C34	0.5526 (2)	−0.5422 (4)	0.4072 (2)	4.1 (2)
C35	0.5918 (2)	−0.5271 (5)	0.4552 (2)	4.6 (2)
C36	0.5646 (2)	−0.6392 (6)	0.3679 (2)	5.4 (2)

† Site occupancy = 0.5.

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

Cl1—C1	1.61 (1)	O22—C22	1.202 (5)
$Cl1^i$—C1	1.79 (1)	N21—N22	1.340 (5)
Cl2—C1	1.83 (1)	N21—C25	1.330 (6)
F11—C16	1.337 (6)	N22—C23	1.329 (5)
F12—C16	1.312 (6)	C22—C23	1.479 (6)
F13—C16	1.339 (6)	C23—C24	1.395 (6)
O11—C11	1.443 (6)	C24—C25	1.361 (6)
O11—C12	1.320 (5)	C24—C26	1.477 (6)
O12—C12	1.194 (5)	F31—C36	1.323 (5)
N11—N12	1.336 (5)	F32—C36	1.336 (5)
N11—C15	1.332 (5)	F33—C36	1.322 (5)
N12—C13	1.336 (5)	O31—C31	1.451 (6)
C12—C13	1.483 (6)	O31—C32	1.324 (5)
C13—C14	1.401 (6)	O32—C32	1.198 (5)
C14—C15	1.348 (6)	N31—N32	1.339 (4)
C14—C16	1.477 (6)	N31—C35	1.335 (5)
F21—C26	1.319 (6)	N32—C33	1.332 (5)
F22—C26	1.331 (6)	C32—C33	1.485 (6)
F23—C26	1.320 (6)	C33—C34	1.402 (5)
O21—C21	1.455 (6)	C34—C35	1.364 (6)
O21—C22	1.321 (5)	C34—C36	1.481 (6)
$Cl1^i$—C1—Cl1	112.7 (8)	C22—C23—C24	134.2 (4)
Cl1—C1—Cl2	112.3 (7)	C23—C24—C25	105.1 (4)
$Cl1^i$—C1—Cl2	104.3 (6)	C23—C24—C26	130.5 (4)
C11—O11—C12	116.9 (4)	C25—C24—C26	124.3 (4)
N12—N11—C15	112.7 (4)	N21—C25—C24	106.6 (5)
N11—N12—C13	104.4 (3)	F21—C26—F22	105.1 (5)
O11—C12—O12	125.5 (4)	F21—C26—F23	105.0 (5)
O11—C12—C13	110.7 (4)	F21—C26—C24	113.9 (5)
O12—C12—C13	123.8 (4)	F22—C26—F23	107.7 (5)
N12—C13—C12	116.4 (4)	F22—C26—C24	113.4 (4)
N12—C13—C14	110.5 (4)	F23—C26—C24	111.2 (5)
C12—C13—C14	133.1 (4)	C31—O31—C32	117.2 (4)
C13—C14—C15	105.1 (4)	N32—N31—C35	112.2 (4)
C13—C14—C16	130.5 (4)	N31—N32—C33	105.0 (3)
C15—C14—C16	124.5 (4)	O31—C32—O32	124.5 (4)
N11—C15—C14	107.3 (5)	O31—C32—C33	111.7 (4)
F11—C16—F12	106.9 (5)	O32—C32—C33	123.7 (4)
F11—C16—F13	105.7 (5)	N32—C33—C32	116.5 (4)
F11—C16—C14	113.2 (5)	N32—C33—C34	110.8 (4)
F12—C16—F13	106.4 (5)	C32—C33—C34	132.8 (4)
F12—C16—C14	113.8 (5)	C33—C34—C35	104.6 (4)
F13—C16—C14	110.3 (4)	C33—C34—C36	130.9 (4)
C21—O21—C22	115.8 (4)	C35—C34—C36	124.5 (4)
N22—N21—C25	113.1 (4)	N31—C35—C34	107.4 (4)
N21—N22—C23	104.2 (4)	F31—C36—F32	106.0 (4)
O21—C22—O22	124.2 (4)	F31—C36—F33	106.2 (4)
O21—C22—C23	112.0 (4)	F31—C36—C34	113.7 (4)
O22—C22—C23	123.8 (4)	F32—C36—F33	106.4 (4)
N22—C23—C22	114.8 (4)	F32—C36—C34	112.8 (4)
N22—C23—C24	111.0 (4)	F33—C36—C34	111.3 (4)

