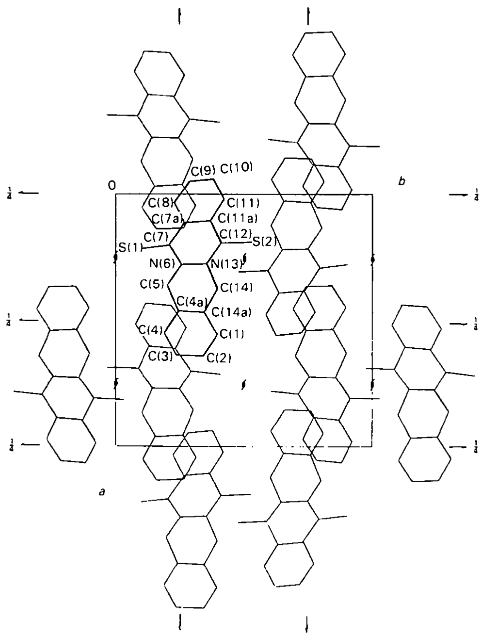

Fig. 2. Crystal packing viewed down **c**.

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Structure of (*S*)-2-Methyl-1-[(*R*)-1-phenylethylamino]-1-propanephosphonic Acid Monohydrate

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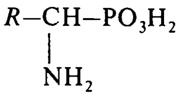
Abstract. $C_{12}H_{20}NO_3P.H_2O$, $M_r = 275\cdot3$, orthorhombic, $C222_1$, $a = 10\cdot167\ (3)$, $b = 18\cdot970\ (10)$, $c = 15\cdot580\ (7)$ Å, $U = 3005$ Å^3, $Z = 8$, $D_m = 1\cdot22\ (1)$, $D_x = 1\cdot22$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot19$ mm^{-1}, $F(000) = 1184$, $T = 293$ K, $R = 0\cdot06$ for 1617 nonzero independent amplitudes. The title compound exists as a zwitterion, Ph—CHMe—NH_2^+—CH(CHMe$_2$)—PO$_3$H$^-$. The conformation of the molecule is *gauche–gauche*, angles χ^1 [P—C(1)—N—C] and χ^2 [C(1)—N—C—C(phenyl)] being 68·3 (4) and 60·9 (5)°, respectively. Two short P—O···H···O—P hydrogen bonds of 2·554 (5) and 2·526 (4) Å occur between molecules related by a twofold rotation axis. The absolute configuration of the molecule was assigned as *S*,*R* with reference to the known *R* configuration of (+)-(*R*)-1-phenylethylamine.

Introduction. The determination of the molecular structure and absolute configuration of 1-aminoalkanephosphonic acids (1) is of considerable importance in view of the established inhibition of enzymes involved in the metabolism of amino acids by the phosphonic acid analogues of substrates (Neuzil & Cassaigne, 1980; Adams, Mukherjee & Dunathan, 1974; Brand & Lowenstein, 1978; Neale, 1970; LaCoste, Cassaigne & Neuzil, 1972; Lejczak, Starzemska & Mastalerz, 1981).

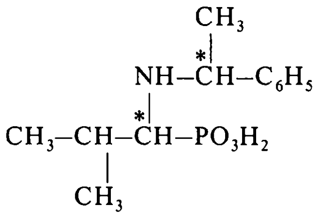
It appears that replacement of the COOH group by the PO_3H_2 function does not prevent some enzymes from recognizing (1) as similar to carboxylic amino acids, but the better understanding of biological effects based on structural antagonism between compounds of type (1) and the corresponding carboxylic amino acids requires that the molecular structures of the former are known with the same degree of exactitude as that of protein amino acids. X-ray data are, however, rather scarce and have been reported only for the phosphonic acid analogues of glycine (Darriet, Darriet, Cassaigne & Neuzil, 1975), alanine (Allen, Atherton, Hall, Hassall, Holmes, Lambert, Nisbet & Ringrose, 1978), valine and phenylglycine (Głowiak, Sawka-Dobrowolska, Kowalik, Mastalerz, Soroka & Zoń, 1977) and phenylalanine (Kowalik, Sawka-Dobrowolska & Głowiak, 1984).

In continuation of our studies on the crystal structure and configuration of optically active 1-aminoalkanephosphonic acids we now report X-ray results for the title compound (2).



