

at C(3) is in an axial position. The sulfur—carbon single-bond lengths [1.808 (3)–1.838 (2) Å] are similar to those reported by Grand, Robert & Filhol (1977) and Noordik, Smits, Sicherer-Roetman, Jansen & de Groot (1985).

The crystalline cohesion is ensured by a pair of symmetry-related intermolecular N⋯N' bonds spanning a centre of symmetry at ($\frac{1}{2}, 1, \frac{1}{2}$), leading to bonded dimers. The intermolecular distances and angles are N⋯N' 3.073, H(1)⋯N' 2.720, H(1)⋯H(1') 2.669 Å, N—H(1)⋯N' 103 and H(1)—N⋯H(1') 77°. All these distances are far too large for conventional hydrogen bonding and it seems that the usual van der Waals interactions hold the molecules together.

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Structure of (*R*)-3-Amino-3-phosphonopropionic Acid

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Abstract. C₃H₈NO₃P, *M_r* = 169.1, orthorhombic, *P*2₁2₁2₁, *a* = 5.103 (2), *b* = 15.209 (6), *c* = 8.114 (3) Å, *V* = 629.7 (4) Å³, *Z* = 4, *D_m* = 1.78 (1), *D_x* = 1.783 (1) Mg m⁻³, λ(Cu Kα) = 1.5418 Å, μ = 3.68 mm⁻¹, *F*(000) = 352, *T* = 293 K, final *R* = 0.037 for 704 observed reflexions. The molecule exists as a zwitterion; the amino group is protonated, the carboxyl group un-ionized, and the phosphonic acid group ionized. The conformation about the C^α—C^β bond is *trans-gauche*, the angles P—C—C—C and N—C—C—C are 176.5 (3) and -60.0 (4)°, respectively. There is extensive intermolecular hydrogen bonding, two of the three N—H⋯O hydrogen bonds are bifurcated. The crystal contains short intermolecular hydrogen bonds of 2.617 (2) (O—H⋯O=P) and 2.629 (4) Å (P—OH⋯O=P).

Introduction. A large number of phosphorus analogs of amino acids, containing a phosphonic instead of

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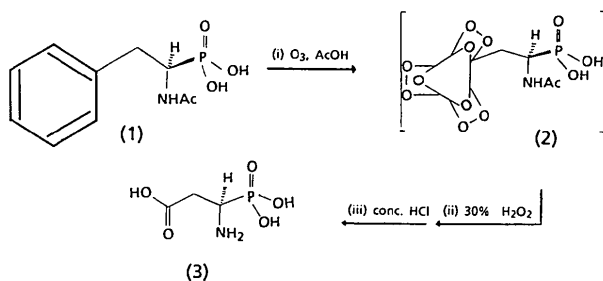
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carboxylic moiety are now known. Almost all counterparts of naturally occurring protein amino acids have been synthesized in various laboratories. The range of applications of α-aminophosphonic acids, e.g. as antibiotics, herbicides, insecticides and enzyme inhibitors (Kafarski & Mastalerz, 1984), shows that they are particularly interesting from a biological viewpoint.

In order to study interactions between aminophosphonates and biological material it is obviously important to have significant amounts of the optically active aminophosphonic acids with known absolute configurations. Recently, we have described the synthesis, molecular structure and absolute configuration of optically active (1-amino-2-phenylethyl)phosphonic acid (PheP), an analog of phenylalanine (Kowalik, Sawka-Dobrowolska & Głowiak, 1984). Here we describe the preparation of the phosphonic analog of aspartic acid, AspP (laevorotary), from the *N*-acetyl derivative of optically pure (–)-PheP, (1). Since all reactions took place outside the asymmetric center, the absolute configurations of

(-)-PheP and (-)-AspP must be the same, *i.e.* *R*. The X-ray structure of (3) is presented here.



Experimental. Treatment of (-)-*N*-acetyl-PheP (1) with a stream of ozone at 273 K for 48 h gave the ozonide (2), which was not isolated. The ozonolysis product was further oxidized by means of 30% hydrogen peroxide to give *N*-acetyl-AspP and the acetyl group was removed by acid hydrolysis to yield the required optically active (-)-AspP (3), m.p. 507–509 K, $[\alpha]_{578}^{20\text{C}} = -35.1^\circ$ ($c = 2.1$ in H_2O).

