, Parthasarathy & Natarajan, 1978), an antagonist of phenylalanine and of 2-butenylglycine

(Swaminathan & Chacko, 1979), an antagonist of methionine, have already been investigated.

Thienylserine (I) is an amino acid analogue of serine (as well as of threonine) with one of the methylene H atoms at the C^β position of serine (or C^γ in threonine) replaced by a thienyl ring. Mathew & Nord (1951) have observed that (I) could act as an antagonist for serine in protein synthesis leading to serine deficiency. (I) also has two asymmetric C atoms and the configuration about these centres is of interest.

Needle-shaped crystals were obtained from the Sigma Chemical Company, USA. Preliminary cell dimensions and the space group were established from

(I)

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Weissenberg photographs. Accurate cell dimensions were determined from 2θ parameters for 30 reflections on a diffractometer.

A crystal $0\cdot1 \times 0\cdot1 \times 0\cdot3$ mm was used for data collection on a Picker diffractometer with c parallel to the φ axis. The θ–2θ scan mode was employed with $2°$ min^{-1} scan speed. The scan range was $2°$ with background measured on either side of the peak for 10 s. 1440 reflections with $2\theta \leq 130°$ had $I > 2\sigma(I)$. The data were corrected for Lorentz and polarization factors and initially scaled by Wilson's method.

The S atom was located from a Patterson map ($R = 0\cdot54$). A Fourier synthesis gave all the non-hydrogen atom locations which were refined by a full-matrix least-squares method (program *LALS* of Gantzel, Sparks & Trueblood, 1961) to $R = 0\cdot13$ with isotropic temperature factors. A difference map computed at this stage gave all H atoms which were included in fixed positions. Anisotropic temperature factors were applied and refinement converged at $R = 0\cdot078$. The weighting scheme employed was that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) with $w = 1/(A + |F_o| + C|F_o|^2)$ where A and C were $8\cdot0$ and $0\cdot02$ respectively.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and an f' ($= 0\cdot3$) correction was applied for S.

Table 1. *Final positional parameters* ($\times 10^4$) *of the non-hydrogen atoms*

	x	y	z
S	1882 (1)	4076 (2)	6035 (2)
C(1)	260 (1)	3209 (4)	7999 (6)
C(2)	680 (1)	4179 (4)	7534 (7)
C(3)	1127 (2)	3897 (4)	8841 (7)
C(4)	1548 (1)	4682 (4)	8053 (7)
C(5)	1705 (2)	5946 (5)	8674 (8)
C(6)	2096 (2)	6413 (6)	7455 (9)
C(7)	2229 (2)	5534 (6)	5974 (9)
N	526 (1)	5613 (3)	7799 (6)
O(1)	−142 (1)	3725 (3)	8261 (5)
O(2)	358 (1)	1967 (3)	8012 (5)
O(3)	1051 (1)	4316 (3)	10889 (5)
OW	961 (1)	6517 (4)	4053 (6)

Table 2. H *atom positions* ($\times 10^3$) *and isotropic temperature factors*

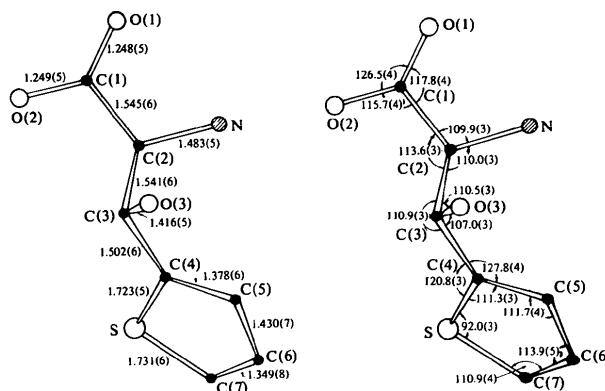|	x	y	z	B (Å^2)
H(1)N	68	593	649	2·35
H(2)N	17	600	755	2·35
H(3)N	36	590	925	2·35
H(4)C(2)	77	398	594	2·06
H(5)C(3)	120	284	882	2·69
H(6)O(3)	82	386	1175	2·70
H(7)C(5)	154	652	991	3·55
H(8)C(6)	228	737	778	3·11
H(9)C(7)	252	572	485	3·35
H(10)OW	66	642	324	3·14
H(11)OW	100	578	308	3·14

Fig. 1. Bond lengths (Å) and angles (°).

The final coordinates, which correspond to the L-configuration, are given in Tables 1 and 2.* Fig. 1 gives bond lengths and angles.

Discussion. The molecule exists as a zwitterion with the N in the NH_3^+ state with the carboxyl group as COO^-. Bond lengths and angles are comparable with values reported for other amino acids. C(3)—C(4), $1\cdot502$ Å, is shorter than C(1)—C(2) and C(2)—C(3); this may be due to the effect of the conjugated thienyl ring at C(4). The C—C bond lengths of the thienyl ring and the C—S distance exhibit partial double-bond character. As expected C(4)—C(5) and C(6)—C(7) exhibit more double-bond character than C(5)—C(6).

The carboxyl-group atoms together with C(2) form a plane (Table 3), from which N deviates by $0\cdot172$ Å (plane 1). As expected the thienyl ring is essentially planar, but S deviates from the plane through the C atoms of the ring by $0\cdot022$ Å (Table 3, plane 2).

