synchro twist $S(++)$ (Acharya, Tavale & Guru Row, 1984).

The molecules are held together by van der Waals interactions.

References

ACHARYA, K. R., TAVALE, S. S. & GURU ROW, T. N. (1984). *Proc. Indian Acad. Sci. (Chem. Sci.)*, **93**, 271–282.

AMMON, H. L., ZHANG, D., CHOI, C. S., SANDUS, O., MARCHAND, A. P. & SURI, S. C. (1985). *Acta Cryst.* C**41**, 404–406.

BRYCE-SMITH, D. & GILBERT, A. (1976). *Tetrahedron*, **32**, 1309–1326.

EATON, P. E., RAVI SHANKER, B. K., PRICE, G. D., PLUTH, J. J., GILBERT, E. E., ALSTER, J. & SANDUS, O. (1984). *J. Org. Chem.* **49**, 185–186.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *LALS*. Program for the full-matrix refinement of positional and thermal parameters and scale factors. Univ. of California, USA.

GEORGE, C., GILLARDI, R., FLIPPEN-ANDERSON, J. L., CHOI, C. S., MARCHAND, A. P. & REDDY, D. S. (1985). *Acta Cryst.* C**41**, 788–791.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MEHTA, G., MURTHY, A. N., REDDY, D. S. & REDDY, A. V. (1986). *J. Am. Chem. Soc.* **108**, 3443–3452.

SOLOTT, G. P. & GILBERT, G. E. (1980). *J. Org. Chem.* **45**, 5405–5408.

WATSON, W. H., MARCHAND, A. P. & DAVE, P. R. (1987). *Acta Cryst.* C**43**, 1569–1571.

WENDER, P. A. (1983). *Selectivity – A Goal for Synthetic Efficiency*, edited by W. BARTMAN & B. M. TROST, pp. 335–348. Berlin: Verlag Chemie.

Acta Cryst. (1988). C**44**, 2193–2195

Structure of 2-Amino-4-(methylphosphinico)butyric Acid Hydrochloride

BY W. SAWKA-DOBROWOLSKA

Institute of Chemistry, University of Wrocław, 14 F. Joliot-Curie Street, 50–383 Wrocław, Poland

(*Received* 8 *April* 1988; *accepted* 12 *July* 1988)

Abstract. $C_5H_{13}NO_4P^+.Cl^-$, $M_r = 217{\cdot}8$, monoclinic, $P2_1/n$, $a = 12{\cdot}642\ (5)$, $b = 5{\cdot}474\ (3)$, $c = 14{\cdot}233\ (5)$ Å, $\beta = 105{\cdot}10\ (5)°$, $V = 950{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}52\ (1)$, $D_x = 1{\cdot}52$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}55$ mm^{-1}, $F(000) = 456$, $T = 292$ K, $R = 0{\cdot}038$ for 1359 observed reflexions. The molecule exists in a cationic form in which the amino group is protonated and the carboxylic and the phosphinic acid groups are neutral. The N–C–COOH moiety is nearly planar, the torsion angle ψ' is $-2{\cdot}0\ (4)°$; $C^\gamma(1)$ is *gauche* to both C(4) and N with torsion angles χ^1 and χ^2 at $-49{\cdot}1\ (4)$ and $73{\cdot}8\ (3)°$ respectively; P is *trans* to $C^\alpha(3)$ [$P–C^\gamma(1)–C^\beta(2)–C^\alpha(3) = -163{\cdot}9\ (3)°$]. There is extensive intermolecular hydrogen bonding in the structure.

Introduction. It has been known for more than twenty years (Mastalerz, 1959) that the phosphonic and phosphinic acid analogues of glutamic acid possess inhibitory properties towards glutamine synthetase. Phosphinothricin [2-amino-4-(methylphosphinico)-butyric acid] has been isolated from cultures of *Streptomyces viridochromogenes* (Bayer *et al.*, 1972) and *Streptomyces hygroscopicus* as the tripeptide, phosphinothricyl-alanyl-alanine. This tripeptide is active against Gram-positive and Gram-negative bacteria and also against the fungi *Botrytis cinerea*, sheath blight and rice blast (Kondo *et al.*, 1973). The two alanine residues allow the penetration of this tripeptide through the cell wall. Inside the cell it is assumed that phosphinothricin is liberated by 'lethal cleavage of an inactive material'.

