Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

S(1)—C(1)	1·708 (4)	S(1)—C(5)	1·781 (7)
S(2)—C(2)	1·706 (7)	S(2)—C(11)	1·876 (5)
O(1)—C(4)	1·193 (6)	O(2)—C(3)	1·191 (6)
C(1)—C(2)	1·379 (6)	C(1)—C(4)	1·490 (7)
C(2)—C(3)	1·501 (6)	C(3)—C(4)	1·543 (6)
C(5)—C(6)	1·378 (6)	C(5)—C(10)	1·376 (6)
C(6)—C(7)	1·381 (7)	C(7)—C(8)	1·373 (8)
C(8)—C(9)	1·380 (7)	C(9)—C(10)	1·382 (7)
C(11)—C(12)	1·368 (6)	C(11)—C(16)	1·383 (8)
C(12)—C(13)	1·381 (8)	C(13)—C(14)	1·365 (9)
C(14)—C(15)	1·367 (9)	C(15)—C(16)	1·382 (8)
C(1)—S(1)—C(5)	100·7 (3)	C(2)—S(2)—C(11)	103·9 (2)
S(1)—C(1)—C(4)	129·1 (4)	S(1)—C(1)—C(2)	137·4 (3)
C(2)—C(1)—C(4)	93·4 (4)	S(2)—C(2)—C(1)	130·8 (3)
C(1)—C(2)—C(3)	92·8 (4)	S(2)—C(2)—C(3)	136·2 (4)
O(2)—C(3)—C(2)	136·8 (6)	C(2)—C(3)—C(4)	86·7 (4)
O(2)—C(3)—C(4)	136·4 (5)	O(1)—C(4)—C(3)	137·5 (5)
O(1)—C(4)—C(1)	135·4 (6)	S(1)—C(5)—C(10)	119·3 (3)
S(1)—C(5)—C(6)	119·9 (5)	C(6)—C(5)—C(10)	120·7 (5)
C(5)—C(6)—C(7)	119·4 (5)	C(6)—C(7)—C(8)	120·0 (5)
C(7)—C(8)—C(9)	120·5 (7)	C(8)—C(9)—C(10)	119·6 (6)
C(5)—C(10)—C(9)	119·6 (5)	S(2)—C(11)—C(16)	118·3 (4)
S(2)—C(11)—C(12)	120·7 (5)	C(12)—C(11)—C(16)	120·5 (6)
C(11)—C(12)—C(13)	119·6 (5)	C(12)—C(13)—C(14)	120·0 (5)
C(13)—C(14)—C(15)	120·5 (7)	C(14)—C(15)—C(16)	120·1 (7)
C(11)—C(16)—C(15)	119·0 (6)		
S(1)—C(1)—C(2)—S(2)	3·5 (12)	S(1)—C(1)—C(4)—O(1)	−1·8 (13)
S(2)—C(2)—C(3)—O(2)	−3·5 (14)	O(2)—C(3)—C(4)—O(1)	1·6 (16)
C(5)—S(1)—C(1)—C(2)	11·5 (9)	C(11)—S(2)—C(2)—C(3)	8·4 (9)
C(1)—S(1)—C(5)—C(10)	77·6 (6)	C(2)—S(2)—C(11)—C(16)	103·0 (6)

double bond which can explain the observed lack of reactivity.

The molecules are held in the crystal by van der Waals forces. The packing of the molecules in the unit cell is illustrated in Fig. 2.

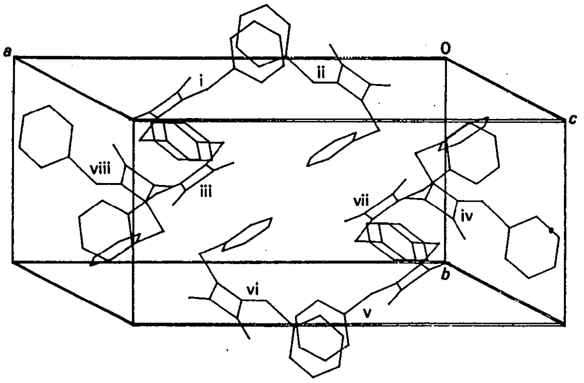

Fig. 2. Packing diagram of the contents of the unit cell. (i) x, y, z; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $1-x, 1-y, 1-z$; (vi) $x, 1-y, \frac{1}{2}+z$; (vii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (viii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

