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Structures of Glycine Monophosphate and Glycine *cyclo*-Triphosphate

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Abstract. $C_2H_6NO_2^+.H_2PO_4^-$, $M_r = 173\cdot06$, monoclinic, $Z = 4$, $P2_1/c$, $a = 9\cdot580$ (2), $b = 7\cdot840$ (2), $c = 9\cdot249$ (3) Å, $\beta = 114\cdot7$ (2)°, $V = 631\cdot1$ (6) Å^3, $D_x = 1\cdot821$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0\cdot423$ mm^{-1}, $F(000) = 360$, $T = 293$ K, final $R = 0\cdot024$ for 1360 independent reflexions. $3C_2H_6NO_2^+.P_3O_9^{3-}$, $M_r = 465\cdot14$, monoclinic, $Z = 4$, $P2_1/c$, $a = 12\cdot223$ (8), $b = 14\cdot52$ (1), $c = 10\cdot229$ (7) Å, $\beta = 100\cdot47$ (5)°, $V = 1785$ (4) Å^3, $D_x = 1\cdot730$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0\cdot424$ mm^{-1}, $F(000) = 960$, $T = 293$ K, final $R = 0\cdot030$ for 2855 independent reflexions. The glycine monophosphate structure is built up of layers of $H_2PO_4^-$ groups alternating with layers of $C_2H_6NO_2^+$ groups. In the glycine *cyclo*-triphosphate the phosphoric group is a non-acidic one: P_3O_9, interconnected by hydrogen bonds to three crystallographically independent $C_2H_6NO_2^+$ groups.

Experimental. (I) Crystals of glycine monophosphate were prepared by slow evaporation at room temperature of an aqueous solution of glycine and monophosphoric acid in stoichiometric ratio. Crystals appear as colourless stout monoclinic prisms. Prism fragment 0·32 × 0·32 × 0·29 mm. Density not measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $h0l$: $l = 2n$; $0k0$: $k = 2n$. 24 reflexions ($12 < \theta < 14°$) for refining the unit-cell dimensions. ω scan. Scan width: 1·20°, scan speed, variable, between 0·04 and 0·02° s^{-1}, total background measuring time: between 15 and 30 s. 2062 reflexions measured ($3 < \theta < 30°$), 1943 unique; $R_{\rm int} = 0\cdot011$; $\pm h,k,l$, $h_{\rm max} = 13$, $k_{\rm max} = 10$, $l_{\rm max} = 12$. Two intensity ($\bar{5}20$ and $5\bar{2}0$) and two orientation (520 and $\bar{5}\bar{2}0$) reference reflexions: no significant variation. Lorentz and polarization corrections, no absorption correction. Direct methods (*MULTAN*77; Main, Lessinger, Woolfson, Germain & Declercq, 1977) used for structure determination. H atoms located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement (on F) for non-hydrogen atoms, isotropic for H atoms. Unit weights. Final refinement with 1360 independent reflexions ($I > 9\sigma_I$). Final $R = 0\cdot024$, $wR = 0\cdot030$, $S = 0\cdot523$, max. $\Delta/\sigma = 0\cdot0$. Max. peak height in the final difference Fourier map 0·33 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: VAX 780.

(II) Crystals of glycine *cyclo*-triphosphate were prepared by a metathesis reaction deriving from that described by Boullé (1941) for the preparation of water-soluble inorganic *cyclo*-triphosphates. A slurry in water of the sparingly soluble silver *cyclo*-triphosphate monohydrate is added to an aqueous solution of glycine hydrochloride with stoichiometric ratio 1:3. The reaction is

$$Ag_3P_3O_9 + 3(NH_3.CH_2.COOH)Cl \rightarrow 3AgCl + [NH_3.CH_2.COOH]_3P_3O_9.$$