Colorless transparent crystals, dimensions $0.15 \times 0.2 \times 0.3$ mm, density by flotation in carbon tetrachloride/ethylene bromide; orthorhombic $P2_12_12_1$ from Weissenberg photographs; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $25 \leq 2\theta \leq 36^\circ$; 726 independent reflexions; $2\theta_{\text{max}} = 140^\circ$; variable θ - 2θ scans, scan rate 2.0 – $29.3^\circ \text{ min}^{-1}$, depending on intensity. Two standards (236, 322) measured every 50 reflexions, variation in intensities $\pm 2\%$; data corrected for Lorentz and polarization effects, not for absorption. 704 reflexions with $I > 1.96\sigma(I)$ used for structure determination; index range h 0 to 6, k 0 to 18, l 0 to 9; calculations performed with Syntex (1976) *XTL/XTLE* system; scattering factors for neutral atoms and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974, Vol. IV). Structure solved by direct methods with a Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares on F , minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$; H atoms located from difference synthesis; non-H atoms refined with anisotropic thermal parameters, H atoms refined with isotropic factors; max. $(\Delta/\sigma) = 0.01$, max. and min. electron density in final difference map 0.12 and $-0.11 \text{ e } \text{\AA}^{-3}$; $R = 0.037$, $wR = 0.042$, $S = 4.51$ (the refinement of the parameters for the inverted structure gave $R = 0.039$, $wR = 0.043$).

The absolute configuration was assigned as *R* on the basis of the configuration of the starting material used in the synthesis. It is confirmed additionally by the Hamilton (1965) \mathcal{R} test.

Table 1. Positional parameters and isotropic temperature factors with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum B_{ii}$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}} (\text{\AA})^2$
P	0.0937 (2)	0.3815 (1)	0.0046 (1)	1.0 (1)
O(1)	0.3971 (5)	0.3663 (2)	-0.0178 (4)	1.6 (2)
O(2)	-0.0294 (6)	0.3007 (2)	0.0798 (3)	1.5 (2)
O(3)	0.0574 (6)	0.4673 (2)	0.0929 (3)	1.6 (2)
O(4)	0.1194 (7)	0.2979 (2)	-0.6100 (3)	2.3 (2)
O(5)	-0.2064 (7)	0.3873 (2)	-0.5353 (4)	2.7 (2)
N	-0.0224 (7)	0.4896 (2)	-0.2534 (4)	1.5 (2)
C(1)	-0.0420 (7)	0.3942 (2)	-0.2049 (4)	1.2 (2)
C(2)	0.1045 (9)	0.3393 (2)	-0.3320 (5)	1.5 (2)
C(3)	-0.0127 (7)	0.3443 (2)	-0.5018 (6)	1.5 (2)

Table 2. Bond distances (\AA), bond angles ($^\circ$) and hydrogen-bond geometry (\AA , $^\circ$) with *e.s.d.*'s in parentheses

P—O(1)	1.576 (3)	C(1)—C(2)	1.523 (5)	
P—O(2)	1.509 (3)	C(2)—C(3)	1.504 (6)	
P—O(3)	1.500 (3)	C(3)—O(4)	1.313 (5)	
P—C(1)	1.846 (4)	C(3)—O(5)	1.215 (5)	
C(1)—N	1.504 (5)			
O(2)—P—O(1)	109.6 (2)	P—C(1)—C(2)	112.5 (3)	
O(1)—P—O(3)	107.7 (2)	N—C(1)—C(2)	110.6 (3)	
O(1)—P—C(1)	106.1 (2)	C(1)—C(2)—C(3)	113.4 (3)	
O(2)—P—O(3)	117.7 (2)	O(4)—C(3)—O(5)	123.8 (4)	
O(2)—P—C(1)	107.5 (2)	O(4)—C(3)—C(2)	112.4 (3)	
O(3)—P—C(1)	107.7 (2)	O(5)—C(3)—C(2)	123.8 (4)	
P—C(1)—N	110.0 (3)			
D—H...A		D—H	H...A	D—H...A
O(1)—H(1)...O(2')	2.617 (2)	0.99 (5)	1.65 (5)	164 (5)
N—H(5)...O(5 ⁱⁱ)	2.878 (5)	0.78 (6)	2.15 (6)	158 (6)
N—H(5)...O(3)	2.876 (4)	0.78 (6)	2.45 (6)	116 (5)
N—H(6)...O(3 ⁱⁱⁱ)	2.982 (5)	1.01 (7)	2.02 (7)	158 (6)
N—H(6)...O(5)	2.890 (5)	1.01 (7)	2.36 (7)	112 (5)
N—H(7)...O(3 ^{iv})	2.847 (5)	0.97 (6)	1.88 (6)	175 (5)
O(4)—H(8)...O(2'')	2.629 (4)	1.00 (7)	1.63 (7)	174 (6)