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

The data were collected in terms of a triclinic cell and later transformed and merged to give Miller indices of the reported equivalent centred monoclinic cell of twice the volume. For each of the three substituted pyrazole molecules, the positions of the H atoms H1 and H5 attached to the rings were refined isotropically. Methyl H atoms were placed in calculated positions. Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SHELX*76 (Sheldrick, 1976). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984); *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1985). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *CIF* (Hall, Allen & Brown, 1991).

The CAD-4 diffractometer was funded by the SERC which is also thanked for funding the Chemical Databank Service, *CSSR* (1984), used for crystallographic literature searches.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Hydroxyephedrinium Dihydrogenphosphate

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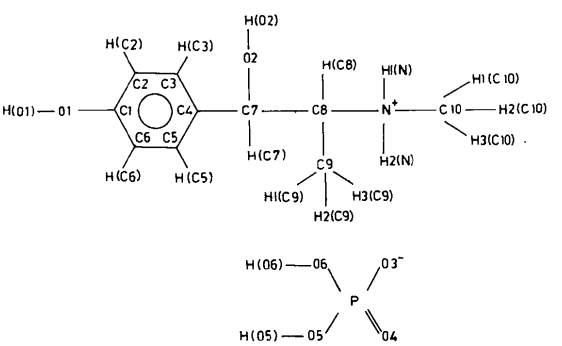
Abstract

The structural investigation of the title compound, [1-hydroxy-1-(4-hydroxyphenyl)-2-propyl]-methylammonium dihydrogenphosphate, $C_{10}H_{16}NO_2^+.H_2PO_4^-$, has been carried out by single-crystal X-ray diffraction. The ethylamine side chain

has a *trans* conformation relative to the phenyl ring and is nearly fully extended and approximately perpendicular to the phenyl ring plane. The $H_2PO_4^-$ group possesses a slightly distorted tetrahedral configuration. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds with the *p*-hydroxyl, ethanolic hydroxyl and amino groups of the *p*-hydroxyephedrine cation hydrogen bonded to the O atoms of the phosphate anion, indicating a putative environment of these drug molecules at their storage and receptor sites in biological systems.

Comment

p-Hydroxyephedrine is a sympathomimetic amine (Triggle, 1970) having a phenylethylamine skeleton. It resembles *p*-aminoephedrine, which is more active but less toxic than ephedrine (McLean, 1960). It is known from various studies that the phenylethylamines form complexes with adenosine triphosphate (ATP) in storage vesicles and receptor sites and that the interaction supposedly involves only a single phosphate group (Triggle, 1970; Klein, Lagercrantz & Zimmermann, 1982; Pai & Maynert, 1972; Brand & Westfall, 1970; Weiner & Jardetzky, 1964). Involvement of both guanosine triphosphate (GTP) and guanosine diphosphate (GDP) in the regulation of catecholamine-induced adenylate cylase systems is also well known (Cassel & Selinger, 1978; Lad, Nielson, Preston & Rodbell, 1980; Rodbell, 1980). The structure of *p*-hydroxyephedrine hydrochloride has been reported (Dattagupta, Pattanayek & Saha, 1981). The crystal structure analysis of the present compound (I) was undertaken as part of our study of the phosphate-binding properties of sympathomimetic phenylethylamines.



