1073 independent reflections
1627 observed reflections
$[I>3.0\sigma(I)]$
$R_{\text{int}} = 0.01$

2 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.043$
$wR = 0.045$
$S = 0.536$
1073 reflections
121 parameters
All H-atom parameters refined
$w = 1$

$(\Delta/\sigma)_{\text{max}} = 0.04$
$\Delta\rho_{\text{max}} = 0.498$ e Å^{-3}
$\Delta\rho_{\text{min}} = 0.359$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for the phosphite derivative*

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

	x	y	z	$B_{\text{eq}}/B_{\text{iso}}$
P	0.44767 (9)	0.27094 (8)	0.1702 (1)	2.97 (1)
O1	0.3434 (3)	0.2567 (2)	0.3392 (3)	3.97 (5)
O2	0.3703 (3)	0.2499 (3)	−0.0143 (3)	4.19 (6)
O3	0.3925 (3)	0.7044 (3)	0.3005 (4)	4.57 (6)
C1	0.0039 (5)	0.4381 (3)	0.3689 (6)	3.81 (8)
C2	0.1759 (5)	0.9690 (4)	0.1386 (7)	5.0 (1)
C3	0.1038 (7)	0.4893 (4)	0.2139 (9)	6.6 (1)
N	0.0163 (3)	0.3208 (2)	0.3515 (4)	2.94 (5)
HO3	0.307 (6)	0.715 (4)	0.391 (6)	5 (1)

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *for the phosphite derivative*

P	O1	O2	O3	H
O1	1.490 (2)	2.546 (3)	2.459 (3)	2.35 (5)
O2	117.5(1)	1.489 (3)	2.529 (3)	2.42 (5)
O3	107.3 (1)	111.9(2)	1.563 (3)	2.19 (5)
H	109 (2)	114 (2)	95(2)	1.40(5)

P—O3—HO3	116 (3)		
C1—N	1.495 (5)	N—C1—C2	108.6 (3)
C1—C2	1.514 (6)	N—C1—C3	109.1 (3)
C1—C3	1.522 (7)	C2—C1—C3	112.2 (4)

O(N)—H···O	O(N)—H	H···O	O(N)···O	O(N)—H···O
O3—HO3···O2	0.96 (5)	1.65 (5)	2.581 (3)	161 (4)
N—H1N···O2	0.87 (4)	1.97 (4)	2.839 (4)	175 (4)
N—H2N···O1	0.87 (4)	1.93 (4)	2.781 (3)	163 (4)
N—H3N···O1	0.82 (4)	2.02 (4)	2.803 (3)	158 (4)

The monophosphate was prepared by slow evaporation at room temperature of a diluted aqueous solution containing H_3PO_4 and isopropylamine with the required stoichiometry. Several dissolutions followed by carefully controlled recrystallizations are often necessary to obtain good quality crystals. A similar process was used for the synthesis of the phosphite derivative.

Data collection: Nonius CAD-4 software. Cell refinement: Nonius CAD-4 software. Data reduction: *SDP* (Enraf-Nonius, 1977). Program used to solve structures: *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Program used to refine structure: *SDP*. Molecular graphics: *STRUPLO* (Fischer, 1985). Software used to prepare material for publication: *SDP*.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55751 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1023]

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Structures of Glycinium Phosphite and Glycylglycinium Phosphite

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Abstract

The structure of glycinium phosphite consists of a layer arrangement of planes containing infinite $[H(HPO_3)]_n^{n-}$ chains alternating with planes built by the organic anions, both layers developing parallel to the *bc* plane. Strong hydrogen bonds corresponding to O—O distances of 2.482 and 2.518 Å are responsible for the cohesion between the HPO_3 tetrahedra along this 'macroanion'. The same type of infinite $[H(HPO_3)]_n^{n-}$ chain is observed in the glycylglycinium derivative which differs from the first compound in that the organic entities are connected by hydrogen bonds. A comparison between these two atomic arrangements and the corresponding monophosphates is given.

