the title compound (Fig. 2) and which is a general packing motif.

We thank Dr W. T. Robinson, Department of Chemistry, University of Canterbury, Christchurch, New Zealand, for kindly arranging for the data collection, and the UGC and CSIR for financial assistance to BSG and SSP.

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Acta Cryst. (1993). C**49**, 1111–1113

Structure of 1-Amino-3-(methylthio)propylphosphonic Acid

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(*Received* 1 *April* 1991; *accepted* 7 *April* 1992)

Abstract. $C_4H_{12}NO_3PS$, $M_r = 185.18$, monoclinic, $P2_1/c$, $a = 14.508$ (8), $b = 6.095$ (4), $c = 9.532$ (5) Å, $\beta = 97.93$ (4)°, $V = 834.8$ Å^3, $Z = 4$, $D_m = 1.47$ (1), $D_x = 1.473$ (1) Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, μ = 4.8 mm^{-1}, $F(000) = 392$, $T = 292$ K, $R = 0.052$ for 1588 observed reflexions. The molecule exists as a zwitterion with the amino group being protonated and the phosphonic acid group being ionized. The conformation of the molecule is *trans*, *gauche* and *gauche* {angles χ^1[N—C(1)—C(2)—C(3)], χ^2[C(1)—C(2)—C(3)—S] and χ^3[C(2)—C(3)—S—C(4)] are 175.7 (4), −62.5 (5) and −69.9 (5)°, respectively} and the side chain is strongly folded. There is extensive intermolecular hydrogen bonding and one of the three N—H···O hydrogen bonds is bifurcated. The crystal contains a short P—OH···O intermolecular hydrogen bond of 2.526 (3) Å.

Introduction. Aminophosphonic acids are analogues of aminocarboxylic acids, the —COOH group being replaced by a —PO_3H_2 group. These acids are of considerable interest because of their occurrence in many living organisms and their biological activity. The neutral and synthetic aminophosphonic acids and their derivatives (phosphonopeptides, phosphonolipids, phosphonoglycolipids, *etc.*) include neuroactive compounds, antibiotics and herbicides (Kafarski & Mastalerz, 1984). Their biological

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activity is displayed mainly through their inhibition of various enzymes containing amino acid substrates. The difference in size, shape and basicity of the carboxylate and phosphonate groups may be important factors in the differences in the enzyme–substrate interactions.

Experimental. The synthesis of 1-amino-3-(methylthio)propanephosphonic acid has been described by Tam, Mattoks & Tisher (1982). Clear colourless crystals grown from water at room temperature, dimensions 0.20 × 0.15 × 0.30 mm; D_m by flotation in carbon tetrachloride/ethylene bromide; monoclinic $P2_1/c$ from Weissenberg photographs. All measurements were made on a Kuma KM4 computer-controlled κ-axis diffractometer with graphite monochromator; cell parameters by least squares from 25 reflexions, $15 < \theta < 20°$; 1790 independent reflexions, $2\theta_{max} = 164°$; variable $\omega/2\theta$ scans, scan rate 0.9–9° min^{-1}, scan width $\Delta\omega = (1.2 + 0.35\tan\theta)°$; three standards ($\bar{1}\bar{1}2$, 311, $2\bar{1}3$) every 50 reflexions, variation in intensities +3.5%; correction for Lorentz and polarization factors, but not for absorption; 1588 reflexions with $I > 3\sigma(I)$ used for structure determination; index range h 0 to 18, k 0 to 7, l −12 to 12; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); direct methods solution (*SHELXS*86; Sheldrick, 1986); block-diagonal least-squares refinement (Syntex, 1976) minimizing $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2 + (0.001F_o)^2]^{-1}$; difference synthesis revealed H atoms; non-H atoms refined with anisotropic thermal parameters and H atoms isotropically; max. $\Delta/\sigma = 0.03$, $\Delta\rho$ within +0.20 and −0.18 e Å^{-3}, $R = 0.052$, $wR = 0.049$.

