C11—C12	1.373 (4)	C4—C5	1.391 (3)
C4—N4	1.429 (3)	O9*A*—N9	1.210 (3)
C1—C6	1.407 (4)	O9*B*—N9	1.210 (3)
C3—C4	1.389 (3)	O11*A*—N11	1.220 (3)
C5—C6	1.371 (4)	O11*B*—N11	1.216 (3)
C8—O8	1.328 (3)	O4*A*—N4	1.230 (3)
C14—O13	1.476 (4)	O4*B*—N4	1.233 (3)
C11—N11	1.461 (3)		
C13—O13—C14	117.3 (3)	O9*A*—N9—O9*B*	122.8 (3)
O9*A*—N9—C9	119.1 (3)	O9*B*—N9—C9	118.0 (2)
O11*A*—N11—O11*B*	124.0 (2)	O11*A*—N11—C11	118.2 (3)
O11*B*—N11—C11	117.9 (2)	C8—C7—C13	118.7 (2)
C12—C7—C13	120.6 (2)	O8—C8—C7	121.2 (2)
O8—C8—C9	121.1 (2)	O1—C13—O13	123.2 (3)
O1—C13—C7	122.4 (3)	O4*A*—N4—O4*B*	121.1 (2)
O4*A*—N4—C4	120.2 (2)	O4*B*—N4—C4	118.6 (2)
N1—C1—C2	120.9 (2)	N1—C1—C6	120.8 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8···O1	0.92 (4)	1.74 (4)	2.547 (4)	144 (3)
O8—H8···O4*B*	0.92 (4)	2.41 (4)	2.968 (3)	119 (4)
N1—H1*A*···O4*B*^{i}	0.83 (3)	2.22 (3)	2.984 (4)	152 (3)
N1—H*B*···O8^{i}	0.94 (3)	2.56 (3)	3.147 (3)	121 (4)
N1—H1*B*···O9*A*^{i}	0.94 (3)	2.07 (3)	3.008 (4)	172 (3)

Symmetry code: (i) $x+\frac{1}{2}, -\frac{1}{2}-y, z-\frac{1}{2}$.

Atom O9*A* has an unusually large B_{eq} value, reflecting highly anisotropic displacement parameters. This could be due to disorder, so the anisotropic atom was replaced with two isotropic half atoms. Refinement of this model converged with $R = 0.056$ and $wR = 0.074$, significantly worse than the anisotropic model. We are left with no explanation for this large anisotropy; it does not appear to be due to disorder between two distinct positions.

The non-H atoms were refined anisotropically. All H atoms except H1*A*, H1*B* and H8, for which all parameters were refined isotropically, were included in the calculations placed in idealized positions (C—H 0.95 Å) with $B_{iso} = 1.2B_{eq}$ of the atoms to which they are bonded.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984), *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1232). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-Leucyl-L-alanine Dimethyl Sulfoxide Solvate

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Abstract

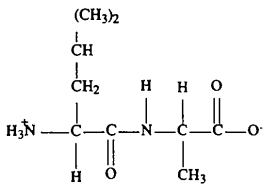
In the title compound, $C_9H_{18}N_2O_3.C_2H_6OS$, the dipeptide molecule exists as a zwitterion and the backbone adopts an extended conformation. The peptide unit is *trans* and shows a slight deviation from planarity [ω_1 = 174.4 (3)°]. The leucyl side chain adopts the $t(g^+t)$ conformation. The crystal packing gives rise to channels which are occupied by the disordered DMSO solvent molecules.

Comment

Structural studies on peptides represent an ongoing project in our laboratory aimed at identifying stable peptide conformations for use in models for protein folding. The present study forms part of the work on several Leu-*X* peptides.

† DCB Contribution No. 873.