After about one hour of mechanical stirring the insoluble silver chloride is eliminated by filtration. The resulting aqueous solution is then kept at room temperature. Colourless long flat prisms of glycine *cyclo*-triphosphate appear after some days of evaporation. Prism fragment 0·3 × 0·3 × 0·08 mm. Density not measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $h0l$: $l = 2n$; $0k0$: $k = 2n$. 20 reflexions ($10\cdot5 < \theta < 13\cdot5°$) for refining the unit-cell dimensions. ω scan. Scan width: 1·20°, scan speed variable, between 0·16 and 0·02° s^{-1}, total background measuring time: between 4 and 30 s. 4442 reflexions measured ($2 < \theta < 27\cdot5°$), 4206 unique; $\pm h,k,l$, $R_{\rm int} = 0\cdot02$; $h_{\rm max} = 15$, $k_{\rm max} = 18$, $l_{\rm max} = 12$. Two intensity ($\bar{5}\bar{1}\bar{4}$ and $\bar{4}2\bar{5}$) and two orientation ($\bar{5}\bar{3}\bar{4}$ and $\bar{5}3\bar{4}$) reference reflexions: no significant variation. Lorentz and polarization corrections, no absorption correction. Structure determination strategy identical to that used for the first compound. Final refinement with 2855 independent reflexions ($I > 4\sigma_I$). Final $R = 0\cdot030$, $wR = 0\cdot032$, $S = 0\cdot904$, max. $\Delta/\sigma = 0\cdot19$. Max. peak height in the final difference Fourier map 0·33 e Å^{-3}. No extinction correction. Computer used: Microvax-II.

Discussion. *Glycine monophosphate.* Table 1 reports the final atomic coordinates for this salt while Fig. 1 is a projection of its arrangement along the b axis.*

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* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44324 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates for glycine monophosphate*

	x	y	z	B_{iso}/B_{eq}(Å^2)
P	0·09984 (4)	0·84591 (5)	0·77730 (4)	1·175 (6)
O(1)	0·8417 (1)	0·2915 (2)	0·3062 (1)	1·93 (2)
O(2)	0·0467 (1)	0·4219 (2)	0·8579 (1)	1·82 (2)
O(3)	0·7804 (1)	0·0205 (2)	0·1446 (1)	1·81 (2)
O(4)	0·0514 (1)	0·7510 (2)	0·8909 (1)	1·67 (2)
O(5)	0·6107 (2)	0·4799 (2)	0·8891 (2)	3·08 (3)
O(6)	0·5182 (1)	0·3952 (2)	0·6366 (1)	2·50 (3)
N	0·2481 (2)	0·1985 (2)	0·1191 (2)	1·80 (3)
C(1)	0·3615 (2)	0·1364 (2)	0·2748 (2)	1·75 (3)
C(2)	0·5104 (2)	0·0815 (2)	0·2723 (2)	1·75 (3)
H(1)	0·128 (3)	0·778 (3)	0·091 (3)	3·7 (6)*
H(2)	0·042 (3)	0·986 (4)	0·366 (3)	5·4 (7)*
H(3)	0·624 (3)	0·074 (4)	0·143 (3)	4·9 (7)*
H(1N)	0·241 (2)	0·126 (3)	0·035 (2)	2·9 (5)*
H(2N)	0·846 (2)	0·793 (3)	0·874 (2)	3·1 (5)*
H(3N)	0·280 (3)	0·301 (3)	0·096 (3)	3·5 (6)*
H(1C1)	0·319 (3)	0·039 (3)	0·300 (3)	3·2 (5)*
H(2C1)	0·623 (2)	0·727 (3)	0·150 (2)	2·5 (5)*

Starred atoms have been refined isotropically.

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j.\beta_{ij}$.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in glycine monophosphate*

P	O(1)	O(2)	O(3)	O(4)
O(1)	1·559 (2)	104·9 (1)	111·1 (1)	106·4 (1)
O(2)	2·470 (3)	1·556 (2)	111·8 (1)	108·1 (1)
O(3)	2·522 (3)	2·529 (3)	1·497 (2)	113·4 (1)
O(4)	2·459 (2)	2·483 (3)	2·521 (2)	1·510 (2)

P—P 4·8628 (4) and 4·2980 (5) Å

NH_3—CH_2—COOH group

N—C(1)	1·478 (3) Å	N—C(1)—C(2)	113·3 (2)°
C(1)—C(2)	1·500 (3)	C(1)—C(2)—O(5)	120·5 (2)
C(2)—O(5)	1·206 (3)	C(1)—C(2)—O(6)	114·4 (2)
C(2)—O(6)	1·301 (3)	O(5)—C(2)—O(6)	125·1 (2)

Hydrogen bonds

	O—H N—H	H···O	O—O N—O	O—H···O N—H···O
O(1)—H(1)···O(4)	0·87 (4)	1·70 (4)	2·568 (2)	175 (4)
O(2)—H(2)···O(4)	0·73 (5)	1·87 (5)	2·596 (3)	174 (5)
O(6)—H(3)···O(3)	1·01 (4)	1·56 (4)	2·569 (2)	176 (4)
N—H(1N)···O(3)	0·94 (3)	1·96 (4)	2·900 (3)	178 (3)
N—H(2N)···O(4)	0·93 (4)	1·94 (4)	2·859 (3)	170 (3)
N—H(3N)···O(5)	0·91 (4)	1·99 (4)	2·877 (3)	164 (3)

