References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A24, 321–324.

Danopoulos, A. A., Wilkinson, G., Hussain-Bates, B. & Hursthouse, M. B. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1855–1860.

Engler, E. M., Patel, V. V., Andersen, J. N., Schumaker, R. R. & Fukushima, A. A. (1978). *J. Am. Chem. Soc.* 100, 3769–3776.

Hiemstra, H. & Kiers, C. T. (1979). *Acta Cryst.* B35, 1140–1143.

Ozturk, T. (1996). *Tetrahedron Lett.* 37, 2821–2824.

Ozturk, T., Rice, C. R. & Wallis, J. D. (1995). *J. Mater. Chem.* pp. 1553–1556.

Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES.* Version 11 September 1989. Delft Instruments, Delft, The Netherlands.

Rosenfield, R. E., Parthasarathy, R. & Dunitz, J. D. (1977). *J. Am. Chem. Soc.* 99, 4860–4862.

Santalo, H., Veciana, J., Rovira, C., Molins, E., Miravitlles, C. & Claret, J. (1991). *Synth. Met.* 42, 2205–2209.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* University of Göttingen, Germany.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A39, 158–166.

Williams, J. M., Beno, M. A., Wang, H. H., Leung, P. C. W., Emge, T. J., Geiser, U. & Carlson, K. D. (1985). *Acc. Chem. Res.* 18, 261–267.

Zsolnai, L. & Pritzkow, H. (1996). *ZORTEP. An Interactive ORTEP Program.* University of Heidelberg, Germany.

L-Histidyl-L-alanine Dihydrate

THOMAS STEINER

Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany. E-mail: steiner@chemie.fu-berlin.de

Abstract

The title dipeptide, $C_9H_{14}N_4O_3.2H_2O$, crystallizes as a zwitterion. The side chain of the histidine residue is uncharged. The peptide C=O group does not accept any conventional hydrogen bonds, only C—H···O interactions.

Comment

The crystal structure of the dipeptide L-His-L-Ala, (I), was determined in order to study the possible occurrence of weak hydrogen-bonding effects.
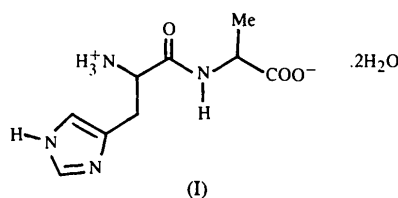
As expected, dipeptide (I) crystallized from aqueous solution as a zwitterion with the imidazole moiety of the histidine residue uncharged (Fig. 1). Two water molecules are co-crystallized per dipeptide. The conformation of the peptide backbone is conventional. The histidine conformation is characterized by the torsion angles C2—C1—C5—C6 −177.3 (2) and C1—C5—C6—C7 98.9 (3)°, *i.e.* the Cβ—Cγ bond (C5—C6) is oriented *trans* with respect to the Cα—CO bond (C1—C2) and the imidazole plane is roughly perpendicular to Cα—Cβ—Cγ (C1—C5—C6); this is one of the most frequently observed histidine conformations (Steiner, 1996a). Bond lengths and angles have normal values.
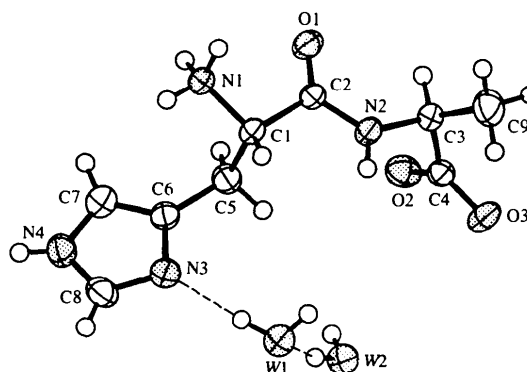

Fig. 1. The molecular structure and atom labelling of the title compound. Displacement ellipsoids are drawn at the 50% probability level. O and N atoms are shaded, and $W1$ and $W2$ represent $OW1$ and $OW2$, respectively.

The system of conventional N—H···O, O—H···O and O—H···N hydrogen bonds is shown in Fig. 2; for numerical data, see Table 3. The NH_3^+ and COO^- groups of neighbouring peptide molecules are connected by an infinite chain of hydrogen bonds joining the N1 atom to O3 atoms above and below in the *a*-axis direction. The co-crystallized water molecules form an infinite chain in the *a*-axis direction; ···H—$OW2$—H···$OW1$···H—$OW2'$—H···$OW1'$.