The title dipeptide molecule (Leu-Ala), (I), exists as a zwitterion with terminal NH_3^+ and COO^- groups. Fig. 1 shows an *ORTEP* plot of the molecule (Vickovic, 1994). The peptide unit is *trans* and shows a slight deviation from planarity. The non-planarity of the peptide unit arises not only as a result of rotation around the C′—N bond, but also from out-of-plane bending of the bonds attached to the C′ or N, as noted by Ramachandran & Sasisekharan (1968). Two parameters, χ_C and χ_N, were introduced by Winkler & Dunitz (1971) to describe the out-of-plane bending which has the effect of changing the hybridization of the orbitals attached to C′ and N (χ_C is defined as the dihedral angle between planes C1*A*, C′, N2 and O1, C′, N2 while χ_N is the dihedral angle between planes C1′, N2, H6 and C1′, N2, C2*A*). In the present structure, χ_C = 0.3 while χ_N = 13.4° indicating that the N-atom orbitals are slightly pyramidal. The backbone adopts an extended conformation.



(I)

The side chain of the leucyl residue adopts one of the energetically favourable conformations $t(g^+t)$ (Benedetti, Morelli, Nemethy & Scheraga, 1983). The peptide chains are oriented with their longest dimension along the *b* axis and are packed head-to-tail along this axis with the protonated N terminus interacting with the ionized C terminus of a neighbouring molecule. The N terminus also forms a strong hydrogen bond with the O atom of the solvent (DMSO) molecule. The carboxyl group is planar and forms a dihedral angle of 24.3° with the plane of the adjacent peptide unit. This relative orientation favours the formation of an intramolecular hydrogen bond between N2 and O22′. The packing of molecules in the lattice gives rise to channels which are occupied by the DMSO solvent molecules. The S atom of the solvent molecule is disordered; this involves the S atom occupying alternative sites which are nearly mirror images of each other in the plane of the other three atoms.

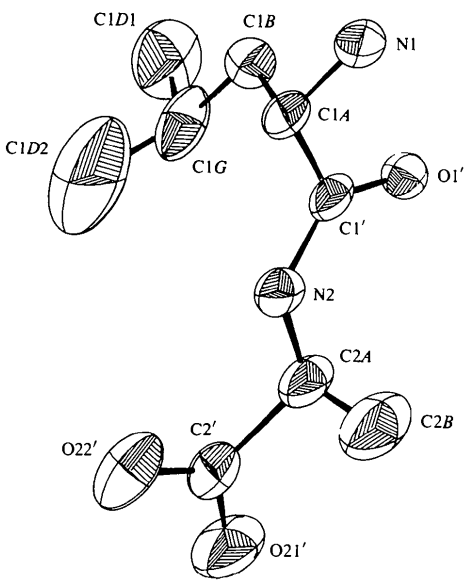


Fig. 1. *ORTEP* (Vickovic, 1994) plot of the molecule with displacement ellipsoids at the 50% probability level.

Experimental

Crystals obtained by slow evaporation of an aqueous solution of the dipeptide in the presence of traces of DMSO.