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Structure of *N*-Phosphonomethyl-L-proline

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Abstract. $C_6H_{12}NO_5P$, $M_r = 209\cdot15$, orthorhombic, $P2_12_12_1$, $a = 5\cdot623$ (2), $b = 7\cdot857$ (2), $c = 19\cdot635$ (5) Å, $V = 867\cdot5$ (4) Å^3, $Z = 4$, $D_m = 1\cdot60$ (1), $D_x = 1\cdot60$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot32$ mm^{-1}, $F(000) = 440$, $T = 293$ K, $R = 0\cdot038$ for 1009 reflexions with $I > 1\cdot96\sigma(I)$. The title compound was prepared by reaction of the sodium salt of L-proline, formaldehyde and diethylphosphite. The molecule exists as a zwitterion; the amino group is protonated and the carboxyl group is un-ionized, the phosphonic acid group being ionized. The pyrrolidine ring adopts a half-chair [$\Delta C_2 = 2\cdot8$ (7)°] conformation.

Introduction. *N*-Phosphonomethyl-L-proline (2) was prepared in the course of our work on the synthesis and

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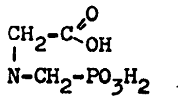
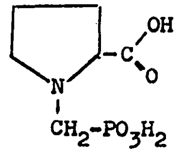
crystal structure of phosphorus analogues of the natural α-amino acids which are known as useful biologically active compounds (Schwerdtle, Bieringer & Finke, 1981; Atherton, Hall, Hassall, Lambert & Ringrose, 1979). The title compound is a new analogue of *N*-phosphonomethyl-glycine (glyphosphate) (1) known as a very effective herbicide.



(1)



(2)

It appears that (2) may be a potential substrate or inhibitor of the enzyme which uses proline as its reagent. As a continuation of our research on the *N*-blocked aminophosphonic acids (Sawka-Dobrowolska, 1985; Sawka-Dobrowolska, Głowiak, Kowalik & Mastalerz, 1985; Sawka-Dobrowolska, Głowiak & Siatecki, 1987; Sawka-Dobrowolska, Głowiak & Barycki, 1988), the X-ray structure of (2) is presented here.

Experimental. The synthesis of *N*-phosphonomethyl-L-proline (Moedritzer & Irani, 1966; Issleib, Wache & Balszuweit, 1979) has been carried out by reaction of the sodium salt of L-proline, formaldehyde and diethylphosphite. M.p. (uncorrected) = 527 K, determined on a Boetius apparatus. Colourless transparent crystals 0·2 × 0·25 × 0·45 mm. D_m 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 $18 \leq 2\theta(\mathrm{Mo}) \leq 31°$ measured on diffractometer; 1185 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 (112, 202) every 50 reflexions, variation in intensities ±2%; data corrected for Lorentz–polarization, but not for absorption and extinction, 1009 reflexions with $I \geq 1{\cdot}96\sigma(I)$ used for structure determination; index range *h* 0 to 7, *k* 0 to 10, *l* 0 to 25; calculations performed with the Syntex (1976) *XTL/XTLE* 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); block-diagonal least squares, 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 temperature factors; max. $(\Delta/\sigma) = 0{\cdot}01$; max. and min. electron density in final difference map 0·14 and –0·13 e Å^{-3}; $R = 0{\cdot}038$, $wR = 0{\cdot}037$, $S = 2{\cdot}293$.

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

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

	x	y	z	B_{eq}(Å^2)
P	0·0430 (2)	0·2387 (1)	0·1820 (1)	1·44 (5)
O(1)	0·0788 (5)	0·2659 (3)	0·2607 (1)	2·1 (2)
O(2)	–0·0244 (5)	0·0531 (3)	0·1730 (1)	2·1 (2)
O(3)	–0·1133 (4)	0·3684 (3)	0·1504 (1)	2·0 (2)
O(4)	0·6116 (5)	0·3924 (4)	–0·0025 (1)	3·1 (2)
O(5)	0·2943 (5)	0·5100 (4)	–0·0542 (1)	2·6 (2)
N	0·4209 (5)	0·4251 (4)	0·1241 (1)	1·3 (2)
C(1)	0·3389 (6)	0·2529 (5)	0·1443 (2)	1·5 (2)
C$^{\delta}$(2)	0·4224 (7)	0·5590 (4)	0·1796 (2)	1·9 (3)
C$^{\gamma}$(3)	0·4385 (9)	0·7214 (5)	0·1392 (2)	2·9 (3)
C$^{\beta}$(4)	0·2807 (9)	0·6939 (5)	0·0800 (2)	3·2 (4)
C$^{\alpha}$(5)	0·2893 (7)	0·5029 (5)	0·0638 (2)	1·8 (3)
C′(6)	0·4203 (8)	0·4599 (4)	–0·0014 (2)	1·9 (3)