(I)

The bond lengths and angles of the present drug molecule are normal and do not deviate much from those in *p*-hydroxyephedrine hydrochloride (Dattagupta, Pattanayek & Saha, 1981) and in the model obtained by averaging pertinent bond lengths and angles for 34 similar compounds (Hebert, 1979). The average C—C distance in the aromatic ring is 1.385 Å. The C8—N distance is greater than the average model value of 1.486 Å (Hebert, 1979) but close to the standard C—N value of 1.505 Å (Hahn, 1957), the corresponding bond lengths of 1.527 (7) Å in *p*-hydroxyephedrine hydrochloride (Dattagupta, Pattanayek & Saha, 1981) and 1.511 (molecule *A*) and 1.525 Å (molecule *B*) in synephrine monohydrogenphosphate monohydrate (Dattagupta, Meyer & Mukhopadhyay, 1982). The phenyl ring is planar within 0.01 Å and the exocyclic atoms O1 and C7 are slightly displaced from the plane by −0.011 (3) and −0.020 (5) Å, respectively. The ethylamine side chain is also planar within experimental error; the dihedral angle between the phenyl ring plane and the side-chain plane is 103.0 (2)°. The relevant torsion angles, C5—C4—C7—C8 = −76.3 (5) and C4—C7—C8—N = 164.5 (3)°, indicate that the side chain has a *trans* conformation relative to the phenyl ring and is approximately perpendicular to the phenyl ring plane. The distance D_N of the amino N atom from the centre of the phenyl ring is 5.128 (5) Å and the height of this N atom from the phenyl ring plane is 1.301 (4) Å. It has been found in other biologically active amines that the D_N distance is around 5 Å (Hebert, 1979; Post & Kennard, 1974; Giesecke, 1973); this appears to be a preferred conformation necessary for activity at the receptor site (Carlström, Bergin & Falkenberg, 1973). Such conformational features are also observed for phenylethylamines in interactive situations (Dattagupta, Meyer & Mukhopadhyay, 1982; Mukhopadhyay, Dattagupta & Simonetta, 1989; Hearn, Freeman & Bugg, 1973; Hebert, 1978) in a similar manner to other monohydrogenphosphates and dihydrogenphosphates. The *trans* conformation of the phenylethylamines with extended ethylamine side chains is also preserved in the complexation of these drugs with phosphates.

In the crystal packing the molecules are linked by a three-dimensional network of hydrogen bonds. Alternate polar columns of hydrophilic moieties (dihydrogenphosphate anions, amino N atoms, ethanolic O atoms and phenolic O atoms) and nonpolar regions of hydrophobic aromatic phenyl moieties extend along the **b** direction. The amino, ethanolic and phenolic hydroxyl groups point towards the polar column and are involved in hydrogen bonds with the O atoms of the $H_2PO_4^-$ anions. The present structure and earlier related crystallographic studies indicate that such hydroxyl–phosphate and amino–phosphate hydrogen bonding may be present in complexes between phenylethylamines and ATP, GTP and GDP in biological systems. In the $H_2PO_4^-$ group the P atom is situated at the centre of a distorted tetrahedron. The P—O bond distances and O—P—O angles conform to the values obtained in other sympathomimetic drug

phosphates such as hordenine monohydrogenphosphate dihydrogenphosphate monohydrate (Mukhopadhyay, Dattagupta & Simonetta, 1989), ephedrine monohydrogenphosphate (Hearn, Freeman & Bugg, 1973), amphetamine dihydrogenphosphate (Herbert, 1978) and synephrine monohydrogenphosphate monohydrate (Dattagupta, Meyer & Mukhopadhyay, 1982).

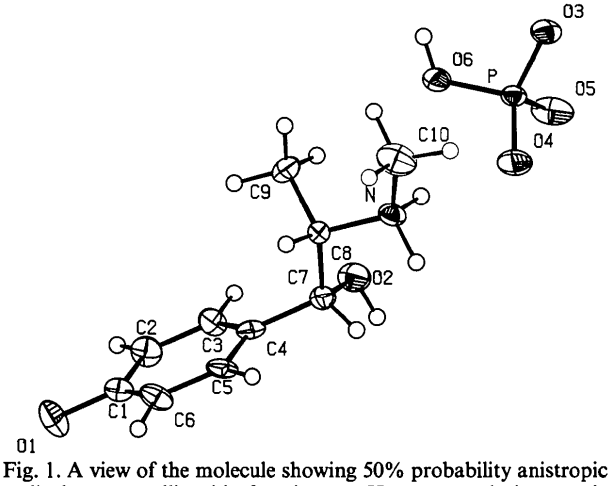


Fig. 1. A view of the molecule showing 50% probability anistropic displacement ellipsoids for the non-H atoms and the atomic numbering scheme.