Crystal data

$C_9H_{18}N_2O_3.C_2H_6OS$
M_r = 280.4
Orthorhombic
$P2_12_12_1$
a = 5.197 (2) Å
b = 16.097 (2) Å
c = 18.718 (2) Å
V = 1565.9 (7) Å^3
Z = 4
D_x = 1.19 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 15 reflections
θ = 12–16°
μ = 1.88 mm^{-1}
T = 298 K
Needle
0.4 × 0.2 × 0.1 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.71, T_{max} = 0.83
1786 measured reflections
1727 independent reflections
1306 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.013
θ_{max} = 65°
h = 0 → 6
k = 0 → 19
l = 0 → 22
3 standard reflections monitored every 200 reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F
R = 0.075
wR = 0.083
S = 1.020
1306 reflections
206 parameters
w = $1/[\sigma^2(F) + 0.012F^2]$
$(\Delta/\sigma)_{max}$ = 0.2
$\Delta\rho_{max}$ = 0.3 e Å^{-3}
$\Delta\rho_{min}$ = −0.3 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{eq/iso}$
N1	−0.2128 (7)	0.7957 (2)	0.6965 (2)	4.11 (8)
C1*A*	−0.3028 (8)	0.8593 (2)	0.7484 (2)	3.70 (8)
C1*B*	−0.2556 (9)	0.8249 (2)	0.8234 (2)	4.7 (1)
C1*G*	−0.3154 (13)	0.8826 (4)	0.8856 (3)	6.7 (2)
C1*D*1	−0.5833 (19)	0.9098 (8)	0.8868 (4)	11.9 (3)
C1*D*2	−0.237 (2)	0.8377 (5)	0.9536 (3)	9.9 (3)
C1′	−0.1541 (7)	0.9386 (2)	0.7356 (2)	3.61 (8)
O1′	0.0765 (5)	0.9372 (2)	0.7248 (2)	4.51 (7)
N2	−0.2915 (6)	1.0080 (2)	0.7374 (2)	4.05 (8)
C2*A*	−0.1791 (8)	1.0911 (2)	0.7326 (2)	4.2 (1)
C2*B*	−0.1516 (18)	1.1148 (3)	0.6537 (3)	7.9 (2)
C2′	−0.3464 (9)	1.1533 (2)	0.7713 (2)	4.6 (1)
O21′	−0.2578 (7)	1.2251 (1)	0.7785 (2)	6.1 (1)
O22′	−0.5644 (7)	1.1329 (2)	0.7906 (3)	7.1 (1)
Solvent molecule				
S1†	0.0659 (6)	0.1503 (2)	0.0329 (1)	7.88 (7)
S2†	−0.0570 (9)	0.0861 (2)	0.0137 (2)	6.9 (8)
O3	−0.2197 (12)	0.1414 (4)	0.0590 (2)	9.9 (2)
C1	0.020 (2)	0.1416 (5)	−0.0631 (4)	11.7 (4)
C2	0.207 (2)	0.0541 (7)	0.0562 (5)	11.6 (3)

† S1 and S2 were refined with site-occupancy factors of 0.62 and 0.38, respectively.

Table 2. *Selected torsion angles (°) involving non-H atoms*

N1—C1*A*—C1′—N2	(ψ_1)	137.3 (3)
C1*A*—C1′—N2—C2*A*	(ω_1)	174.4 (3)
N1—C1*A*—C1*B*—C1*G*	($^1\chi_1$)	175.6 (4)
C1*A*—C1*B*—C1*G*—C1D1	($^1\chi_{21}$)	59.1 (7)
C1*A*—C1*B*—C1*G*—C1D2	($^1\chi_{22}$)	−176.1 (5)
C1′—N2—C2*A*—C2′	(φ_2)	−151.8 (4)
N2—C2*A*—C2′—O21′	(ψ_{21})	171.9 (3)
N2—C2*A*—C2′—O22′	(ψ_{22})	−11.8 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O21′^{i}	1.02 (7)	1.74 (7)	2.737 (5)	163 (5)
N1—H2···O3^{ii}	0.79 (7)	2.02 (7)	2.788 (6)	164 (7)
N1—H3···O22′^{iii}	0.69 (7)	2.21 (7)	2.875 (5)	161 (7)
N2—H6···O22′	0.79 (7)	2.33 (6)	2.654 (5)	106 (6)

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

H atoms of terminal groups in side chains showed abnormal B_j's and hence were only included in the structure-factor calculations. The other H atoms in the peptide molecule were refined isotropically.

Data collection: *SDP* (Enraf–Nonius, 1979). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1978). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1976); *ORTEP* (Vickovic, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1038). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dalspinosin

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Abstract

The title compound, 3-(3,4-dimethoxyphenyl)-5,7-dihydroxy-6-methoxy-4*H*-1-benzopyran-4-one, $C_{18}H_{16}O_7$, consists of two phenyl rings (*A* and *B*) and a heterocyclic ring *C*. Rings *A* and *B* are planar and ring *C* is slightly puckered. The packing of the molecules in the unit cell is governed by van der Waals interactions and hydrogen bonds.

Comment

Dalspinosin (I) is an isoflavone derivative having a unique 3′,4′ arrangement of the methoxy groups in ring *B*. Isoflavanoids have oestrogenic, insecticidal, pesticidal and antifungal properties (Harborne, Mabry & Mabry, 1975). Fig. 1 is a perspective view of the molecular geometry showing numbering scheme adopted.