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

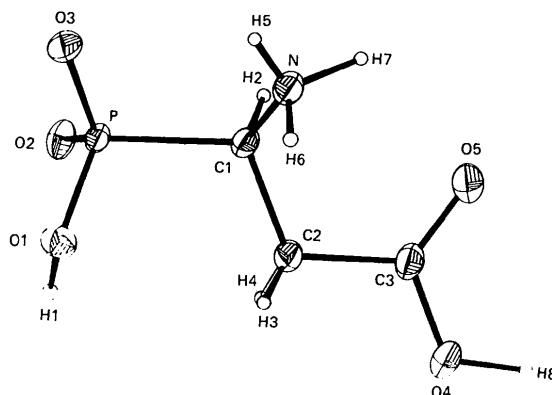


Fig. 1. ORTEP (Johnson, 1976) projection of molecule with the atom-numbering scheme and thermal ellipsoids at the 50% probability level.

Discussion. Final atomic coordinates are given in Table 1.* The molecular structure and atom numbering are shown in Fig. 1. Interatomic distances, valence angles and hydrogen-bond geometry are given in Table 2. The 3-amino-3-phosphonopropionic acid (α -AspP) exists as a zwitterion with the α -amino N protonated and the phosphonic acid group negatively charged; the P—O bond lengths, 1.509 (3) and 1.500 (3) Å, indicate that the charge is equally distributed between O(2) and O(3) — as in β -AspP (Sawka-Dobrowolska, Głowiak, Siatecki & Soroka, 1985). There is extensive hydrogen bonding,

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, torsion angles, H-atom parameters and the full synthesis of the title compound have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54317 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in which all potential donor and acceptor atoms participate.

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Structure of 12,14-Dihydro-2H-dibenzo[*d,i*][1,3,7,6,8]dioxathiadiazecine

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Abstract. $C_{13}H_{12}N_2O_4S$, $M_r = 292.309$, monoclinic, $P2_1/n$, $a = 4.907$ (2), $b = 13.797$ (6), $c = 19.474$ (8) Å, $\beta = 97.20$ (3)°, $V = 1308.02$ (95) Å³, $Z = 4$, $D_x = 1.4843$, $D_m = 1.477$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 22.24$ cm⁻¹, $F(000) = 608$, room temperature, final $R = 0.0494$ for 2121 reflections with $I > 3\sigma(I)$. The ten-membered ring is in a chair conformation. There are two intramolecular and one intermolecular hydrogen bonds of N—H...O type. The molecules form chains in the [100] direction.

Introduction. Bearing in mind that sulfamides find wide application in medicine we tried to obtain and study a new class of related compounds, cyclic sulf-

amides. Some methods of obtaining benzo- and dibenzosulfadiazines on the basis of the reaction of aryldiamines with sulfamide, or sulfur chloride have been described (Knollmuller, 1971, 1974). Following these methods we have carried out the synthesis by using an aminoaryl ether, methylenedioxybis(aminobenzene), and sulfamide. We have obtained the title compound (1) and used it for preliminary screening in antibacterial properties. The pharmacological test showed it had comparatively weak antibacterial activity. The formula of (1) has been confirmed by elemental, IR, NMR and MS methods.

This structure determination has been undertaken to give more detailed information about the bond