C1	0.4436 (2)	0.56885 (11)	0.6988 (2)	0.0533 (5)
C2	0.5181 (2)	0.60889 (13)	0.8237 (2)	0.0640 (5)
C3	0.5669 (2)	0.67641 (13)	0.8085 (2)	0.0650 (5)
C4	0.6041 (2)	0.77288 (12)	0.6413 (3)	0.0682 (6)
C5	0.5876 (2)	0.79812 (12)	0.5005 (3)	0.0707 (6)
C6	0.4921 (2)	0.78615 (13)	0.2185 (3)	0.0768 (6)
C7	0.4120 (3)	0.74959 (15)	0.0915 (3)	0.0872 (8)
C8	0.3493 (2)	0.68824 (13)	0.1075 (3)	0.0757 (6)
C9	0.3082 (2)	0.59389 (11)	0.2754 (2)	0.0582 (5)
C10	0.3308 (2)	0.56449 (11)	0.4161 (2)	0.0545 (5)
C11	0.4129 (2)	0.59988 (10)	0.5512 (2)	0.0478 (4)
C12	0.5456 (2)	0.70643 (11)	0.6644 (2)	0.0564 (5)
C13	0.5088 (2)	0.76172 (11)	0.3660 (3)	0.0610 (5)
C14	0.3659 (2)	0.65992 (11)	0.2540 (2)	0.0569 (5)
C15	0.4461 (2)	0.69703 (10)	0.3845 (2)	0.0516 (4)
C16	0.4667 (2)	0.66821 (10)	0.5342 (2)	0.0489 (4)
C17	0.4055 (2)	0.49140 (11)	0.7200 (2)	0.0580 (5)
C18	0.2371 (2)	0.51793 (11)	0.8095 (2)	0.0552 (5)
C19	0.0998 (2)	0.52796 (12)	0.7611 (2)	0.0586 (5)
C20	−0.0501 (2)	0.57246 (12)	0.8628 (2)	0.0640 (5)
C21	−0.1321 (2)	0.62093 (12)	0.7397 (2)	0.0645 (5)
C22	0.2343 (2)	0.37029 (11)	0.5272 (2)	0.0620 (5)
C23	0.2395 (2)	0.40389 (11)	0.6771 (2)	0.0615 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C20	1.414 (2)	N1—C23	1.465 (2)
O1—C19	1.422 (2)	C1—C17	1.511 (3)
O2—C22^{i}	1.408 (2)	C18—C19	1.496 (2)
O2—C21	1.414 (2)	C20—C21	1.494 (3)
N1—C18	1.459 (2)	C22—O2^{i}	1.408 (2)
N1—C17	1.464 (2)	C22—C23	1.506 (3)
C20—O1—C19	114.06 (14)	C18—N1—C23	111.77 (15)
C22^{i}—O2—C21	113.02 (15)	N1—C17—C1	114.76 (15)
C18—N1—C17—C1	−69.1 (2)	C17—N1—C18—C19	163.5 (2)
C23—N1—C17—C1	166.0 (2)	C23—N1—C18—C19	−72.1 (2)
C2—C1—C17—N1	112.8 (2)	O2^{i}—C22—C23—N1	−57.8 (2)

Symmetry code: (i) $-x, 1-y, 1-z$.

All H atoms were located at ideal positions and included in the refinement, but were restrained to ride on their bonded atoms. The isotropic displacement parameters of the H atoms were held fixed to $1.2U_{eq}$ of their riding atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *Xtal GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL93*.

This work was supported by a Grant-in-Aid for Encouragement of Young Scientists from the Ministry of Education, Science and Culture, Japan (08740554).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 134–136

L-Histidinol Phosphate Tetrahydrate

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(*Received 28 May 1996; accepted 7 October 1996*)

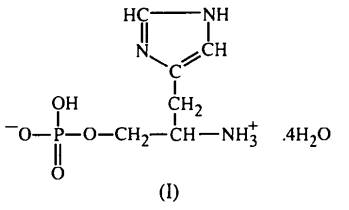
Abstract

In the crystal structure of the title compound, $C_6H_{12}N_3O_4P.4H_2O$, the amino group is protonated by the phosphate group. The phosphate group is *trans* planar to the central asymmetric C atom and projects out the plane of the imidazole ring. The crystal structure is stabilized by a three-dimensional network of all possible hydrogen bonds.

Comment

L-Histidinol phosphate is an intermediate in histidine biosynthesis (Ames & Mitchell, 1955; Ames & Horecker, 1956). It is derived enzymatically from imidazoleacetate phosphate catalyzed by imidazoleacetol phosphate transaminase and further converted to histidinol by histidinol phosphate aminotransferase (Martin & Goldberger, 1967; Henderson & Snell, 1973). Recently, the homology of aspartate, tyrosine and histidinol phosphate aminotransferases has been reported from the investigation on evolutionary relationships among vitamine B_6-dependent aminotransferases (Metha, Hale & Christen, 1989, 1993). It is important, therefore, to determine the fine structure of the substrate for these transferases in order to elucidate the structural mechanism of the enzymatic action.