Discussion. Final positional parameters are given in Table 1.* The molecular structure and atom numbering are shown in Fig. 1. Interatomic distances and angles and selected torsion angles are given in Table 2. [The atom-labelling scheme used in this paper is that recommended by the IUPAC–IUB Commission on Biochemical Nomenclature (1970).]

The 1-amino-3-(methylthio)propanephosphonic acid exists as a zwitterion with the N atom of the amino group protonated and the phosphonic acid group negatively charged. The near equality of the bond lengths P—O(2) and P—O(3) indicates that the single negative charge is nearly equally distributed between O(2) and O(3). The coordination of phosphorus departs significantly from a regular tetrahedron (Table 2) as in other aminophosphonic acids. The conformations about the C(1)—C(2), C(2)—C(3) and C(3)—S bonds are *trans*, *gauche* and *gauche*

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å^2)

$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
P	0.1120 (1)	0.1782 (1)	0.3852 (1)	2.56 (3)
S	0.3782 (1)	−0.0450 (2)	0.3351 (1)	6.0 (1)
O(1)	0.1705 (2)	0.2924 (3)	0.2803 (2)	3.7 (1)
O(2)	0.1313 (2)	0.3064 (3)	0.5215 (2)	3.6 (1)
O(3)	0.0123 (2)	0.1495 (3)	0.3276 (2)	3.3 (1)
N	0.0879 (2)	−0.2535 (4)	0.4433 (3)	3.0 (1)
C(1)	0.1626 (2)	−0.0999 (4)	0.4112 (3)	3.1 (1)
C(2)	0.2466 (3)	−0.1184 (5)	0.5210 (4)	3.9 (1)
C(3)	0.3290 (3)	0.0189 (7)	0.4920 (5)	5.0 (2)
C(4)	0.4293 (6)	−0.3034 (13)	0.3857 (9)	9.8 (5)

Table 2. *Molecular geometry* (Å, °) *with e.s.d.'s in parentheses*

P—O(1)	1.562 (2)	C(1)—N	1.495 (4)
P—O(2)	1.509 (2)	C(2)—C(3)	1.515 (6)
P—O(3)	1.484 (2)	C(3)—S	1.786 (5)
P—C(1)	1.850 (3)	C(4)—S	1.779 (8)
C(1)—C(2)	1.498 (5)		

O(1)—P—O(2)	105.5 (1)	C(3)—S—C(4)	99.5 (3)
O(1)—P—O(3)	113.9 (1)	P—C(1)—N	108.4 (2)
O(2)—P—O(3)	115.8 (1)	P—C(1)—C(2)	115.7 (2)
O(1)—P—C(1)	104.6 (1)	N—C(1)—C(2)	110.7 (3)
O(2)—P—C(1)	109.6 (1)	C(1)—C(2)—C(3)	114.7 (3)
O(3)—P—C(1)	106.9 (1)	S—C(3)—C(2)	116.7 (3)

O(1)—P—C(1)—N	−151.1 (3)	χ^1[N—C(1)—C(2)—C(3)]	175.7 (4)
O(2)—P—C(1)—N	96.2 (3)	χ^2[C(1)—C(2)—C(3)—S]	−62.5 (5)
O(3)—P—C(1)—N	−30.0 (3)	χ^3[C(2)—C(3)—S—C(4)]	−69.9 (5)
P—C(1)—C(2)—C(3)	−60.6 (4)		

D—H···A	D—H	H···A	D···A	D—H···A
O(1)—H(1)···O(2^i)	0.70 (4)	1.84 (3)	2.526 (3)	168 (4)
N—H(3)···O(3^{ii})	1.05 (3)	1.84 (3)	2.856 (4)	164 (3)
N—H(3)···O(2^{ii})	1.05 (3)	2.53 (3)	3.260 (4)	126 (2)
N—H(4)···O(2^{iii})	0.99 (3)	1.87 (3)	2.832 (3)	163 (3)
N—H(5)···O(3^{iv})	0.82 (4)	2.10 (4)	2.845 (3)	151 (4)
Short contact				
N—H(5)···O(3)	0.82 (4)	2.59 (4)	2.850 (3)	100 (4)

Symmetry code: (i) x, $0.5 - y$, $-0.5 + z$; (ii) $-x$, $-y$, $1 - z$; (iii) x, $-1 + y$, z; (iv) $-x$, $-0.5 + y$, $0.5 - z$.