D,L-Phosphinothricin is an active glutamine synthetase inhibitor (Mastalerz, 1959; Leason, Cunliffe, Parkin, Lea & Miflin, 1982) and shows herbicidal properties (Rupp, Finke, Beringer & Lagenlueddeke, 1977). Recently, the crystal structures of DL- and L-phosphinothricin have been reported by Paulus & Grabley (1982). This paper reports the first X-ray structure of an aminophosphinic acid hydrochloride.

Experimental. The free phosphinothricin was prepared by the method developed by Dr E. Gruszecka-Kowalik at the Institute of Organic and Physical Chemistry, Technical University of Wrocław, Poland. Clear colourless crystals were obtained by slow evaporation from a saturated aqueous solution with excess 20% hydrochloric acid. Crystal of dimensions $0{\cdot}28 \times 0{\cdot}40 \times 0{\cdot}45$ mm: D_m by flotation in carbon tetrachloride/ethylene bromide: monoclinic $P2_1/n$ from Weissenberg photographs. Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation

0108-2701/88/122193-03$03.00

counter, Mo $K\alpha$ radiation, graphite monochromator. Cell parameters by least squares from setting angles of 15 reflexions with $15 \le 2\theta \le 24°$ measured on the diffractometer. 1614 independent reflexions: $2\theta_{max} = 55{\cdot}0°$; variable θ–2θ scans, scan rate 2·0–29·3° min^{-1}, depending on intensity: two standards (233, 32$\bar{6}$) measured every 50 reflexions. Variation in intensities ±2%; data corrected for Lorentz and polarization but not for absorption; 1359 with $I > 3\sigma(I)$ used for structure determination: index range h 0 to 14, k 0 to 6, l ±16. All calculations performed with Syntex (1976) *XTL/XTLE* system: neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); direct methods *via* Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$; difference synthesis revealed H atoms: non-H atoms refined with anisotropic thermal parameters and H atoms isotropically; max. $\Delta/\sigma = 0{\cdot}01$, $\Delta\rho$ within +0·2 and −0·18 e Å^{-3}, $R = 0{\cdot}038$, $wR = 0{\cdot}041$, $S = 2{\cdot}60$.

Discussion. Final atomic parameters are in Table 1.* Interatomic distances and selected torsion angles are in Table 2. The atom-labelling scheme (IUPAC-IUB Commission on Biochemical Nomenclature, 1970) is illustrated in Fig. 1, which shows that the phosphinic acid and α-carboxyl groups are in their neutral forms.

The α-carboxyl group is planar. The C=O and C—OH bond lengths are 1·208 (4) and 1·297 (4) Å, similar to those found in L-glutamic acid hydrochloride (Sequeira, Rajagopal & Chidambaram, 1972). The C—OH bond length in the protonated α-carboxyl group in L-Glu hydrochloride and the present compound are shorter [1·296 (8) and 1·297 (4) Å] than the values observed for γ-carboxyl groups [1·313 (1), 1·312 (2) 1·315 (8) Å, mean 1·313 Å] (Lehmann, Koetzle & Hamilton, 1972; Lehmann & Nunes, 1980). The two O—C—C angles differ from each other, being 122·5 (3) and 111·5 (3)° (see Marsh & Donohue, 1967). The angle O—C—O of 122·5 (3)° is normal for amino acids.

The maximum deviation from the least-squares plane through the carboxyl group, O(3), O(4), C′(4) and $C^{\alpha}(3)$ is 0·005 (3) Å. The distance of the N atom from this plane is 0·034 (3) Å and the O(3)—C′(4)—$C^{\alpha}(3)$—N torsion angle (ψ^1) is −2·0 (4)°. This angle is greater [−11·5 (2)°] in DL-phosphinothricin (Paulus & Grabley, 1982).