The molecular structure and atom-numbering scheme of L-histidinol phosphate tetrahydrate, (I), are shown in Fig. 1. In the crystal structure, the hydrated L-histidinol phosphate molecule exists in a zwitterionic form in which the amino group is protonated by a phosphate proton. The ester O(1)—C(1) bond is *gauche* to both the C(2)—N(1) and C(2)—C(3) bonds giving torsion angles O(1)—C(1)—C(2)—N(1) of −58.3 (4)° and O(1)—C(1)—C(2)—C(3) of 63.2 (4)°. The orientation of the phosphate group with respect to C(2) is almost *trans* planar, with the P(1)—O(1)—C(1)—C(2) torsion angle −164.7 (2)°. The imidazole ring is roughly coplanar with the plane formed by N(1), C(2) and C(3), as shown by the torsion angles N(1)—C(2)—C(3)—C(4) of −172.0 (4)° and C(2)—C(3)—C(4)—N(2) of −165.0 (4)°. The phosphate group projects out of the plane of the imidazole ring. The crystal structure is stabilized by all possible hydrogen bonds between the deprotonated phosphoric acid group, the imidazole N atoms, the protonated amino group and the water molecules, as indicated by contact distances (Table 3).



(I)

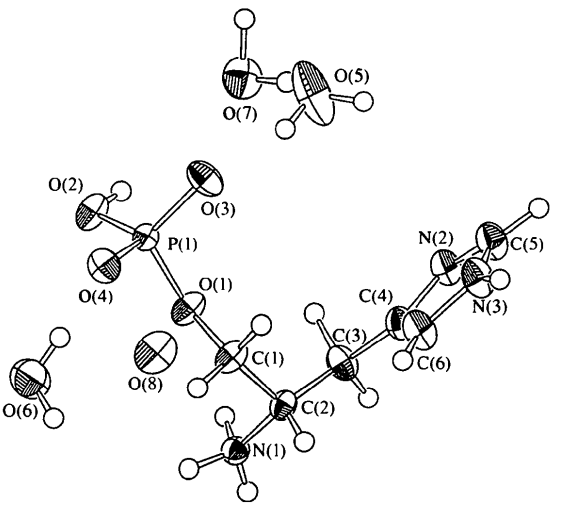


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

Experimental

The colorless plate-shaped crystal of (I) was obtained by the vapor diffusion technique. An aqueous solution of L-histidinol phosphate in an open beaker was placed in a desiccator containing pure ethanol and equilibrated with ethanol vapor.

Crystal data

$C_6H_{12}N_3O_4P.4H_2O$
M_r = 293.22
Monoclinic
$P2_1$
a = 9.405 (1) Å
b = 7.669 (2) Å
c = 9.436 (1) Å
β = 104.177 (9)°
V = 659.9 (4) Å^3
Z = 2
D_x = 1.476 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 19.35–22.45°
μ = 0.236 mm^{-1}
T = 296 K
Plate
0.5 × 0.2 × 0.1 mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
1719 measured reflections
1627 independent reflections
1465 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.014
θ_{max} = 27.5°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 9$
$l = -12 \rightarrow 11$
3 standard reflections monitored every 150 reflections
frequency: 66 min
intensity decay: none

Refinement

Refinement on F
R = 0.036
wR = 0.049
S = 1.870
1465 reflections
162 parameters
H atoms not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.015
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 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 (Å^2)*

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

	x	y	z	B_{eq}
P(1)	0.41344 (8)	0.1670	0.77578 (9)	1.67 (3)
O(1)	0.4514 (3)	−0.0344 (4)	0.7570 (3)	2.5 (1)
O(2)	0.5580 (3)	0.2573 (4)	0.7852 (3)	2.6 (1)
O(3)	0.2948 (3)	0.2222 (4)	0.6443 (3)	2.9 (1)
O(4)	0.3592 (2)	0.1836 (5)	0.9143 (2)	2.5 (1)
O(5)	0.2585 (3)	0.2398 (7)	0.3480 (3)	5.9 (2)
O(6)	0.7583 (4)	−0.0150 (6)	1.0095 (4)	5.0 (2)
O(7)	0.9731 (3)	0.2068 (5)	0.1503 (3)	3.9 (1)
O(8)	0.1469 (3)	−0.0013 (5)	1.0075 (4)	3.9 (1)
N(1)	0.5323 (3)	−0.3867 (4)	0.7913 (3)	2.1 (1)
N(2)	0.1978 (3)	−0.2639 (5)	0.3146 (3)	2.6 (1)
N(3)	−0.0163 (3)	−0.2795 (5)	0.3593 (3)	3.0 (1)
C(1)	0.3453 (4)	−0.1602 (5)	0.7747 (4)	2.4 (1)
C(2)	0.3811 (3)	−0.3342 (6)	0.7129 (4)	2.0 (1)
C(3)	0.3721 (3)	−0.3338 (8)	0.5508 (4)	2.5 (1)
C(4)	0.2205 (4)	−0.3074 (6)	0.4595 (4)	2.3 (1)
C(5)	0.0534 (4)	−0.2464 (7)	0.2587 (4)	3.1 (2)
C(6)	0.0868 (4)	−0.3173 (8)	0.4875 (4)	2.9 (1)