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

P–O(1)	1·572 (2)	C$^{\delta}$(2)–C$^{\gamma}$(3)	1·509 (5)
P–O(2)	1·518 (3)	C$^{\gamma}$(3)–C$^{\beta}$(4)	1·513 (6)
P–O(3)	1·482 (3)	C$^{\beta}$(4)–C$^{\alpha}$(5)	1·535 (6)
P–C(1)	1·824 (3)	C$^{\alpha}$(5)–C′(6)	1·515 (5)
C(1)–N	1·484 (5)	C(6)–O(4)	1·200 (5)
N–C$^{\delta}$(2)	1·515 (4)	C(6)–O(5)	1·317 (4)
N–C$^{\alpha}$(5)	1·523 (4)		
O(1)–P–O(2)	106·1 (1)	C$^{\alpha}$(5)–N–C$^{\delta}$(2)	106·4 (3)
O(1)–P–O(3)	113·2 (1)	N–C$^{\delta}$(2)–C$^{\gamma}$(3)	102·1 (3)
O(1)–P–C(1)	105·9 (2)	C$^{\delta}$(2)–C$^{\gamma}$(3)–C$^{\beta}$(4)	102·8 (3)
O(2)–P–O(3)	117·6 (2)	C$^{\gamma}$(3)–C$^{\beta}$(4)–C$^{\alpha}$(5)	106·2 (3)
O(2)–P–C(1)	103·8 (2)	N–C$^{\alpha}$(5)–C$^{\beta}$(4)	104·3 (3)
O(3)–P–C(1)	109·2 (2)	C$^{\beta}$(4)–C$^{\alpha}$(5)–C′(6)	114·1 (3)
P–C(1)–N	116·6 (2)	O(4)–C(6)–O(5)	126·9 (4)
C(2)–N–C(1)	116·2 (3)	O(4)–C(6)–C(5)	123·3 (3)
C(1)–N–C(5)	115·1 (3)	O(5)–C(6)–C(5)	109·7 (3)
N–C(5)–C(6)–O(4)	–8·0 (4)	H(1)–O(1)–P–C(1)	95 (3)
N–C(5)–C(6)–O(5)	173·0 (3)	O(1)–P–C(1)–N	–88·5 (3)
H(2)–O(5)–C(6)–C(5)	–135 (1)	O(2)–P–C(1)–N	160·0 (2)
N–C$^{\delta}$(2)–C$^{\gamma}$(3)–C$^{\beta}$(4)	42·5 (4)	O(3)–P–C(1)–N	33·7 (3)
C$^{\delta}$(2)–C$^{\gamma}$(3)–C$^{\beta}$(4)–C$^{\alpha}$(5)	–33·9 (4)	P–C(1)–N–C(2)	56·6 (3)
C$^{\gamma}$(3)–C$^{\beta}$(4)–C$^{\alpha}$(5)–N	11·6 (3)	P–C(1)–N–C(5)	–68·8 (3)
C$^{\beta}$(4)–C$^{\alpha}$(5)–N–C$^{\delta}$(2)	15·0 (3)	C(1)–N–C(2)–C(3)	–166·0 (3)
C$^{\alpha}$(5)–N–C$^{\delta}$(2)–C$^{\gamma}$(3)	–36·0 (3)	C(1)–N–C(5)–C(4)	145·3 (4)
C′(6)–C$^{\alpha}$(5)–N–C$^{\delta}$(2)	137·4 (3)	C(1)–N–C(5)–C(6)	–92·3 (3)
C′(6)–C$^{\alpha}$(5)–C$^{\beta}$(4)–C$^{\gamma}$(3)	–107·5 (5)		

The absolute configuration was assigned as *S* on the basis of the configuration of the starting material used in the synthesis.