The hydrogen-bond coordination of the peptide C=O group, which is known to be a strong acceptor group (Jeffrey & Saenger, 1991), is of interest. The shortest
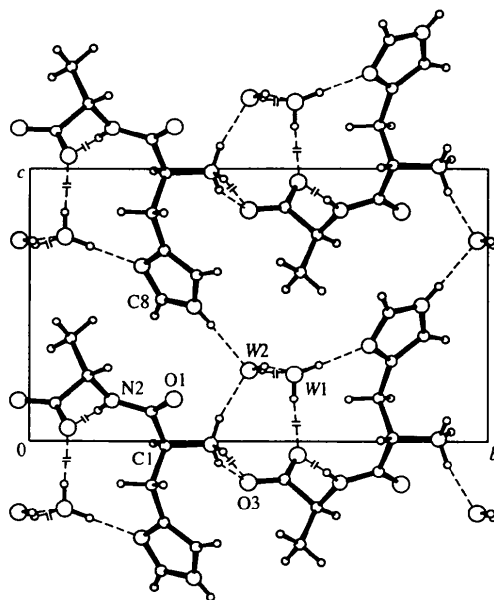
Fig. 2. The crystal-packing scheme and pattern of conventional hydrogen bonds (W1 and W2 represent OW1 and OW2, respectively).

intermolecular contact to an O or N atom is $O1\cdots OW2$ of 3.336 (2) Å. In a macromolecular crystal structure where H-atom positions are not located, this would be interpreted as 'suggestive of hydrogen bonding'. In fact, no hydrogen bond is formed; both $OW2$—H bonds point away from the O1 atom (and towards OW1, see Fig. 2). Instead, C=O accepts two weak C—H···O interactions (see Table 3). These are formed by C1—H (Cα—H of His) and by C8—H (Cε—H of His), which are both relatively strong C—H hydrogen-bond donors (see Desiraju, 1991; Steiner, 1996b). This resembles the situation observed for water acceptors, which also tend to resort to C—H···O interactions if no stronger donors are available, so that the water acceptor potential is not left completely unsatisfied (Steiner & Saenger, 1993; Steiner, 1995).

The imidazole moiety of (I) is coordinated by hydrogen-bonding functional groups in an almost planar geometry; both C—H groups are engaged in long C—H···O contacts. This coordination, however, is not as tight as is typically observed for protonated histidine side chains (Steiner, 1996a).

Experimental

The title compound is commercially available (Sigma). It was recrystallized by vapour diffusion of ethanol into an aqueous solution of (I).

Crystal data

$C_9H_{14}N_4O_3.2H_2O$
$M_r = 262.27$
Monoclinic
$P2_1$
$a = 4.6709 (2)$ Å
$b = 14.9289 (7)$ Å
$c = 9.0408 (9)$ Å
$\beta = 90.131 (11)°$
$V = 630.43 (7)$ Å^3
$Z = 2$
$D_x = 1.382$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54176$ Å
Cell parameters from 25 reflections
$\theta = 10.1–31.1°$
$\mu = 0.962$ mm^{-1}
$T = 293 (2)$ K
Rod
$0.70 \times 0.07 \times 0.05$ mm
Colourless

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
ω scans
Absorption correction:
ψ scan (North, Phillips & Matthews, 1968)
$T_{min} = 0.929$, $T_{max} = 0.997$
1956 measured reflections
982 independent reflections

966 observed reflections
$[I > 2\sigma(I)]$
$R_{int} = 0.0107$
$\theta_{max} = 59.91°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 16$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: 1.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0204$
$wR(F^2) = 0.0564$
$S = 1.072$
979 reflections
235 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 0.0541P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.091$ e Å^{-3}
$\Delta\rho_{min} = -0.127$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = -0.2 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
OW1	1.3647 (3)	0.57677 (12)	0.2484 (2)	0.0464 (4)
OW2	0.8714 (4)	0.47736 (11)	0.2625 (2)	0.0439 (4)
O1	0.5661 (3)	0.81279 (9)	-0.1563 (2)	0.0439 (4)
O2	0.2834 (3)	0.58390 (12)	-0.0493 (2)	0.0478 (4)
O3	0.5427 (3)	0.47616 (10)	-0.1509 (2)	0.0456 (4)
N1	0.9772 (4)	0.89358 (11)	0.0106 (2)	0.0343 (4)
N2	0.8000 (4)	0.67885 (11)	-0.1512 (2)	0.0342 (4)
N3	1.2015 (4)	0.74365 (13)	0.3540 (2)	0.0409 (4)
N4	1.1086 (4)	0.85637 (15)	0.5024 (2)	0.0467 (5)
C1	0.9542 (4)	0.79433 (13)	0.0150 (2)	0.0301 (4)
C2	0.7559 (4)	0.76389 (13)	-0.1099 (2)	0.0297 (4)
C3	0.5992 (4)	0.62721 (13)	-0.2416 (2)	0.0330 (5)
C4	0.4661 (4)	0.55581 (13)	-0.1406 (2)	0.0314 (4)
C5	0.8179 (5)	0.76439 (15)	0.1611 (2)	0.0393 (5)
C6	0.9723 (4)	0.79139 (14)	0.2981 (2)	0.0352 (5)
C7	0.9150 (5)	0.8615 (2)	0.3889 (3)	0.0440 (5)
C8	1.2736 (5)	0.7855 (2)	0.4766 (2)	0.0448 (5)
C9	0.7436 (7)	0.5895 (2)	-0.3781 (3)	0.0568 (7)