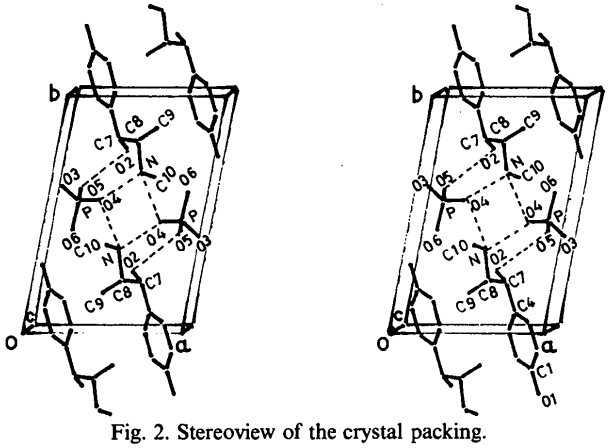


Fig. 2. Stereoview of the crystal packing.

Experimental

Crystal data

$C_{10}H_{16}NO_2^+.H_2PO_4^-$
M_r = 279.23
Triclinic
$P\bar{1}$
a = 10.308 (2) Å
b = 11.315 (2) Å
c = 6.056 (1) Å
α = 90.17 (2)°
β = 105.68 (2)°
γ = 75.55 (2)°
V = 657.0 (2) Å^3
Z = 2
D_x = 1.411 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 2.1-7.6°
μ = 2.056 mm^{-1}
T = 293 K
Rectangular parallelepiped
0.50 × 0.30 × 0.25 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1741 measured reflections
1463 independent reflections
1404 observed reflections [$F > 5\sigma(F)$]
R_{int} = 0.0432
θ_{max} = 55°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 12$
$l = 0 \rightarrow 6$
3 standard reflections monitored every 100 reflections
intensity variation: <2%

Refinement

Refinement on F
R = 0.074
wR = 0.079
S = 0.743
1404 reflections
163 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.022628F^2]$
$(\Delta/\sigma)_{max}$ = 0.351
$\Delta\rho_{max}$ = 0.514 e Å^{-3}
$\Delta\rho_{min}$ = −0.583 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)

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

	x	y	z	U_{eq}
P	0.1885 (1)	0.5594 (1)	0.0857 (2)	0.021 (5)
O1	0.9986 (3)	−0.2853 (3)	0.4961 (6)	0.038 (1)
O2	0.6033 (3)	0.2565 (3)	0.1705 (6)	0.037 (1)
O3	0.0516 (3)	0.6253 (3)	0.1276 (6)	0.032 (1)
O4	0.3193 (3)	0.5557 (3)	0.2632 (6)	0.038 (1)
O5	0.1996 (3)	0.6215 (3)	−0.1380 (6)	0.045 (1)
O6	0.1874 (3)	0.4245 (3)	0.0337 (7)	0.042 (2)
N	0.4722 (4)	0.3378 (3)	0.5342 (6)	0.025 (2)
C1	0.9169 (5)	−0.1674 (4)	0.4664 (8)	0.027 (2)
C2	0.8298 (5)	−0.1175 (4)	0.2513 (8)	0.031 (2)
C3	0.7471 (5)	0.0021 (4)	0.2294 (8)	0.028 (2)
C4	0.7491 (4)	0.0720 (4)	0.4178 (8)	0.024 (2)
C5	0.8373 (4)	0.0205 (4)	0.6280 (7)	0.026 (2)
C6	0.9187 (4)	−0.0988 (4)	0.6549 (8)	0.030 (2)
C7	0.6588 (4)	0.2025 (4)	0.3990 (8)	0.025 (2)
C8	0.5348 (4)	0.2057 (4)	0.4950 (8)	0.023 (2)
C9	0.4246 (5)	0.1530 (4)	0.3401 (9)	0.036 (2)
C10	0.3663 (6)	0.3547 (5)	0.6667 (10)	0.046 (2)