Discussion. Final atomic coordinates are given in Table 1.[*] Interatomic distances, valence angles and torsion angles are in Table 2. [The atom-labelling scheme in

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles and bond distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51348 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

this paper is that recommended by the IUPAC–IUB Commission on Biochemical Nomenclature (1970).] Fig. 1 shows that the phosphonic acid group is ionized, the proton being transferred to the N atom of L-proline. The planar carboxyl group is in the un-ionized form with C=O and C=OH bonds of 1·200 (5) and 1·317 (4) Å. The two O—C—C (5) angles differ from each other, being 123·3 (3) and 109·7 (3)° (Marsh & Donohue, 1967). The angle O—C—O of 126·9 (4)° compares well with those found in other amino acids. The maximum deviation from the least-squares plane through the carboxyl group, O(4), O(5), C′(6) and $C^{\alpha}(5)$, is 0·006 (4) Å. The distance of N from this plane is 0·182 (3) Å.

With the exception of the bonds involving N, the bond distances of the pyrrolidine ring in (2) are similar to those in other structures (Ashida & Kakudo, 1974; Ashida, Tanaka, Shimonishi & Kakudo, 1977; Benedetti, Palumbo, Bonora & Toniolo, 1976; Tanaka, Kozima, Ashida, Tanaka & Kakudo, 1977). As anticipated, the protonation at N is accompanied by a lengthening of the N—$C^{\alpha}(5)$, N—$C^{\delta}(2)$ bonds. The respective values of 1·523 (4) and 1·515 (4) Å found for these bonds in (2) are much longer than the average values of 1·461 and 1·470 Å reported by Ashida & Kakudo (1974) for unprotonated proline. They are, however, entirely consistent with values reported for protonated proline residues in DL-proline hydrochloride [1·47 (1), 1·52 (1) Å: Mitsui, Masamichi & Iitaka, 1969], L-proline hydrochloride benzyl ester [1·493 (6), 1·500 (6) Å: Kamwaya, Oster & Bradaczek, 1981] and L-prolyl-L-glutamic acid dihydrate [1·501 (1), 1·516 (1) Å: Eggleston & Hodgson, 1982]. Similarly the $C^{\alpha}(5)$—N—$C^{\delta}(2)$ bond angle of 106·4 (3)° found here is appreciably smaller than the mean value of 113·0 (9)° in unprotonated proline, but is consistent with values of 104·6 (7), 106·4 (3) and 108·1 (1)° in the protonated forms cited above.

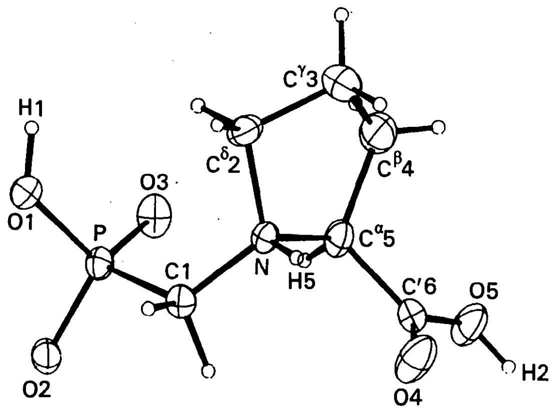

Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme.

The bond lengths in the aminomethylphosphonic acid part of the molecule are in good agreement with those found in aminomethylphosphonic acid, β-AMPh (Darriet, Darriet, Cassaigne & Neuzil, 1975), 4-amino-4-phosphonobutyric acid (Sawka-Dobrowolska & Gruszecka-Kowalik, 1987, and references cited therein) and N-phosphonomethyl-L-threonine (Sawka-Dobrowolska *et al.*, 1988). In the present structure there is O⋯P⋯O resonance as indicated by the bond lengths, P—O(2) and P—O(3), which are 1·518 (3) and 1·482 (3) Å respectively. The P—O(1) bond length of 1·572 (2) Å indicates a single bond.

The coordination around the P atom departs significantly from regular tetrahedral, the angles varying from 117·7 (2)° [O(2)—P—O(3)] to 103·8 (2)° [O(2)—P—C(1)]. The smallest angle involves C(1) and an unprotonated O atom although as a general rule the smallest O—P—C angle involves the C atom and the protonated O in organic phosphates (Corbridge, 1974). The P—C(1)—N angle in the title compound [116·6 (2)°] is greater than the corresponding angle in β-AMPh [110·9 (1)°], this may be a result of the N substitution by proline.