The torsion angles defining the conformation of the backbone and the side chain of amino acids (Lakshminarayanan, Sasisekharan & Ramachandran, 1967) are given in Table 4. The side-chain conformations $\chi^{1,1}$ and $\chi^{1,2}$ about C(2)—C(3) $(C^\alpha-C^\beta)$ giving the positions of O^ν and C^ν with respect to N are

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33917 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Least-squares-plane calculations*

Deviations of atoms from plane are in Å $\times 10^3$.

Plane 1: C(1), C(2), O(1) and O(2)
$$0\cdot191x + 0\cdot062y + 0\cdot980z = 5\cdot446$$
Deviations: C(1) −11, C(2) 3, O(1) 4, O(2) 4, N −172

Plane 2: C(4), C(5), C(6) and C(7)
$$0\cdot641x − 0\cdot434y + 0\cdot633z = 4\cdot118$$
Deviations: C(4) 0, C(5) 0, C(6) 0, C(7) 0, S −22

expected to be close to 60° (position I), 180° (II) or 300° (III). C^ν is at position III (292·8°) and O^ν at position I (51·4°). In reported serine structures O^ν always occurs in position I. DL-Serine and L-serine.H_2O (Frey, Lehman, Koetzle & Hamilton, 1973) have $\chi^1 = 70\cdot0$ and 70·2° respectively, while in L-serine (Benedetti, Pedone & Sirigu, 1972) $\chi^1 = 60\cdot2°$. The side-chain conformation here corresponds to that in glycyl-L-threonine dihydrate (Yadava & Padmanabhan, 1973) which adopts positions III and I (298 and 61°). However, L-threonine (Shoemaker, Donohue, Schomaker & Corey, 1950) adopts positions II and III (185·5 and 305·2°) and L-allothreonine (Swaminathan & Srinivasan, 1975) positions I and III (65·1 and 302·9°).

The planar thienyl ring is nearly perpendicular to the C(2)–C(3)–C(4) plane. S is nearly *trans* to O(3) and is in a conformationally more favoured position than the *cis* position, when the bulkiness of S compared to C(5) is taken into consideration. The configuration of atoms about the asymmetric centres at C(2) and C(3) shows that the molecule could be compared to the erythrose series.

The structure viewed down c is given in Fig. 2 which also shows the hydrogen bonding. NH_3^+ forms strong

Table 4. Torsion angles (°)

IUPAC-IUB
designation

ψ^1	N–C(2)–C(1)–O(1)	8·5 (5)
$\chi^{1,1}$	N–C(2)–C(3)–O(3)	51·4 (4)
$\chi^{1,2}$	N–C(2)–C(3)–C(4)	292·8 (4)
$\chi^{2,1}$	C(2)–C(3)–C(4)–S	277·5 (4)
$\chi^{2,2}$	C(2)–C(3)–C(4)–C(5)	93·3 (5)
	O(3)–C(3)–C(4)–S	156·9 (3)
	O(3)–C(3)–C(4)–C(5)	332·7 (6)

Fig. 2. Projection of the structure down c.

Table 5. Hydrogen-bond distances (Å) and angles (°)

D–H$\cdots A$	$D\cdots A$	H$\cdots A$	$\angle D$–H$\cdots A$
N–H(1)$\cdots$OW	2·88	1·86	179
N–H(2)$\cdots$O(2)^b	2·86	1·79	168
N–H(3)$\cdots$O(1)^d	2·87	1·77	174
O(3)–H(6)$\cdots$O(2)^e	2·70	1·74	173
OW–H(10)$\cdots$O(1)^c	2·76	1·76	178
OW–H(11)$\cdots$O(3)^a	3·00	2·03	176

Symmetry code

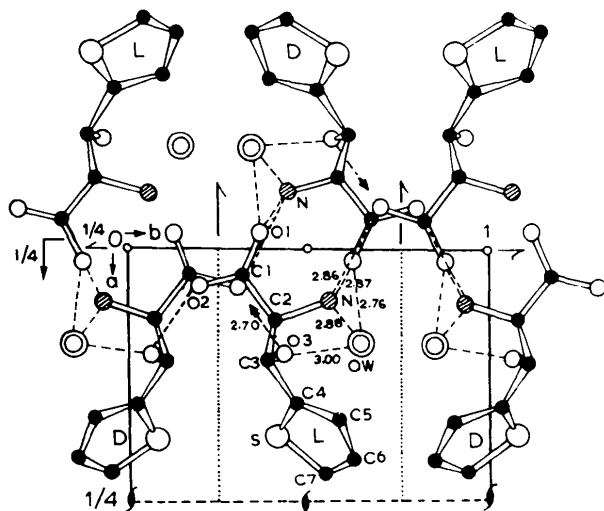|							
(a)	x,	y,	$z-1$	(d)	$-x$,	$1-y$,	$1-z+1$
(b)	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z+1$	(e)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z-1$
(c)	$1-x$,	$1-y$,	$1-z$				

hydrogen bonds with symmetry-related carboxyl O(1) and O(2) and the water O W at 2·87, 2·86 and 2·88 Å respectively. The H atom at O(3) forms a strong hydrogen bond with symmetry-related O(2) of length 2·70 Å. The water O W forms hydrogen bonds with O(1) and O(3) at 2·76 and 3·00 Å respectively. The relevant distances and angles are given in Table 5. The H$\cdots A$ distances and D–H$\cdots A$ angles show that all the hydrogen bonds are strong and nearly linear.

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