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

P—O3	1.510 (3)	C1—C6	1.377 (7)
P—O4	1.471 (3)	C2—C3	1.393 (6)
P—O5	1.572 (4)	C3—C4	1.385 (7)
P—O6	1.560 (4)	C4—C5	1.379 (5)
O1—C1	1.371 (5)	C4—C7	1.522 (6)
O2—C7	1.421 (6)	C5—C6	1.384 (6)
N—C8	1.519 (5)	C7—C8	1.534 (7)
N—C10	1.497 (8)	C8—C9	1.512 (7)
C1—C2	1.393 (6)		
O5—P—O6	106.4 (2)	C3—C4—C7	122.3 (4)
O4—P—O6	107.3 (2)	C3—C4—C5	118.1 (4)
O4—P—O5	106.0 (2)	C5—C4—C7	119.7 (4)
O3—P—O6	109.5 (2)	C4—C5—C6	121.8 (4)
O3—P—O5	107.9 (2)	C1—C6—C5	119.7 (4)
O3—P—O4	119.1 (2)	O2—C7—C4	114.0 (4)
C8—N—C10	114.7 (4)	C4—C7—C8	110.1 (4)

O1—C1—C6	119.0 (4)	O2—C7—C8	107.1 (4)
O1—C1—C2	121.3 (4)	N—C8—C7	107.9 (4)
C2—C1—C6	119.8 (4)	C7—C8—C9	113.4 (4)
C1—C2—C3	119.4 (4)	N—C8—C9	110.3 (4)
C2—C3—C4	121.2 (4)		
C10—N—C8—C7	−169.5 (4)	C5—C4—C7—C8	−76.3 (5)
C10—N—C8—C9	66.1 (5)	O2—C7—C8—N	−71.0 (4)
C3—C4—C7—O2	−16.2 (6)	C4—C7—C8—N	164.5 (3)
C5—C4—C7—O2	163.3 (4)	C4—C7—C8—C9	−73.1 (5)
C3—C4—C7—C8	104.2 (5)	O2—C7—C8—C9	51.4 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1(N)···O4	1.08	1.95	2.818 (4)	135.4 (2)
N—H2(N)···O4^{i}	1.08	1.65	2.727 (5)	172.1 (2)
O6—H(O6)···O3^{ii}	0.87	1.74	2.594 (5)	168.5 (3)
O2—H(O2)···O5^{iii}	0.97	1.84	2.773 (5)	162.1 (2)
O1—H*···O3^{iv}	-	-	2.583 (5)	-
O1—H*···O5^{v}	-	-	2.599 (4)	-

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, -z$; (iii) $1-x, 1-y, -z$; (iv) $1+x, y-1, z$; (v) $1+x, y-1, 1+z$.

* This H atom could not be located.

Refinement was by full-matrix least-squares methods. Of 18 H atoms, only four were located on the difference Fourier map, 12 were calculated and the other two could not be located. The high *R* values may be due to the poor quality of the crystal. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used for geometrical calculations and to prepare material for publication: *PARST* (Nardelli, 1983). All calculations were performed on a Super 32 computer (VECC, Calcutta).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-(*N*-Benzyloxycarbonyl-L-1,2,3,4-tetrahydroisoquinol-3-ylcarbonyl)-L-phenylalanine Methyl Ester, Z-L-Tic-L-Phe-OMe

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Abstract

The title compound, $C_{28}H_{28}N_2O_5$, is a terminally blocked dipeptide, conformationally constrained by the presence of a 1,2,3,4-tetrahydroisoquinoline residue (Tic). The conformation of the peptide linkage is *trans* [$\omega_1 = -177.0\ (3)°$] and the main chain conformation is determined by the parameters $\varphi_1 = -86.7\ (4)$, $\psi_1 = 171.5\ (3)$, $\varphi_2 = -77.2\ (4)$, $\psi_\tau = 160.1\ (3)°$. The side chain of Tic is in a g^+ conformation [$\chi_1^1 = 56.0\ (4)°$], whereas the phenylalanine side chain is in a g^- conformation [$\chi_2^1 = -68.8\ (5)°$]. In