The structure can be described as layers of $H_2PO_4^-$ groups, parallel to the *bc* plane, alternating with layers of $C_2H_6NO_2^+$ groups. Inside the first type of layers, the P—P distances are rather short (4·298 and 4·863 Å). Each $H_2PO_4^-$ group is connected by hydrogen bonds with its four neighbours, to build a two-dimensional network illustrated by Fig. 2.

Table 2 reports the main interatomic distances and bond angles in such a layer. As may be expected the two P—OH distances are significantly longer (1·559 and 1·556 Å) than the P—O distances (1·497 and 1·510 Å).

The glycine groups are located between these phosphate layers (Fig. 1). The carboxylic group is not deprotonated and its H atom is involved in a hydrogen bond with an O atom of the $H_2PO_4^-$ group with a relatively short O—O distance (2·569 Å). Two H atoms of the NH_3 group are linked by hydrogen bonds with O atoms of the phosphoric groups while the third is connected to an O atom of the carboxylic group to form an intermolecular bond along the *b* axis. No intermolecular bonds exist along the *c* axis between the glycine groups.

Glycine cyclo-triphosphate. Table 3 reports the final atomic coordinates. The atomic arrangement is here built up by the stacking of $C_2H_6NO_2^+$ groups and of non-acidic phosphate groups: $P_3O_9^{3-}$ (Fig. 3). In most of the previously described interaction compounds between phosphoric acid and amines or amino acids the phosphoric anion is an acidic one, such as $H_2PO_4^-$ in glycine monophosphate (present work) and in two L-histidine phosphates, L-His.$2H_3PO_4$ (Blessing, 1986) and L-His.H_3PO_4 (Averbuch-Pouchot & Durif, 1988), and HPO_4^{2-} in ethylenediamine monophosphate (Averbuch-Pouchot & Durif, 1987).

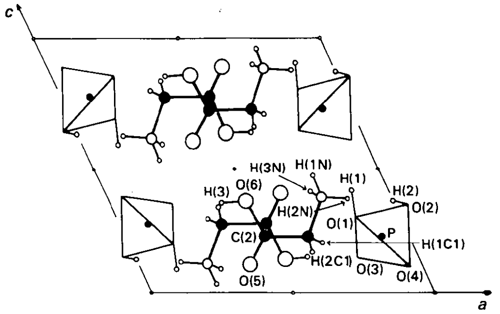

Fig. 1. Projection along the *b* axis of the atomic arrangement of glycine monophosphate.

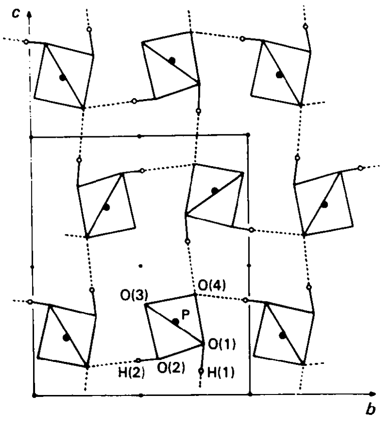

Fig. 2. Projection along the *a* axis of the two-dimensional network of the phosphoric groups.

