C4	1.1210 (4)	0.4289 (5)	0.3344 (2)	0.062 (1)
C5	0.9089 (4)	0.4475 (5)	0.2222 (2)	0.057 (1)
C6	0.7429 (5)	0.4112 (5)	0.1866 (2)	0.057 (1)
C7	0.6012 (4)	0.3270 (5)	0.2237 (2)	0.0479 (8)
C8	0.6305 (4)	0.2868 (4)	0.2972 (2)	0.0435 (9)
C9	0.8016 (4)	0.3206 (4)	0.3365 (2)	0.0409 (8)
C10	0.9453 (4)	0.4013 (5)	0.2972 (2)	0.0483 (9)
C11	1.0600 (6)	0.2471 (6)	0.5263 (2)	0.074 (1)
C12	0.4233 (5)	0.2796 (6)	0.1815 (2)	0.064 (1)

Table 2. *Selected geometric parameters (Å, °)*

Br—C1	1.911 (3)	C5—C6	1.359 (5)
C1—C2	1.386 (4)	C5—C10	1.409 (5)
C1—C9	1.405 (5)	C6—C7	1.405 (5)
C2—C3	1.409 (5)	C7—C8	1.365 (5)
C2—C11	1.505 (6)	C7—C12	1.504 (5)
C3—C4	1.341 (6)	C8—C9	1.417 (4)
C4—C10	1.419 (4)	C9—C10	1.423 (4)
Br—C1—C2	117.9 (3)	C6—C7—C8	118.9 (3)
Br—C1—C9	118.6 (2)	C6—C7—C12	119.5 (3)
C2—C1—C9	123.5 (3)	C8—C7—C12	121.6 (3)
C1—C2—C3	116.2 (3)	C7—C8—C9	122.4 (3)
C1—C2—C11	124.0 (3)	C1—C9—C8	124.6 (3)
C3—C2—C11	119.8 (3)	C1—C9—C10	117.7 (3)
C2—C3—C4	123.3 (3)	C8—C9—C10	117.7 (3)
C3—C4—C10	120.5 (3)	C4—C10—C5	122.5 (3)
C6—C5—C10	121.4 (3)	C4—C10—C9	118.8 (3)
C5—C6—C7	120.8 (3)	C5—C10—C9	118.7 (3)

The structure was solved by Patterson and Fourier methods. Initially, data were collected using a weakly scattering crystal and Cu $K\alpha$ radiation. The structure was solved using these data, but the refinement did not yield satisfactory results. A crystal was found which scattered strongly and Mo $K\alpha$ radiation was chosen to collect data from this crystal to take advantage of the lower absorption and higher resolution available. The Mo $K\alpha$ data collection crystal was sealed in a capillary to prevent sublimation. Ring H atoms were refined isotropically, while methyl H atoms were placed in calculated positions (C—H 0.95 Å), guided by difference maps. $R = 0.038$ for 1499 data having $I > 3\sigma(I)$.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF IN*.

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1195). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(Phosphonomethyl)acrylic Acid Hemihydrate and Ammonium 2-(Phosphonomethyl)acrylate: Analogues of Phosphoenolpyruvate (PEP)

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(*Received 16 March 1995; accepted 19 July 1995*)

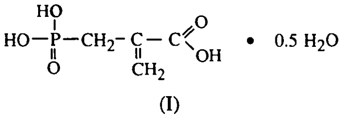
Abstract

The structures of hydrated 2-(phosphonomethyl)acrylic acid, $C_4H_7O_5P.0.5H_2O$, (I), and its ammonium salt, $NH_4^+.C_4H_6O_5P^-$, (II), are described. In (I), the two crystallographically independent 2-(phosphonomethyl)-acrylic acid residues differ slightly in the orientation of the phosphonic group relative to the rest of the molecule. In both compounds, the phosphonic group projects out the plane of the 2-methyleneacrylate system. The carboxylic hydroxyl is *trans* planar to the terminal $=CH_2$ group in (II) but is *syn* planar in (I). In both crystals, all OH and NH groups are involved in intermolecular hydrogen bonds.

Comment

Numerous phosphoenolpyruvate (PEP) analogues are used for the study of enzyme-catalyzed reactions (Stubbe & Kenyon, 1972; Wirsching & O'Leary, 1988; Sikkema & O'Leary, 1988). 2-(Phosphonomethyl)-acrylic acid, a phosphonate analogue of PEP in which the bridging O atom of the phosphate ester has been substituted by a methylene group, has served as inhibitor and potential substrate in the pyruvate kinase and enolase reactions (Stubbe & Kenyon, 1972). This paper about a phosphonate analogue of PEP provides information for a detailed structural comparison which could be useful in studies of the interaction of PEP with the above-mentioned enzymes and of the mechanisms of these reactions. It follows our investigation of PEP acid and its salts (Weichsel & Lis, 1994). There is an earlier report on another phosphonate analogue of PEP, namely tris(cyclohexylammonium) phosphonopyruvate dihydrate (Schwalbe & Freeman, 1990).