$R\text{–}\underset{\underset{\textstyle NH_2}{|}}{CH}\text{–}PO_3H_2$

(1)



(2)

Experimental. (2) prepared by addition of diisopropyl phosphate to the aldimine prepared from isobutyraldehyde and (+)-(*R*)-1-phenylethylamine, followed by acid hydrolysis of the addition product, *i.e.* the diisopropyl ester (2). ^{31}P NMR indicated that the addition product was a mixture of two diastereoisomers in a ratio of 5 to 1. ^{31}P chemical shifts in $CDCl_3$ relative to external H_3PO_4 were −27·2 and −26·7 p.p.m., respectively. Crystallization of crude (2) from water yielded pure (2), m.p. 512–513 K. Colourless, transparent crystals 0·4 × 0·4 × 0·2 mm. D_m by flotation in benzene/1,1,2,2-tetrachloroethane. Preliminary crystal data from oscillation and Weissenberg photographs. Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator. Cell parameters by least squares from setting angles of 15 reflections, $16° \leq 2\theta \leq 25°$. 2227 independent reflections, $2\theta \leq 60°$, variable θ–2θ scans, scan rate 2·0–29·3° min^{-1} depending on intensity. Two standards every 50 reflections with average intensities and e.s.d.'s of 171 748 (2196) and 42 231 (810). Corrections for Lorentz–polarization, but not for absorption or extinction. 1637 reflections with $I > 1{\cdot}96\sigma(I)$ used for structure determination. Index range *h* 0 to 14, *k* 0 to 26, *l* 0 to 21. 20 reflections showing a large $(F_o - F_c)/\sigma(F_o)$ ratio excluded in the final stages of refinement. Calculations performed with the Syntex (1976) *XTL* system. Scattering factors for neutral atoms, corrected for anomalous dispersion, from *International Tables for X-ray Crystallography* (1974). Structure solved by direct methods with a Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F)$; 16 H atoms from difference synthesis, remaining H atoms placed at computed positions; H atoms of the water molecule could not be located; non-H atoms with anisotropic thermal parameters and H atoms with fixed coordinates and thermal parameters ($B = 5{\cdot}0$ Å^2); 1617 observations, 163 variables; max. in final least-squares cycle $(\Delta/\sigma)_{max} = 0{\cdot}1$; residual electron density in final difference map within −0·20 and 0·25 e Å^{-3}; $R = 0{\cdot}060$, $wR = 0{\cdot}061$, $S = 4{\cdot}04$.* The absolute configuration of the molecule was assigned as *S*,*R* and is consistent with the known *R* configuration of 1-phenylethylamine.

Discussion. Final atomic parameters are given in Table 1. The molecular structure and atom numbering are shown in Fig. 1. Bond distances and angles and selected torsion angles are in Table 2.

One of the interesting aspects of this crystal structure is the hydrogen-bonding pattern (details deposited). The phosphate protons are located on the twofold rotation axis parallel to **b**. The O atoms O(1),O(1′) and O(3),O(3′) (related by the twofold axis) are involved in short hydrogen bonds [2·554 (5) and 2·526 (4) Å, respectively]. The distances H(O1)···O(1) and H(O3)···O(3) are 1·28 and 1·27 Å and both O—H···O angles are 179·9°. Similar short hydrogen bonds have been observed in L-*O*-serine phosphate (Sundaralingam & Putkey, 1970), in DL-*O*-serine phosphate (Putkey & Sundaralingam, 1970) and in compounds cited therein.

The phosphate groups are arranged about the twofold rotation axis and are bound together through the —P—O···H···O—P— hydrogen bonds to form a dimer (Fig. 2). These dimers are held together in the **a** direction *via* N—H(4)···O(2) [2·736 (5) Å] and O(*W*)···O(1) [2·855 (9) Å] hydrogen bonds. Although the H atoms of the water molecule have not been located, the distance O(*W*)···O(1) indicates the existence of an O(*W*)—H···O(1) hydrogen bond. The second H atom of the NH_2^+ group participates in a hydrogen bond involving O(*W*) at $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$.

The P—C and P—O(2) bond distances (Table 2) are close to the normal values, while the P—O(1) and P(1)—O(3) bonds involving the short hydrogen bonds

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and hydrogen-bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42397 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are 1·556 (4) and 1·523 (3) Å, respectively, and intermediate in character between the P—O (1·490 Å) and P—OH (1·568 Å) bond distances found in other aminophosphonic acids.

The coordination around the P atom departs significantly from regular tetrahedral (Table 2). The equal sharing of a proton by two phosphate O atoms has also influenced the bond angles at P. The two largest O—P—O angles of 114·3 (2) and 112·6 (2)° involve the unprotonated O(2) and hemi-protonated O(1) and O(3). The smallest angle of 105·2 (2)° involves the C atom and the unprotonated O atom, although as a general rule the smallest C—P—O angle involves the C atom and the protonated O atom in organic phosphates (Corbridge, 1974).