In the present structure P—O(1) = 1·494 (2) and P—O(2) = 1·560 (2) Å, indicative of double and single

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51239 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}|a_i^*|\,|a_j^*|\,(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}
P	0·1765 (1)	0·1079 (2)	0·4692 (1)	1·83 (1)
Cl	0·1370 (1)	0·3242 (2)	0·7069 (1)	2·73 (2)
O(1)	0·2799 (2)	0·2536 (4)	0·4886 (2)	2·45 (6)
O(2)	0·0805 (2)	0·2504 (4)	0·4942 (2)	2·66 (6)
O(3)	−0·0024 (2)	−0·1537 (5)	0·0984 (2)	3·64 (7)
O(4)	0·1523 (2)	0·0590 (5)	0·1196 (2)	3·42 (7)
N	−0·0984 (2)	0·1812 (6)	0·1853 (2)	2·48 (7)
$C^{\gamma}(1)$	0·1202 (3)	0·0434 (6)	0·3430 (2)	2·30 (8)
$C^{\beta}(2)$	0·0915 (2)	0·2743 (6)	0·2815 (2)	2·25 (8)
$C^{\alpha}(3)$	0·0153 (2)	0·2304 (6)	0·1802 (2)	2·10 (8)
C′(4)	0·0536 (3)	0·0224 (7)	0·1274 (2)	2·40 (8)
C(*M*)	0·1972 (3)	−0·1697 (7)	0·5343 (3)	3·14 (10)

Table 2. *Molecular geometry* (*e.s.d.'s in parentheses*)

(*a*) Bond lengths (Å)

P—O(1)	1·494 (2)	$C^{\beta}(2)$—$C^{\alpha}(3)$	1·529 (4)
P—O(2)	1·560 (2)	$C^{\alpha}(3)$—C′(4)	1·512 (5)
P—C(1)	1·786 (3)	$C^{\alpha}(3)$—N	1·482 (4)
P—C(*M*)	1·764 (4)	C′(4)—O(3)	1·208 (4)
$C^{\gamma}(1)$—$C^{\beta}(2)$	1·527 (5)	C′(4)—O(4)	1·297 (4)

(*b*) Valence angles (°)

O(1)—P—O(2)	112·7 (1)	$C(1)^{\gamma}$—$C(2)^{\beta}$—$C^{\alpha}(3)$	114·1 (3)
O(1)—P—C(1)	113·1 (1)	N—$C^{\alpha}(3)$—$C^{\beta}(2)$	111·3 (3)
O(1)—P—C(*M*)	111·1 (2)	N—$C^{\alpha}(3)$—C′(4)	109·1 (3)
O(2)—P—C(1)	101·4 (1)	$C^{\beta}(2)$—$C^{\alpha}(3)$—C′(4)	112·4 (3)
O(2)—P—C(*M*)	109·2 (2)	O(3)—C′(4)—O(4)	126·0 (3)
C(1)—P—C(*M*)	108·9 (2)	$C^{\alpha}(3)$—C′(4)—O(3)	122·5 (3)
P—$C(1)^{\gamma}$—$C^{\beta}(2)$	112·7 (2)	O(4)—C′(4)—$C^{\alpha}(3)$	111·5 (3)

(*c*) Torsion angles (°)

C(*M*)—P—C(1)—C(2)	175·8 (3)	χ^1 $C^{\gamma}(1)'$—$C^{\beta}(2)$—$C^{\alpha}(3)$—C′(4)	−49·1 (4)
O(1)—P—$C^{\gamma}(1)$—$C^{\beta}(2)$	−60·2 (3)	χ^2 $C^{\gamma}(1)$—$C^{\beta}(2)$—$C^{\alpha}(3)$—N	73·8 (3)
O(2)—P—$C^{\gamma}(1)$—$C^{\beta}(2)$	60·7 (3)	χ^1 O(3)—C′(4)—$C^{\alpha}(3)$—N	−2·0 (4)
H(1)—O(2)—P—$C^{\gamma}(1)$	178·2 (28)	χ^2 O(4)—C′(4)—$C^{\alpha}(3)$—N	178·8 (3)
P—$C^{\gamma}(1)$—$C^{\beta}(2)$—$C^{\alpha}(3)$	−163·9 (3)	H(13)—O(4)—C′(4)—$C^{\alpha}(3)$	−173·5 (36)