Table 2. *Selected torsion angles (°)*

N1—C1—C2—O1	-28.1 (3)	O1—C2—N2—C3	-10.0 (3)
N1—C1—C2—N2	156.8 (2)	O1—C2—C1—C5	91.0 (2)
C1—C2—N2—C3	164.9 (2)	N1—C1—C5—C6	-59.2 (3)
C2—N2—C3—C4	-109.6 (2)	C2—C1—C5—C6	-177.3 (2)

C2—N2—C3—C9	125.1 (2)	C1—C5—C6—C7	98.9 (3)
N2—C3—C4—O2	74.2 (2)	C1—C5—C6—N3	−83.0 (2)
N2—C3—C4—O3	−105.0 (2)		

Table 3. Hydrogen-bond distances (Å)

Data for normalized H-atom positions are based on bond lengths of O—H = 0.98, N—H = 1.04 and C—H = 1.08Å.

D···A	D···A	H_{norm}···A
OW1···N3	2.775 (3)	1.81
OW1···O2^i	2.720 (2)	1.75
OW2···OW1	2.744 (3)	1.80
OW2···OW1^{ii}	2.796 (2)	1.82
N1···O3^{iii}	2.854 (2)	1.89
N1···OW2^{iii}	2.858 (2)	1.84
N1···O3^{iv}	3.007 (2)	2.00
N1···O2^{iv}	3.111 (2)	2.44
N2···OW^i	2.819 (2)	1.78
N4···OW2^v	2.791 (3)	1.76
C1···O1^i	3.266 (3)	2.46
C5···OW1^{ii}	3.600 (3)	2.78
C5···N3^{ii}	3.384 (3)	2.66
C7···O3^{iv}	3.481 (3)	2.62
C8···O1^{vi}	3.609 (3)	2.80

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

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*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

References

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jeffrey, G. A. & Saenger, W. (1991). In *Hydrogen Bonding in Biological Structures*. Berlin: Springer-Verlag.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Steiner, Th. (1995). *Acta Cryst.* D**51**, 93–97.
Steiner, Th. (1996a). *Acta Cryst.* C**52**, 2266–2269.
Steiner, Th. (1996b). *Cryst. Rev.* In the press.
Steiner, Th. & Saenger, W. (1993). *J. Am. Chem. Soc.* **115**, 4540–4547.

α-5-Adamantyl-4'-thio-2'-deoxyuridine Methanol Solvate

Ming Sun,† Ivan Basnak, Thomas A. Hamor and Richard T. Walker

*School of Chemistry, University of Birmingham, Birmingham B15 2TT, England. E-mail: t.a.hamor@bham.ac.uk*

Abstract

The thiosugar ring of the title compound, $C_{19}H_{26}N_2O_4S.CH_4O$, has the C2'-*endo*, C3'-*exo* conformation. The orientation of the C4'—C5' bond is *trans–gauche*, and the glycosidic torsion angle S4'—C1'—N1—C6 is −26.2 (2)° (*anti*).

Comment

5-Substituted 2'-deoxy-4'-thiouridines are a relatively new group of nucleosides, possessing significant antiviral activity (Dyson, Coe & Walker, 1991; Secrist, Tiwari, Riordan & Montgomery, 1991). Syntheses provide mixtures of α- and β-anomers, of which only the β-anomers manifest antiviral activity (Rahim *et al.*, 1996). In order to provide information about structure–activity relationships in both anomeric series, the crystal structure of the title compound (I), synthesized by Basnak, Sun, Coe & Walker (1996), is presented here. As far as we are aware, it is the first reported crystal structure of an α-anomer within the 2'-deoxy-4'-thiouridine series.

(I)
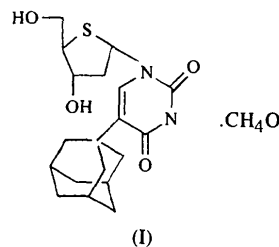
A perspective view of the molecule with atomic numbering is shown in Fig. 1. Bond lengths are normal. The C1'—S4' and C4'—S4' bonds are 1.811 (2) and 1.830 (2) Å, in good agreement with accepted values (Allen *et al.*, 1987). The other bond lengths generally agree well with those found in the crystal structures of 2'-deoxyuridine (Rahman & Wilson, 1972) and α-5-acetyl-2'-deoxyuridine (Hamor, O'Leary & Walker, 1977). The thiosugar ring has the C2'-*endo*, C3'-*exo* conformation (south), these two atoms being displaced by 0.224 (3) and 0.440 (3) Å, respectively, on opposite

† Current address: Department of Chemistry, Tianjin Normal University, Tianjin 300074, People's Republic of China.