The torsion angles (Table 2) and asymmetry parameters of Duax, Weeks & Rohrer (1976), $\Delta C_2 = 2{\cdot}8\ (7)°$ and $\Delta C_s = 7{\cdot}8\ (7)°$, show that in the pyrrolidine ring two pseudosymmetry elements occur, a twofold axis passing through $C^{\alpha}(5)$ and the $C^{\delta}(2)$—$C^{\gamma}(3)$ bond and a mirror plane perpendicular to the $C^{\beta}(4)$—$C^{\alpha}(5)$ bond. $C^{\delta}(2)$ and $C^{\gamma}(3)$ are −0·377 (4) and 0·293 (5) Å out of the plane of $C^{\beta}(4)$—$C^{\alpha}(5)$—N [C′(6) deviates by 1·208 (4) Å]. Thus, the pyrrolidine ring adopts the half-chair conformation. The torsion angles ψ^1 and ψ^2 about C′(6)—$C^{\alpha}(5)$ of −8·0 (4) and 173·0 (3)° are near 0 and 180° as usually observed.

The molecules are held in the crystal by three hydrogen bonds. The protonated O(1) and O(5) form two strong links to the O(2) atom ($-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, -z$). The O⋯O and H⋯O distances are 2·623 (3), 2·593 (3), 1·74 (4) and 1·77 (4) Å and O—H⋯O angles are 175 (4) and 166 (4)°, respectively.

The other hydrogen bond involves N—H and the phosphonic O(3) atom of the molecule at ($1+x, y, z$). The distances N⋯O(3), H⋯O and the N—H⋯O angle are 2·707 (4), 2·05 (4) Å and 136 (3)°, respectively. Fig. 2 is a stereoview of the cell contents.

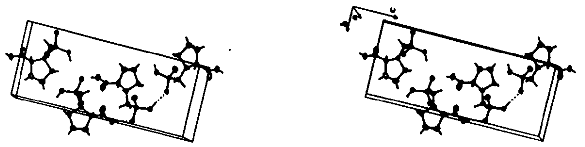

Fig. 2. Stereoview of the unit-cell contents. H bonds are indicated by dashed lines.

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Hexa-2,4-diyne-1,6-diyl Bis(4-hexyloxybenzoate), White Form at 185 K

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Abstract. $C_{32}H_{38}O_6$, $M_r = 518\cdot65$, monoclinic, $P2_1/c$, $a = 18\cdot971\ (7)$, $b = 7\cdot800\ (4)$, $c = 19\cdot615\ (4)$ Å, $\beta = 99\cdot63\ (2)°$, $U = 2861\cdot6$ Å^3, $Z = 4$, $D_x = 1\cdot20$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot076$ mm^{-1}, $F(000) = 1112$, $T = 185$ K, $R = 0\cdot039$ and $wR = 0\cdot0415$ for 3176 reflections. The structure at 185 K shows little change from that found in an earlier room-temperature study [Shklover, Struchkov, Bagirov, Konstantinov & Amerik (1985). *Z. Kristallogr.* **173**, 25–31]. The crystals do not undergo noticeable solid-state polymerization despite relatively short separations (3·83 and 4·29 Å) between reactive acetylenic C atoms in neighbouring molecules. These 1···4 diyne contacts occur between adjacent molecules related by centres of symmetry in contrast to the unit translation stacking arrangement that is commonly found in diacetylene compounds that do undergo crystal-phase polymerization. The banana-shaped hexadiyne unit ($\langle \mathrm{C{-}C{\equiv}C} \rangle = 176\cdot9°$) may result from competition between alternative packing requirements.

Introduction. Part of our studies towards polymeric liquid crystals have been concerned with the syntheses and properties of diacetylenes bearing mesogenic side groups bonded through carboxylate ester linkages and related compounds (Hardy, Milburn, Nyitrai, Horvath, Balazs, Varga & Shand, 1988).

This determination was undertaken to provide information about molecular conformation and packing in a model system where the ester groups are decoupled from the diacetylene unit by only a single methylene group. The restricted mobility of this arrangement

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