Comment

The atomic arrangement in glycine phosphite has a typical layer organization. As shown in Fig. 1, planes built by the phosphoric entities alternate with planes containing the organic groups, the two kinds of layer being parallel to the *bc* plane and separated by a distance of $a/2$. Inside the phosphoric layers, the $\mathrm{H(PO_3H)^-}$ groups assemble so as to build infinite $[\mathrm{H(HPO_3)}]_n^{n-}$ chains spreading along the **c** direction. Inside such a chain, the P—P distances are 4.917 (1) and 4.855 (1) Å. The acidic H atom of the $\mathrm{H(PO_3H)^-}$ group is statistically distributed in two positions located close to the inversion centres adjacent to this group, along the **c** direction. This result of the structure determination is clearly shown by examination of the three P—O distances inside the $\mathrm{PO_3H}$ tetrahedron (1.508, 1.520 and 1.531 Å). The first (and shortest) corresponds to the P—O bond but the latter two (which are almost identical) are too short to be attributed to a normal P—OH bond (generally observed to be around 1.55 Å in this type of anionic group).

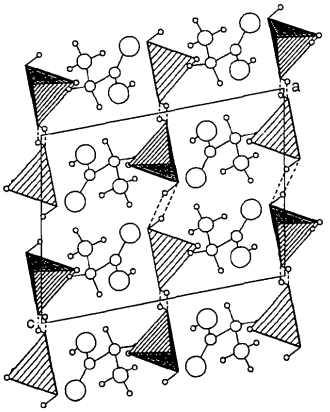

Fig. 1. Projection of glycinium phosphite along the *b* axis. The open circles denote (in decreasing order of size) O, N, C and H atoms. In the polyhedral representation of the $\mathrm{PO_3H}$ tetrahedron, the corner corresponding to the H atom is completed by a circle.

In the organic layers, no hydrogen bond interconnects the organic groups. All the connections are established through the O atoms of the $\mathrm{PO_3H}$ groups. For instance, the $\mathrm{NH_3}$ group of the glycinium entity is connected to three different $\mathrm{PO_3H}$ anions belonging to three different $[\mathrm{H(HPO_3)}]_n^{n-}$ chains. The last hydrogen bond connects the H atom H(O5) of the acidic radical of the glycinium group to the O atom O(1) of the $\mathrm{PO_3H}$ tetrahedron. Table 2 reports the main interatomic distances and bond angles in this arrangement.

The main difference between this compound and the corresponding monophosphate, previously reported by Averbuch-Pouchot, Durif & Guitel (1988), concerns the organization of the phosphoric network. In the title compound, the $\mathrm{H(PO_3H)^-}$ groups build a one-dimensional 'macroanion', while in the monosphosphate derivative the phosphoric groups, $\mathrm{H_2PO_4}$, assemble so as to build infinite two-dimensional layers. Another difference is observed within the layers of the organic groups. In the monophosphate, one hydrogen bond interconnects the glycinium groups to establish chains.

The organization of the anionic components in the glycylglycinium compound is quite similar to that observed in the first salt. The $\mathrm{H(PO_3H)^-}$ groups assemble so as to build infinite $[\mathrm{H(HPO_3)}]_n^{n-}$ chains parallel to the **b** direction (Fig. 2) but, unlike in the glycine salt, the hydrogen bonds connecting the $\mathrm{H(PO_3H)^-}$ groups of the chain do not involve disordered H atoms so that, in this case, the P—OH distance measured inside the $\mathrm{(PO_3H)^-}$ tetrahedron (1.566 Å) is significantly different from the other two P—O distances (1.493 and 1.505 Å).

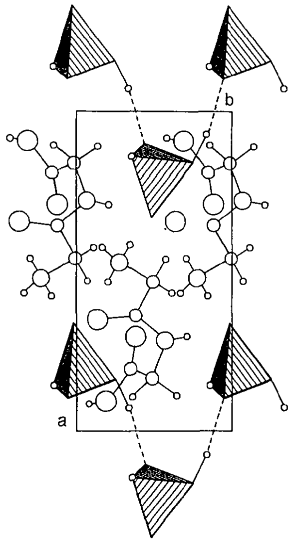

Fig. 2. Projection of glycylglycinium phosphite along the *c* axis. The open circles denote (in decreasing order of size) O, N, C and H atoms. In the polyhedral representation of the $\mathrm{PO_3H}$ tetrahedron, the corner corresponding to the H atom is completed by a circle.