(*d*) Hydrogen-bond geometry (Å,°)

D—H···*A*	*D*···*A*	*D*—H	H···*A*	*D*—H···*A*
O(2)—H(1)···Cl	2·952 (2)	0·77 (3)	2·19 (3)	170 (3)
O(4)—H(13)···O(1)—P	2·567 (3)	0·99 (4)	1·59 (4)	166 (4)
N—H(12)···Cl^{ii}	3·262 (3)	0·97 (3)	2·29 (3)	173 (3)
N—H(11)···Cl^{iii}	3·211 (3)	1·07 (3)	2·16 (4)	167 (3)
N—H(10)···O(1^{iv})—P	2·843 (3)	0·93 (4)	1·92 (4)	172 (3)

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

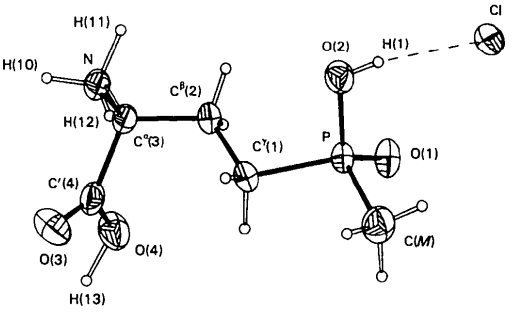

Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme.

bonds respectively. The P–C$^{\gamma}$(1) and P–C(*M*) distances of 1·786 (3) and 1·764 (4) Å are somewhat shorter than the corresponding values [1·825 (6), 1·806 Å] in aminomethyl(methyl)phosphinic acid (Głowiak & Sawka-Dobrowolska, 1977) and in DL-phosphinothricin [1·803 (2) and 1·790 (2) Å: Paulus & Grabley (1982)]. The P-coordination departs significantly from a regular tetrahedron (Table 2). The protonated O atom influences the bond angles at P. The largest two O–P–O and O–P–C angles of 113·1 (1) and 112·7 (1)° involve the unprotonated O(1), the protonated O(2) and C(1). The smallest angle of 101·4 (1)° involves C(1) and the protonated O(2) atom; this angle is considerably smaller than the corresponding angle in L-phosphinothricin (Paulus & Grabley, 1982) [108·0 (1)°].

The two bond angles C$^{\gamma}$(1)–C$^{\beta}$(2)–C$^{\alpha}$(3) and P–C$^{\gamma}$(1)–C$^{\beta}$(2) [114·1 (3) and 112·7 (2)°] are similar to the corresponding angles in L-Glu hydrochloride [115·8 (4) and 112·0 (4)°], DL-glutamic acid [113·6 (2) and 113·6 (2)°] (Ciunik & Głowiak, 1983) and DL-phosphinothricin [113·3 (2) and 112·0 (1)°] (Paulus & Grabley, 1982).

The conformation of the molecule is described by the torsion angles χ^1, χ^2, ψ^1 and ψ^2. The molecule assumes a *gauche–gauche* conformation with χ^1 and χ^2 [torsion angles about C$^{\beta}$(2)–C$^{\alpha}$(3)] = −49·1 (4) and 73·8 (3)° respectively. These are similar to the values found in L- and DL-phosphinothricin [χ^1 = −65·5 (2), 57·8 (3)°; χ^2 = −45·4 (2), 76·7 (2)°; Paulus & Grabley, 1982]. This implies that P is *trans* to C$^{\alpha}$(3) [P–C$^{\gamma}$(1)–C$^{\beta}$(2)–C$^{\alpha}$(3) = −163·9 (3)°], this being the only possible conformation.