Table 3. *Final atomic coordinates for glycine cyclo-triphosphate*

	x	y	z	B_{iso}/B_{eq}(Å^2)
P(1)	0·62041 (5)	0·40452 (4)	0·29324 (5)	2·17 (1)
P(2)	0·84764 (5)	0·39627 (4)	0·25874 (6)	2·53 (1)
P(3)	0·73593 (4)	0·57085 (4)	0·24603 (5)	1·663 (9)
O(*E*11)	0·6175 (2)	0·3597 (1)	0·4219 (2)	3·04 (3)
O(*E*12)	0·5200 (1)	0·4035 (1)	0·1884 (2)	2·97 (3)
O(*L*12)	0·7198 (2)	0·3632 (1)	0·2275 (2)	2·90 (3)
O(*E*21)	0·9043 (2)	0·3554 (1)	0·1570 (2)	3·65 (4)
O(*E*22)	0·8926 (2)	0·3860 (2)	0·3987 (2)	6·02 (6)
O(*L*23)	0·8331 (1)	0·5031 (1)	0·2228 (2)	3·16 (4)
O(*E*31)	0·6728 (1)	0·5971 (1)	0·1158 (2)	2·82 (3)
O(*E*32)	0·7848 (1)	0·6436 (1)	0·3412 (1)	2·16 (3)
O(*L*13)	0·6626 (1)	0·5080 (1)	0·3247 (1)	2·03 (3)
O(11)	0·6767 (2)	0·6936 (1)	0·6091 (2)	3·42 (4)
O(21)	0·1828 (2)	0·4027 (1)	0·3988 (2)	3·66 (4)
C(11)	0·2527 (2)	0·1422 (2)	0·8387 (2)	2·28 (4)
C(21)	0·2322 (2)	0·3784 (2)	0·1922 (2)	2·58 (5)
N(1)	0·3074 (2)	0·3235 (1)	0·1269 (2)	2·33 (4)
O(12)	0·4892 (2)	0·6943 (1)	0·3197 (2)	3·21 (4)
O(22)	0·6374 (2)	0·0862 (1)	0·1673 (2)	4·03 (4)
C(12)	0·4242 (2)	0·8620 (2)	0·7696 (2)	2·30 (4)
C(22)	0·5978 (2)	0·3818 (2)	0·8771 (2)	2·79 (5)
N(2)	0·5337 (2)	0·1821 (1)	0·4450 (2)	2·29 (4)
O(13)	0·9664 (2)	0·8196 (1)	0·5972 (2)	3·73 (4)
O(23)	0·1088 (2)	0·5876 (2)	0·0832 (2)	4·89 (5)
C(13)	0·9573 (2)	0·1333 (2)	0·3527 (2)	2·78 (5)
C(23)	0·0752 (2)	0·8822 (2)	0·7939 (2)	3·01 (5)
N(3)	−0·0138 (2)	0·3205 (1)	0·6311 (2)	2·35 (4)
H(1)	0·197 (3)	0·109 (3)	−0·015 (3)	4·1 (9)*
H(121)	0·758 (2)	0·560 (2)	0·824 (3)	2·1 (7)*
H(221)	0·158 (2)	0·135 (2)	0·655 (3)	1·2 (6)*
H(1N1)	0·700 (2)	0·663 (2)	0·957 (3)	1·7 (6)*
H(2N1)	0·293 (3)	0·240 (2)	0·633 (3)	2·5 (7)*
H(3N1)	0·622 (2)	0·665 (2)	0·839 (3)	1·0 (6)*
H(2)	0·628 (3)	0·107 (3)	0·086 (4)	5 (1)*
H(122)	0·428 (2)	0·943 (2)	0·609 (3)	1·9 (7)*
H(222)	0·669 (2)	0·130 (2)	0·408 (3)	1·1 (6)*
H(1N2)	0·536 (2)	0·165 (2)	0·529 (3)	1·0 (6)*
H(2N2)	0·538 (2)	0·676 (2)	0·089 (3)	2·0 (7)*
H(3N2)	0·448 (3)	0·757 (2)	0·564 (3)	2·8 (8)*
H(3)	0·097 (3)	0·594 (3)	0·006 (4)	5 (1)*
H(123)	0·062 (2)	0·555 (2)	0·314 (3)	2·4 (7)*
H(223)	0·153 (2)	0·864 (2)	0·828 (3)	1·5 (6)*
H(1N3)	0·063 (2)	0·170 (2)	0·155 (3)	1·2 (6)*
H(2N3)	0·035 (3)	0·835 (2)	0·957 (3)	2·4 (7)*
H(3N3)	0·968 (3)	0·256 (2)	0·642 (3)	2·9 (7)*

Starred atoms have been refined isotropically.

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$.

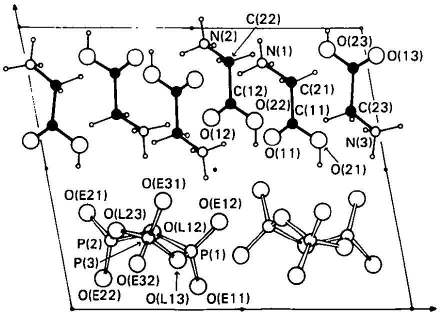

Fig. 3. Projection along the *b* axis of the atomic arrangement of glycine *cyclo*-triphosphate. For clarity the phosphoric anions have been omitted in the upper part of the unit cell and glycine groups omitted in the lower part.