The differences between the organization of this and the glycine salt appear on examination of the organic components of the arrangement. Here the organic cations are interconnected by hydrogen bonds. One of them is established between one H atom of the $\mathrm{NH_3}$ radical and the carboxyl O atom O(5) of the adjacent organic group, the second connects one H atom of the NH radical of the peptidic part to the carbonyl O atom O(4). These two bonds connect the organic entities along the **b** direction. The last two H atoms of the $\mathrm{NH_3}$ radical are bonded to two $\mathrm{HPO_3}$ tetrahedra belonging to two different phosphoric chains and connect them along the **a** direction. The last hydrogen bond involving the H atom of the hydroxyl group of the organic cation establishes a connection of this group with a third $\mathrm{HPO_3}$ tetrahedron.

Some similarities can be observed between the present atomic arrangement and the corresponding monophosphate previously investigated by Freeman, Hearn & Bugg (1972). In both cases, the phosphoric groups assemble so as to build chains through hydrogen bonds; these are slightly shorter in the case of the phosphate (2.571 against 2.649 Å for the title compound). This linear linkage observed for the diacidic H_2PO_4 anion of the monophosphate is explained by the fact that the second H atom of this group is involved in a hydrogen bond with a water molecule. All other types of hydrogen bond are similar in the two compounds.

Experimental

Glycinium phosphite

Crystal data

$C_2H_6NO_2^+.H_2PO_3^-$
$M_r = 157.062$
Monoclinic
$P2_1/a$
$a = 9.792$ (1) Å
$b = 8.487$ (1) Å
$c = 7.411$ (2) Å
$\beta = 100.43$ (2)°
$V = 607.3$ (3) Å^3
$Z = 4$
$D_x = 1.722$ Mg m^{-3}

Ag $K\alpha$ radiation
$\lambda = 0.5608$ Å
Cell parameters from 22 reflections
$\theta = 10\text{-}12°$
$\mu = 0.223$ mm^{-1}
$T = 295$ K
Short stout prisms
0.51 × 0.40 × 0.32 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
3959 measured reflections
2154 independent reflections
2093 observed reflections [$I > 4\sigma(I)$]
$R_{int} = 0.01$
$\theta_{max} = 30°$

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 15$
$l = -13 \rightarrow 12$
2 orientation standard reflections
monitored every 400 reflections
2 intensity standard reflections
frequency: 60 min
intensity variations: none

Refinement

Refinement on F
Final $R = 0.027$
$wR = 0.027$
$S = 0.317$
2093 reflections
611 parameters
Unit weights applied
$(\Delta/\sigma)_{max} = 0.16$ (B of H)

$\Delta\rho_{max} = 0.285$ e Å^{-3}
$\Delta\rho_{min} = -0.255$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for glycinium phosphite*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
P	0.50864 (3)	0.31263 (3)	0.75481 (4)	1.550 (3)
O(1)	0.46665 (8)	0.14342 (8)	0.7155 (1)	1.93 (1)
O(2)	0.4847 (1)	0.3623 (1)	0.9436 (1)	3.48 (2)
O(3)	0.43642 (9)	0.4248 (1)	0.6056 (1)	2.76 (1)
N	0.17719 (9)	0.5731 (1)	0.6469 (1)	1.76 (1)
C(1)	0.2005 (1)	0.6984 (1)	0.7863 (1)	2.01 (1)
C(2)	0.30339 (9)	0.8169 (1)	0.7404 (1)	1.60 (1)
O(4)	0.36358 (8)	0.8011 (1)	0.6130 (1)	2.34 (1)
O(5)	0.3186 (9)	0.9374 (1)	0.8543 (1)	2.53 (1)
H	0.643 (2)	0.321 (2)	0.752 (2)	1.7 (4)*
H(O2)†	0.495 (5)	0.454 (5)	0.952 (6)	4 (1)*
H(O3)†	0.477 (4)	0.460 (5)	0.530 (6)	3 (1)*

* B_{iso}.
†Occupancy = 0.5.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of glycinium phosphite*