Table 2. *Selected geometric parameters (Å, °)*

P(1)—O(1)	1.607 (3)	N(2)—C(5)	1.342 (5)
P(1)—O(2)	1.508 (3)	N(3)—C(5)	1.305 (5)
P(1)—O(3)	1.511 (3)	N(3)—C(6)	1.381 (5)
P(1)—O(4)	1.519 (2)	C(1)—C(2)	1.526 (6)
O(1)—C(1)	1.428 (4)	C(2)—C(3)	1.512 (4)
N(1)—C(2)	1.492 (4)	C(3)—C(4)	1.491 (5)
N(2)—C(4)	1.371 (4)	C(4)—C(6)	1.350 (4)

O(1)—P(1)—O(2)	103.0 (1)	N(1)—C(2)—C(1)	108.7 (3)
O(1)—P(1)—O(3)	108.6 (2)	N(1)—C(2)—C(3)	108.1 (3)
O(1)—P(1)—O(4)	107.8 (2)	C(1)—C(2)—C(3)	115.0 (3)
O(2)—P(1)—O(3)	113.2 (2)	C(2)—C(3)—C(4)	113.1 (3)
O(2)—P(1)—O(4)	113.5 (2)	N(2)—C(4)—C(3)	120.1 (3)
O(3)—P(1)—O(4)	110.2 (1)	N(2)—C(4)—C(6)	106.7 (3)
P(1)—O(1)—C(1)	117.0 (2)	C(3)—C(4)—C(6)	133.1 (3)
C(4)—N(2)—C(5)	108.2 (3)	N(2)—C(5)—N(3)	109.7 (3)
C(5)—N(3)—C(6)	108.3 (3)	N(3)—C(6)—C(4)	107.5 (3)
O(1)—C(1)—C(2)	108.5 (3)		

Table 3. *Contact distances (Å)*

N(1)···O(2^{i})	2.742 (4)	O(6)···O(2)	3.231 (5)
N(1)···O(4^{ii})	2.768 (4)	O(6)···O(4^{ii})	2.731 (5)
N(1)···O(5^{iii})	2.791 (4)	O(7)···O(6^{vii})	2.727 (5)
N(3)···O(3^{iv})	2.613 (4)	O(7)···O(8^{v})	2.775 (5)
O(2)···N(2^{v})	2.692 (4)	O(8)···O(4)	2.762 (4)
O(5)···O(3)	2.737 (4)	O(8)···O(7^{viii})	2.845 (4)
O(5)···O(7^{vi})	2.879 (4)		

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

H atoms were located in successive difference Fourier syntheses, but those bonded to the O(8) atom could not be found.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

This research was supported by a grant from The Japan Private School Promotion Foundation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: TA1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 136–140

Complex of a Lisuride Derivative and (*S*)-Naproxen

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(*Received 28 March 1996; accepted 23 July 1996*)

Abstract

The structure of a complex between (+)-1-allyllisuride and the (+)-(*S*) isomer of 2-(6-methoxy-2-naphthyl)-propionic acid (naproxen), (+)-(5*R*,8*S*)-1-allyl-9,10-didehydro-8-(*N*′,*N*′-diethylureido)-6-methylergolin-6-ium 2-(6-methoxy-2-naphthyl)propionate 2-(6-methoxy-2-naphthyl)propionic acid acetonitrile solvate hydrate, $C_{23}H_{31}N_4O^+.C_{14}H_{13}O_3^-.C_{14}H_{14}O_3.C_3H_8O.H_2O$, has been determined. At the pH of the crystallization conditions, each molecule of allyllisuride is protonated and interacts with two molecules of naproxen in different modes; with one molecule, a π–π interaction seems to occur between aromatic moieties, while with the other, which appears to be deprotonated, hydrogen bonds are present. The electrostatic interactions seem sensitive to the configuration at the asymmetric C atom of naproxen and are likely to be responsible for the enantio-discriminative process. In the asymmetric unit, one molecule of isopropyl alcohol and one molecule of water are present. They are connected through a network of hydrogen bonds to the carbonyl group of allyllisuride and to the carboxyl groups of the two molecules of naproxen.

Comment

The use of liquid chromatography for the resolution of optical isomers requires a chiral selector, usually bonded to an achiral matrix, able to form reversible interactions with the enantiomers and labile diastereoisomeric complexes with different degrees of stability. Since the stability difference between the complexes affects the degree of chiral discrimination and the efficiency of the chiral selector, studies of chiral recognition, which provide the basis for the development of new chiral stationary phases, are particularly relevant.