The torsion angles ψ^1 and ψ^2 (Table 2) are near 0 and 180° as usually observed.

The conformation around P–C$^{\gamma}$(1) is defined by the C(*M*)–P–C(1)–C(2), O(2)–P–C(1)–C(2) and O(1)–P–C(1)–C(2) angles of 175·8 (3), 60·7 (3) and −60·2 (3)°. Thus both O atoms are synclinal with respect to the carbon backbone and C(methyl) is antiperiplanar. These values contrast with the 66·1 (2), −51·2 (2) and −173·4 (1)° observed in L-phosphinothricin.

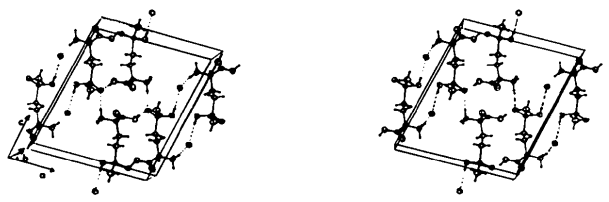

Fig. 2. Stereoview of crystal structure; hydrogen bonds are indicated by dashed lines.

There is extensive hydrogen bonding in the structure, with all potential donor and acceptor atoms participating. Relevant dimensions are in Table 2(*d*) and a stereoscopic drawing of the unit cell is shown in Fig. 2. The amino group interacts with two Cl$^-$ ions and O(1) of the phosphinic acid group. Adjacent molecules are held together by pairs of N$^+$–H···Cl$^-$ hydrogen bonds, related by a centre of symmetry. H(11) and H(12) are donated to two Cl$^-$ ions, and the third amino H atom, H(10), is donated to O(1) of an *n*-glide related molecule. The hydrogen-bonding scheme is completed with the formation of short hydrogen bonds from O(2) (phosphinic) and O(4)(carboxyl) to Cl$^-$ and O(1) (screw related) respectively. These intermolecular hydrogen bonds are similar to the hydrogen bonds found in L-Glu hydrochloride.

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

References

BAYER, E., GUGELE, K. H., HAEGELE, K., HAGENMAIER, H., JESSIPOW, S., KOENIG, W. A. & ZACHNER, H. (1972). *Helv. Chim. Acta*, **55**, 224–226.

CIUNIK, Z. & GŁOWIAK, T. (1983). *Acta Cryst.* C**39**, 1271–1273.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–375.

GŁOWIAK, T. & SAWKA-DOBROWOLSKA, W. (1977). *Acta Cryst.* B**33**, 1522–1525.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KONDO, Y., SHOMURA, T., OGAWA, Y., SUZUKI, T., MORIYAMA, CH., IOSHIDA, J., INONYE, SH. & NIIDA, T. (1973). *Sci. Rep. Meiji Seika Kaisha*, **13**, 34–42.

LEASON, M., CUNLIFFE, D., PARKIN, D., LEA, P. J. & MIFLIN, B. J. (1982). *Phytochemistry*, **21**, 855–858.

LEHMANN, M. S., KOETZLE, T. F. & HAMILTON, W. C. (1972). *J. Cryst. Mol. Struct.* **2**, 225–233.

LEHMANN, M. S. & NUNES, A. C. (1980). *Acta Cryst.* B**36**, 1621–1625.

MARSH, R. E. & DONOHUE, J. (1967). *Adv. Protein Chem.* **22**, 235–256.

MASTALERZ, P. (1959). *Arch. Immunol. Terapii Doświadczalnej*, **7**, 201–203.

PAULUS, E. F. & GRABLEY, S. (1982). *Z. Kristallogr.* **160**, 39–44, 63–68.

RUPP, W., FINKE, M., BERINGER, H. & LAGENLUEDDEKE, P. (1977). German Patent No. 2 717 440, 22 pp.: *Chem. Abstr.* (1978), 88 P 7049 e.

SEQUEIRA, A., RAJAGOPAL, H. & CHIDAMBARAM, R. (1972). *Acta Cryst.* B**28**, 2514–2519.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California, USA.