$C_2H_6NO_2$ group

N—C(1)	1.472 (1)	N—C(1)—C(2)	110.42 (9)
C(1)—C(2)	1.505 (1)	C(1)—C(2)—O(4)	122.98 (9)
C(2)—O(4)	1.207 (1)	C(1)—C(2)—O(5)	112.18 (9)
C(2)—O(5)	1.318 (1)	O(4)—C(2)—O(5)	124.84 (9)

PO_3H tetrahedron

P	O(1)	O(2)	O(3)	H
O(1)	1.508 (1)	2.496 (1)	2.523 (1)	2.27 (2)
O(2)	111.10 (5)	1.520 (1)	2.520 (1)	2.31 (2)
O(3)	112.24 (4)	111.36 (5)	1.531 (1)	2.29 (2)
H	106.5 (8)	108.7 (7)	106.7 (8)	1.32 (2)

P—O(2)—H(O2)	108 (4)	P—O(3)—H(O3)	121 (3)

Hydrogen bonds

O(N)—H···O	O(N)—H	H···O	O(N)···O	O(N)—H···O
O(2)—H(O2)···O(2)	0.78 (5)	1.74 (5)	2.482 (1)	158 (5)
O(3)—H(O3)···O(3)	0.80 (5)	1.73 (5)	2.518 (1)	167 (5)
O(5)—H(O5)···O(1)	0.86 (2)	1.75 (2)	2.598 (1)	171 (2)
N—H(1N)···O(1)	0.88 (2)	2.00 (2)	2.861 (1)	164 (2)
N—H(2N)···O(1)	0.91 (2)	1.97 (2)	2.875 (1)	172 (2)
N—H(3N)···O(3)	0.87 (2)	2.03 (2)	2.899 (1)	177 (2)

Glycylglycinium phosphite

Crystal data

$C_4H_9N_2O_3^+.H_2PO_3^-$
$M_r = 214.112$
Monoclinic
$P2_1$
$a = 10.003$ (4) Å
$b = 4.924$ (1) Å
$c = 9.343$ (2) Å
$\beta = 90.88$ (2)°
$V = 460.1$ (4) Å^3
$Z = 2$
$D_x = 1.545$ Mg m^{-3}

Ag $K\alpha$ radiation
$\lambda = 0.5608$ Å
Cell parameters from 22 reflections
$\theta = 10\text{-}11°$
$\mu = 0.169$ mm^{-1}
$T = 295$ K
Long prism
0.52 × 0.36 × 0.28 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
3026 measured reflections
1942 independent reflections
1924 observed reflections [$I > 4\sigma(I)$]
$\theta_{max} = 30°$
$R_{int} = 0.01$

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 17$
$l = -15 \rightarrow 15$
2 orientation standard reflections
monitored every 400 reflections
2 intensity standard reflections
frequency: 60 min
intensity variations: none

Refinement

Refinement on F
Final $R = 0.028$

$\Delta\rho_{max} = 0.387$ e Å^{-3}
$\Delta\rho_{min} = -0.170$ e Å^{-3}

wR = 0.030
S = 0.231
1924 reflections
161 parameters
Unit weights applied
$(\Delta/\sigma)_{\max}$ = 0.15 [*B* of H(2C1)]

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for glycylglycinium phosphite*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$
P	0.81589 (3)	0.0	0.4513 (4)	2.151 (5)
O(1)	0.6675 (1)	−0.0179 (4)	0.4636 (1)	2.97 (2)
O(2)	0.8971 (1)	−0.0580 (3)	0.5847 (1)	2.90 (2)
O(3)	0.8501 (1)	0.2869 (3)	0.3895 (2)	4.14 (3)
N(1)	0.5247 (1)	0.7745 (4)	0.6866 (2)	2.65 (2)
C(1)	0.4634 (2)	0.9916 (5)	0.7714 (2)	3.03 (3)
C(2)	0.3577 (2)	0.8801 (4)	0.8681 (2)	2.37 (3)
O(4)	0.3452 (1)	0.6349 (3)	0.8894 (2)	3.21 (2)
N(2)	0.2803 (2)	1.0666 (3)	0.9278 (2)	2.98 (3)
C(3)	0.1627 (2)	0.9868 (6)	1.0038 (2)	3.57 (3)
C(4)	0.1914 (2)	0.8472 (4)	1.1443 (2)	2.58 (3)
O(5)	0.2921 (1)	0.8792 (3)	1.2150 (2)	3.19 (2)
O(6)	0.0938 (1)	0.6886 (5)	1.1804 (2)	4.96 (3)
H	0.858 (2)	−0.145 (5)	0.352 (2)	1.2 (4)*
H(O3)	0.927 (3)	0.334 (6)	0.397 (3)	2.8 (6)*

* $B_{\rm iso}$.