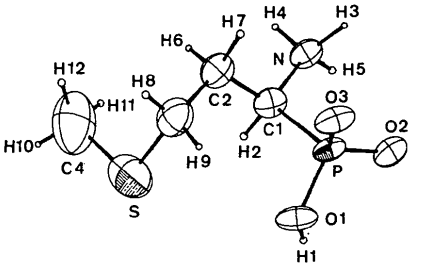

Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme (thermal ellipsoids drawn at the 50% probability level).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and molecular geometry for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55358 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0067]

[175.7 (4), −62.5 (5) and −69.9 (5)°], and the side chain is folded. This conformation is very similar to that of molecule *B* of L-methionine (Torii & Iitaka, 1973).

The molecular structure is stabilized by a network of N—H···O and O—H···O hydrogen bonds (Table 2).

This work was supported by the Polish Ministry of Science and Higher Education (Project RP.II.10) and the Polish Academy of Sciences (Project CPBP.01.12).

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Acta Cryst. (1993). C**49**, 1113–1116

(3*R*,6*R*)-3,4-Dimethyl-1,4-diazabicyclo[4.4.0]decane-2,5-dione

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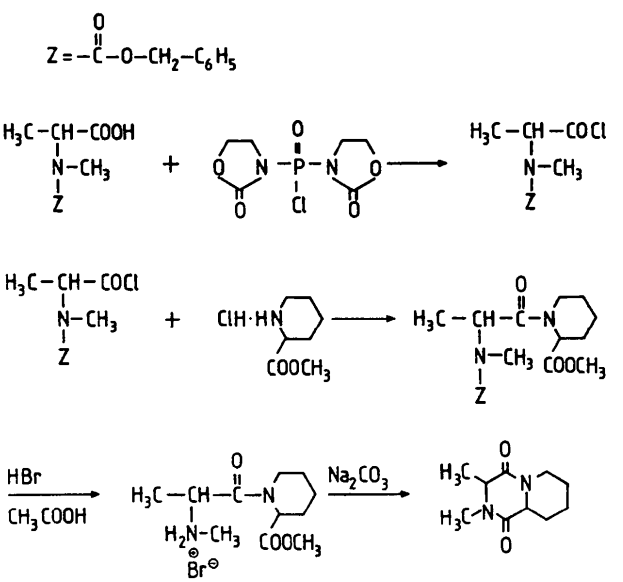
(*Received* 30 *March* 1992; *accepted* 5 *February* 1993)

Abstract. $C_{10}H_{16}N_2O_2$, $M_r = 196.25$, orthorhombic, $P2_12_12_1$, $a = 6.593\ (3)$, $b = 6.755\ (2)$, $c = 23.653\ (4)$ Å, $V = 1053\ (1)$ Å^3, $Z = 4$, $D_x = 1.24$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.08$ mm^{-1}, $F(000) = 424$, room temperature, $R = 0.031$, $wR = 0.038$ for 884 observed reflections [$I \geq 3\sigma(I)$] out of 1302 reflections measured and for 191 variables. The compound, for which the synthesis is also reported, consists of a piperidine ring in the chair form and a diketopiperazine ring in the boat form with C(3) and C(6) as bowsprits. The two rings are *cis*-fused. The methyl group at C(3) is pseudo-axially bonded, while the methyl group at N(4) is pseudo-equatorially bonded. The C=O bonds are of equal length reflecting the absence of hydrogen bonding in the structure.

Introduction. The title compound, shown in Fig. 1, contains the 2,5-diketopiperazine moiety (abbreviated DKP) and is a cyclic dipeptide composed of D-alanine and D-pipecolic acid. The compound, also known as *cis-cyclo*-[-*N*-methyl-D-Ala-D-Pec-], was synthesized in the series of reactions presented below. It belongs to a group of compounds of which some members show antiviral and antimicrobial activity (Sammes, 1975). The restrictions brought



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0108-2701/93/061113-04$06.00