Table 1. *Positional parameters and* B_{eq} (Å^2) *values of the non-*H *atoms, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	x	y	z	B_{eq}
P	0·0209 (1)	0·2128 (1)	0·1184 (1)	3·40 (7)
O(1)	−0·0384 (3)	0·2744 (2)	0·1720 (2)	4·2 (3)
O(2)	−0·0362 (3)	0·2083 (2)	0·0306 (2)	4·4 (3)
O(3)	0·0147 (4)	0·1443 (2)	0·1692 (2)	4·1 (3)
O(*W*)	0·3152 (8)	0·2944 (4)	0·3472 (4)	11·5 (7)
N	0·2075 (4)	0·2775 (2)	0·0200 (2)	3·1 (3)
C(1)	0·1967 (4)	0·2355 (2)	0·1020 (3)	3·2 (3)
C(2)	0·2957 (5)	0·1749 (3)	0·0988 (4)	4·7 (5)
C(3)	0·2569 (8)	0·1154 (4)	0·0400 (5)	6·8 (7)
C(4)	0·3280 (7)	0·1485 (4)	0·1894 (5)	6·2 (6)
C(5)	0·1464 (5)	0·3517 (3)	0·0212 (3)	3·5 (4)
C(6)	0·1578 (6)	0·3812 (3)	−0·0691 (4)	5·0 (5)
C(7)	0·2121 (6)	0·3967 (3)	0·0880 (4)	3·9 (4)
C(8)	0·1434 (7)	0·4178 (3)	0·1590 (4)	5·3 (5)
C(9)	0·2014 (9)	0·4630 (3)	0·2194 (5)	6·6 (7)
C(10)	0·3273 (8)	0·4876 (3)	0·2080 (5)	6·8 (7)
C(11)	0·3978 (7)	0·4661 (4)	0·1363 (6)	7·3 (7)
C(12)	0·3389 (6)	0·4210 (4)	0·0772 (5)	6·0 (6)

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°), *with e.s.d.'s in parentheses*

P—O(1)	1·556 (4)	C(5)—C(6)	1·519 (8)
P—O(2)	1·488 (3)	C(5)—C(7)	1·502 (7)
P—O(3)	1·523 (3)	C(7)—C(8)	1·368 (9)
P—C(1)	1·856 (5)	C(8)—C(9)	1·403 (10)
C(1)—N	1·510 (6)	C(9)—C(10)	1·374 (12)
C(1)—C(2)	1·529 (7)	C(10)—C(11)	1·388 (11)
C(2)—C(3)	1·506 (9)	C(11)—C(12)	1·392 (10)
C(2)—C(4)	1·533 (9)	C(12)—C(7)	1·379 (8)
C(5)—N	1·540 (6)		

O(1)—P—O(2)	112·6 (2)	C(1)—C(2)—C(4)	110·9 (5)
O(1)—P—O(3)	110·2 (2)	C(6)—C(5)—N	107·1 (4)
O(1)—P—C(1)	105·9 (2)	N—C(5)—C(7)	110·4 (4)
O(2)—P—O(3)	114·3 (2)	C(6)—C(5)—C(7)	113·6 (4)
O(2)—P—C(1)	105·2 (2)	C(5)—C(7)—C(8)	120·0 (5)
O(3)—P—C(1)	108·0 (2)	C(5)—C(7)—C(12)	121·4 (5)
P—C(1)—N	108·0 (3)	C(8)—C(7)—C(12)	118·6 (5)
C(1)—N—C(5)	116·3 (3)	C(7)—C(8)—C(9)	120·4 (6)
P—C(1)—C(2)	117·7 (3)	C(8)—C(9)—C(10)	120·8 (7)
N—C(1)—C(2)	108·7 (4)	C(9)—C(10)—C(11)	119·0 (7)
C(1)—C(2)—C(3)	114·2 (5)	C(10)—C(11)—C(12)	119·4 (7)
C(3)—C(2)—C(4)	111·8 (5)	C(7)—C(12)—C(11)	121·8 (6)

	O(1)—P—C(1)—N	−90·1 (4)
	O(2)—P—C(1)—N	29·3 (4)
	O(3)—P—C(1)—N	151·8 (4)
χ^1	P—C(1)—N—C(5)	68·3 (4)
	C(2)—C(1)—N—C(5)	−163·0 (5)
	C(1)—N—C(5)—C(6)	−175·0 (4)
χ^2	C(1)—N—C(5)—C(7)	60·9 (5)
	P—C(1)—C(2)—C(4)	−78·7 (4)
	P—C(1)—C(2)—C(3)	48·7 (6)
χ^{31}	N—C^α(1)—C^β(2)—C^γ(4)	158·2 (5)
χ^{32}	N—C^α(1)—C^β(2)—C^γ(3)	−74·4 (6)
	N—C(5)—C(7)—C(8)	−112·4 (6)
	N—C(5)—C(7)—C(12)	71·4 (7)

The P—C(1)—N angle in the title compound [108·0 (3)°] is smaller than the corresponding angle in (−)-(*S*)-aminomethyl-2-propylphosphonic acid (*P*-valine) (Głowiak *et al.*, 1977; Sawka-Dobrowolska, 1980) [110·6 (4)°]. However, the C(1)—N—C(5) angle [116·3 (3)°] is greater than the tetrahedral angle; this may be a result of the substitution by the bulky groups.