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of glycylglycinium phosphite*

$C_4H_9N_2O_3$ group

N(1)—C(1)	1.470 (3)	N(1)—C(1)—C(2)	111.1 (2)
C(1)—C(2)	1.506 (2)	C(1)—C(2)—N(2)	114.8 (2)
C(2)—O(4)	1.230 (2)	C(1)—C(2)—O(4)	121.9 (2)
C(2)—N(2)	1.329 (2)	O(4)—C(2)—N(2)	123.3 (2)
N(2)—C(3)	1.438 (2)	C(2)—N(2)—C(3)	120.3 (2)
C(3)—C(4)	1.506 (3)	N(2)—C(3)—C(4)	114.1 (1)
C(4)—O(5)	1.206 (2)	C(3)—C(4)—O(5)	124.3 (2)
C(4)—O(6)	1.299 (2)	C(3)—C(4)—O(6)	111.5 (1)
		O(5)—C(4)—O(6)	124.1 (2)

PO_3H tetrahedron

P	O(1)	O(2)	O(3)	H
O(1)	1.493 (1)	2.553 (1)	2.472 (2)	2.27 (2)
O(2)	116.73 (7)	1.505 (1)	2.531 (2)	2.24 (2)
O(3)	107.74 (9)	111.01 (8)	1.566 (2)	2.15 (3)
H	112 (1)	109 (1)	99 (1)	1.25 (2)

P—O(3)—H(O3) 116 (2)

Hydrogen bonds

O(N)—H···O	O(N)—H	H···O	O(N)···O	O(N)—H···O
O(3)—H(O3)···O(2)	0.81 (3)	1.84 (3)	2.649 (2)	180 (3)
O(6)—H(O6)···O(2)	0.80 (3)	1.73 (3)	2.508 (2)	166 (3)
N(1)—H(1N1)···O(1)	0.92 (2)	1.83 (2)	2.742 (2)	172 (2)
N(1)—H(2N1)···O(5)	0.86 (3)	2.00 (3)	2.818 (2)	157 (2)
N(1)—H(3N1)···O(1)	0.80 (2)	1.97 (2)	2.766 (2)	171 (3)
N(2)—H(N2)···O(4)	0.72 (3)	2.18 (3)	2.896 (2)	176 (2)

The two title compounds were prepared by the slow evaporation (over a few days) at room temperature of diluted aqueous solutions containing $H_2(PO_3H)$ and glycine or glycylglycine in stoichiometric ratios.

The H atoms were found by difference Fourier techniques and refined with $B_{\rm iso}$. The structure was determined using *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined with *SDP* (Enraf-Nonius, 1977). The figures were drawn using *STRUPLO* (Fischer, 1985).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and main interatomic bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55726 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1020]

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Acta Cryst. (1993). **C49**, 818–820

X-ray Structure of a New Pyrethroid, RU 52259

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Abstract

The X-ray structure of this intermediate compound, *tert*-butyl α-(*tert*-butylsulfonyl)-β-(methoxysulfinyl)-3,3-dimethyl-2-[(3-phenoxybenzyl)oxycarbonyl]-cyclopropanepropionate, shows the configuration of the asymmetric atoms at sites C1, C2 and S1 (C^α,C^β and β-S) and allows the mechanism of its formation to be established. The bond distances in the molecule are in the expected range.

Comment

Biological activity in pyrethroids is related to molecular structure and strongly dependent on the stereochemistry at the asymmetric centre. For example, the *Z* isomer of norpyrethrates is generally far more active than the *E* isomer (Tessier, Teche & Demoute,.1982).

0108-2701/93/040818-03$06.00