The only example of a non-acidic phosphate anion seems to be the $P_2O_7^{4-}$ group observed in guanidinium pyrophosphate monohydrate (Adams & Ramdas, 1977).

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *in glycine cyclo-triphosphate*

P(1)O_1 tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*13)
O(*E*11)	1·474 (2)	2·548 (2)	2·535 (3)	2·476 (2)
O(*E*12)	119·5 (1)	1·475 (2)	2·471 (3)	2·530 (2)
O(*L*12)	110·6 (1)	106·5 (1)	1·608 (2)	2·481 (2)
O(*L*13)	107·1 (1)	110·5 (1)	101·2 (1)	1·602 (2)

P(2)O_1 tetrahedron

P(2)	O(*L*12)	O(*E*21)	O(*E*22)	O(*L*23)
O(*L*12)	1·610 (2)	2·491 (3)	2·509 (3)	2·465 (2)
O(*E*21)	107·6 (1)	1·476 (2)	2·542 (3)	2·455 (3)
O(*E*22)	110·3 (1)	121·0 (1)	1·445 (2)	2·486 (3)
O(*L*23)	100·5 (1)	106·0 (1)	109·5 (1)	1·597 (2)

P(3)O_1 tetrahedron

P(3)	O(*L*23)	O(*E*31)	O(*E*32)	O(*L*13)
O(*L*23)	1·593 (2)	2·474 (2)	2·498 (2)	2·495 (2)
O(*E*31)	108·0 (1)	1·464 (2)	2·550 (2)	2·521 (2)
O(*E*32)	108·3 (1)	119·6 (1)	1·487 (2)	2·459 (2)
O(*L*13)	103·0 (1)	110·9 (1)	105·8 (1)	1·596 (2)

P(1)–O(*L*12)–P(2)	125·8 (1)	P(1)–P(2)	2·8648 (9)
P(2)–O(*L*23)–P(3)	128·3 (1)	P(1)–P(3)	2·8828 (8)
P(3)–O(*L*13)–P(1)	128·7 (1)	P(2)–P(3)	2·8715 (8)

P(2)–P(1)–P(3)	59·95 (2)
P(1)–P(2)–P(3)	60·34 (2)
P(1)–P(3)–P(2)	59·72 (2)

Glycine groups

Group I

C(11)–O(11)	1·192 (3)	O(11)–C(11)–O(21)	125·5 (2)
C(11)–O(21)	1·312 (3)	O(11)–C(11)–C(21)	123·1 (2)
C(11)–C(21)	1·504 (3)	O(21)–C(11)–C(21)	111·3 (2)
C(21)–N(1)	1·466 (3)	C(11) C(21)–N(1)	109·9 (2)

Group II

C(12)–O(12)	1·190 (3)	O(12)–C(12)–O(22)	125·4 (2)
C(12)–O(22)	1·314 (3)	O(12)–C(12)–C(22)	123·1 (2)
C(12)–C(22)	1·503 (3)	O(22)–C(12)–C(22)	111·5 (2)
C(22)–N(2)	1·469 (3)	C(12)–C(22)–N(2)	109·7 (2)

Group III

C(13)–O(13)	1·195 (3)	O(13)–C(13)–O(23)	125·4 (2)
C(13)–O(23)	1·310 (4)	O(13)–C(13)–C(23)	124·1 (2)
C(13) C(23)	1·497 (3)	O(23) C(13) C(23)	110·5 (2)
C(23)–N(3)	1·471 (3)	C(13)–C(23)–N(3)	111·3 (2)

Hydrogen bonds

O(N)–H···O	O(N)–H	H···O	O(N)–O	O(N)–H···O
O(21)–H(1)···O(*E*32)	0·89 (3)	1·82 (3)	2·702 (2)	174 (3)
O(22)–H(2)···O(*E*11)	0·87 (4)	1·73 (4)	2·599 (2)	175 (4)
O(23)–H(3)···O(*E*21)	0·78 (4)	1·82 (4)	2·570 (3)	160 (4)
N(1)–H(1N1)···O(*E*31)	0·87 (3)	1·95 (3)	2·788 (3)	157 (3)
N(1)–H(2N1)···O(*E*32)	0·94 (3)	1·98 (3)	2·888 (3)	161 (3)
N(1)–H(3N1)···O(*E*12)	0·87 (3)	1·98 (3)	2·812 (3)	156 (2)
N(2)–H(1N2)···O(*E*12)	0·89 (3)	1·95 (3)	2·815 (3)	163 (2)
N(2)–H(2N2)···O(*E*31)	0·88 (3)	1·98 (3)	2·776 (3)	148 (3)
N(2)–H(3N2)···O(*E*11)	0·92 (3)	1·90 (3)	2·802 (3)	169 (3)
N(3)–H(1N3)···O(*E*32)	0·94 (3)	1·89 (3)	2·810 (2)	166 (2)
N(3)–H(2N3)···O(*E*22)	0·92 (3)	1·74 (3)	2·622 (3)	160 (3)
N(3)–H(3N3)···O(*E*21)	0·97 (3)	1·82 (3)	2·774 (3)	168 (3)