The phenyl moiety is nearly planar; the maximum deviation from the best plane through the ring atoms is 0·006 (7) Å. The mean C—C bond length is 1·384 Å as in benzene and C—C—C angles are close to 120°.

The conformation of the molecule is described by the torsion angles χ^1, χ^2, χ^{31} and χ^{32}. The molecule assumes a *gauche–gauche* conformation with χ^1 and χ^2, the torsion angles about C(1)—N and N—C(5), 68·3 (4) and 60·9 (5)° (see Table 2).

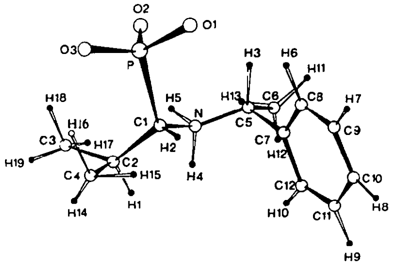

Fig. 1. Perspective view of the title molecule.

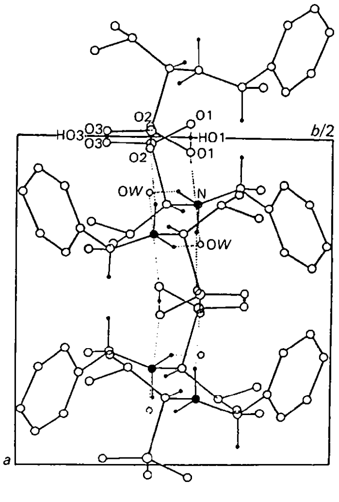

Fig. 2. The crystal structure projected along **c**. Hydrogen bonds are shown by broken lines.

The conformation of the valine residue is defined by the torsion angles χ^{31}[N—C(1)—C(2)—C(4)] and χ^{32}[N—C(1)—C(2)—C(3)] describing the orientation of the two C^{β}—C^{γ} bonds about C^{α}—C^{β}. The values of χ^{31} and χ^{32} are different from those found in *P*-valine where N—C(1) is *gauche* [$\chi^{31} = -49{\cdot}5$ (10), $\chi^{32} = 76{\cdot}4$ (10)°] to both C^{β}—C^{γ} bonds.

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Structures of 3-(*p*-Benzyloxyphenyl)sydnone (1) and 3-(*p*-Isopropoxyphenyl)sydnone (2)

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Abstract. (1): $C_{15}H_{12}N_2O_3$, $M_r = 268$, monoclinic, $P2_1/c$, $a = 6{\cdot}582$ (3), $b = 6{\cdot}190$ (1), $c = 20{\cdot}848$ (2) Å, $\beta = 96{\cdot}77$ (3)°, $V = 1252{\cdot}26$ Å^3, $Z = 4$, $D_m = 1{\cdot}4$ (3), $D_x = 1{\cdot}42$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, μ(Mo $K\alpha$) = 0·094 mm^{-1}, $F(000) = 560$, $T = 298$ K, final $R = 0{\cdot}048$ for 2222 observed reflections. (2): $C_{11}H_{12}N_2O_3$, $M_r = 220$, triclinic, $P\bar{1}$, $a = 6{\cdot}916$ (1), $b = 8{\cdot}089$ (1), $c = 10{\cdot}820$ (2) Å, $\alpha = 108{\cdot}49$ (1), $\beta = 82{\cdot}89$ (1), $\gamma = 108{\cdot}42$ (1)°, $V = 544{\cdot}45$ Å^3, $Z = 2$, $D_m = 1{\cdot}3$ (3), $D_x = 1{\cdot}34$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, μ(Mo $K\alpha$) = 0·093 mm^{-1}, $F(000) = 232$, $T = 298$ K, final $R = 0{\cdot}041$ for 1609 observed reflections. The bond distances in the sydnone ring are similar in both structures and also similar to those in 3-(*p*-ethoxyphenyl)-sydnone and 3-(*p*-tolyl)sydnone [Wang, Lee & Yeh (1984). *Acta Cryst.* C**40**, 1226–1228]. The N(1)—C(7) and C(7)—C(8) distances of (1), (2) and 3-(*p*-ethoxyphenyl)sydnone are significantly shorter than the corresponding bonds in other 3-phenylsydnone derivatives. The dihedral angles between the sydnone ring and the phenyl ring of (1) and (2) are 39·1 (1) and 24·4 (1)°, respectively. The sydnone ring can be described as having a cyclic azomethine-imide type of bonding.

Introduction. There are a few studies on the unique aromaticity of the sydnone ring (Stewart, 1964; Ohta & Kato, 1969). The dominant delocalized form of the

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