Three crystallographically independent glycine groups exist in the atomic arrangement of the P_3O_9 ring anion. Main interatomic distances and bond angles for these three groups are reported in Table 4. For all of them the carboxylic group is not deprotonated and so their configuration is: HOOC–CH_2–NH_3^+. These molecules are almost planar, parallel to the *ac* plane, at

$y \sim \pm 0{\cdot}15$ and $\pm 0{\cdot}35$. It is to be noticed that the planes of the inorganic groups are perpendicular to those of the organic molecules.

Geometrical details of the hydrogen-bond scheme are reported in Table 4. Two points should be noted: there is no intermolecular hydrogen bond between glycine molecules; and the bonding oxygen atoms (*OL*) of the P_3O_9 ring are not involved in hydrogen bonds, while all the external ones are. This fact is to be compared with an almost systematic observation made in inorganic condensed phosphate chemistry, where *OL* bonding oxygen atoms do not take part in cation coordination polyhedra. Each glycine molecule is connected by hydrogen bonds to four different phosphoric groups.

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Structure of 5-Nitro-2-{[(*S*)-1-phenylethyl]amino}pyridine

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Abstract. $C_{13}H_{13}N_3O_2$, $M_r = 243{\cdot}26$, monoclinic, $P2_1$, $a = 17{\cdot}945\,(4)$, $b = 6{\cdot}372\,(1)$, $c = 5{\cdot}401\,(2)$ Å, $\beta = 94{\cdot}70\,(2)°$, $V = 615{\cdot}5\,(3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}31$, $D_x = 1{\cdot}313$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}854$ cm^{-1}, $F(000) = 256$, $T = 295$ K, $R = 0{\cdot}065$ for 770 unique observed reflections. The twist angle of the nitro group out of the pyridine ring and that of the amino group are 2·8 and −8·5°, respectively. The crystal packing is dominated by hydrogen bonds which link the molecules into infinite chains. The title compound proved to have a suitable molecular and crystal structure for nonlinear optical materials.

Introduction. In recent years, conjugated organic molecular crystals have attracted considerable attention as preferable materials in nonlinear optics, such as second harmonic generation (SHG) and optical bistability, owing to their large optical nonlinearities. Among a number of organic compounds examined, the title compound was found to have very high SHG efficiency in the powder form and to have an absorption cut-off in the relatively short-wavelength region (Twieg, Azema, Jain & Cheng, 1982). These properties make this compound highly attractive for application to frequency doubling of the light produced by semiconductor lasers. The present X-ray analysis was undertaken to elucidate the relation between the crystal structure and its large optical nonlinearity.

Experimental. The title compound was synthesized by the method reported previously (Bettoni, Catsiotis, Perrone & Tortorella, 1977). Yellow crystal, thin rectangular plate, recrystallized by slow evaporation from a mixture of hexane–methylene chloride, with dimensions 0·6 × 0·4 × 0·2 mm. Density measured by flotation in a $ZnCl_2$ solution. Rigaku AFC-5 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$. Cell dimensions determined with 20 reflections ($20 < 2\theta < 30°$) by least-squares method. Systematic absences $0k0$ for k odd. Intensity data $2 < 2\theta < 30°$, ω–2θ scan, $30 < 2\theta < 60°$, θ–2θ scan, scan speed 4° min^{-1}. Three standard reflections (410, 112, 040) monitored every 100 reflections showed only random variations within 3% in intensity. 1643 unique reflections ($h = -22$ to 22, $k = 0$ to 8, $l = 0$ to 6) measured, 770 reflections with $|F_o| > 3\sigma(|F_o|)$ observed. No correction for absorption. Structure solved by direct methods with *MULTAN* (Main, Woolfson & Germain, 1971). 12 non-H atoms were obtained from the initial E map and the remaining non-H atoms were located from sub-

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