In 2-(phosphonomethylacrylic)acid hemihydrate, (I), the asymmetric unit comprises two crystallographically independent acid molecules (*A* and *B*). The structure of the acid molecules and the atomic numbering schemes are shown in Fig. 1.



$$\mathrm{HO-\underset{\displaystyle \overset{\|}{O}}{\overset{\displaystyle \overset{HO}{|}}{P}}-CH_2-\underset{\displaystyle \overset{\|}{CH_2}}{C}-C\overset{\displaystyle \nearrow O}{\underset{\displaystyle \searrow OH}{}}} \quad \bullet\ 0.5\,H_2O$$

(I)

The four C atoms and two carboxylic O atoms of the acid define the 2-methyleneacrylate system which corresponds with the enolpyruvate group in PEP. The deviation from planarity of this system is revealed by the angles between the plane of the carboxylic group and the planes formed by the atoms C(12), C(13) and C(14) in *A* and C(22), C(23) and C(24) in *B*. These angles are 1.0 (2) and 7.1 (2)°, respectively, and may be compared with the corresponding angle of 3.6 (2)° in the enolpyruvate system in crystals of PEP acid (Weichsel, Lis & Kuczek, 1989). The hydroxyl O atom of the carboxylic group in both molecules is in the *trans*-planar position with respect to the bridging methylene C atom. The same orientation of the hydroxyl O atom to the ester O atom was observed in PEP acid (Weichsel, Lis & Kuczek, 1989).

The orientation of the phosphonic group with respect to the 2-methyleneacrylate system is defined by the torsion angles P(1)—C(14)—C(12)—C(11) in *A* and P(2)—C(24)—C(22)—C(21) in *B*. These angles (Table 2) show that the phosphonic groups project out of the 2-methyleneacrylate plane in both molecules. In PEP acid and its salts, the phosphate group can assume different orientations relative to the terminal methylene C atom (P—O—C=CH_2 torsion angles are in the range −90 to 90°; Weichsel & Lis, 1994).

The most essential, if predictable, geometric differences between 2-(phosphonomethyl)acrylic and PEP acid concern the bond lengths and angles involving the bridging methylene C atom. The P—C bonds in (II) [1.795 (2) and 1.791 (2) Å] are considerably longer than the high energy P—O(ester) bonds in PEP acid [1.578 (3) and 1.583 (3) Å] or even in the silver barium salt of PEP acid where the P—O(ester) bond is the longest found in all structures of PEP salts (Weichsel & Lis, 1990). Also, the C(14)—C(12) and C(24)—C(22) bonds [1.508 (3) and 1.505 (3) Å] are significantly longer than the corresponding C—O(ester) bonds in PEP acid, and the C(12)—C(14)—P(1) and C(22)—C(24)—P(2) bond angles are smaller than the C—O(ester)—P angles in PEP acid [121.6 (2) and 125.8 (2)°].

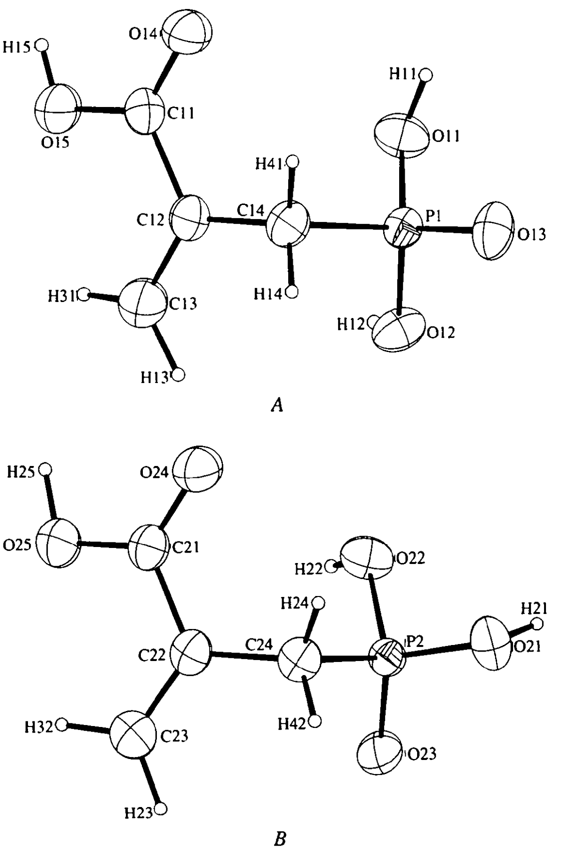


Fig. 1. Molecular geometry and numbering scheme of the two independent molecules (*A* and *B*) in crystals of 2-(phosphonomethyl)acrylic acid. Displacement ellipsoids are shown at the 50% probability level. H atoms are represented as spheres of arbitrary radii.

The crystal packing of (I) and the hydrogen-bonding scheme are shown in Fig. 2, and hydrogen-bond parameters are listed in Table 5. The 2-methyleneacrylate systems of molecules *A* and *B* are nearly coplanar in the crystal. A similar situation was observed in the structure of PEP acid where the enolpyruvate systems are also coplanar although the phosphate group orientations in PEP acid differ from those in (I). All O-bonded H atoms participate in hydrogen bonding. As in PEP acid, there are hydrogen bonds between the crystallographically independent acid molecules but none between the carboxylic and phosphonic groups; in compounds containing a phosphonic and a carboxylate group (Sawka-Dobrowolska, Głowiak & Barycki, 1989;

Sawka-Dobrowolska & Barycki, 1989), these groups are usually linked by hydrogen bonds. Carboxylic groups are involved in hydrogen bonds in the way usually observed, *i.e.* carboxyl to carboxyl. The phosphonic groups participate in hydrogen bonds with one another and with the water O atom, O(1), which forms three hydrogen bonds: two as a donor to O(12) and O(23) phosphonate atoms, and a very short one as an acceptor to O(11) (Table 5).

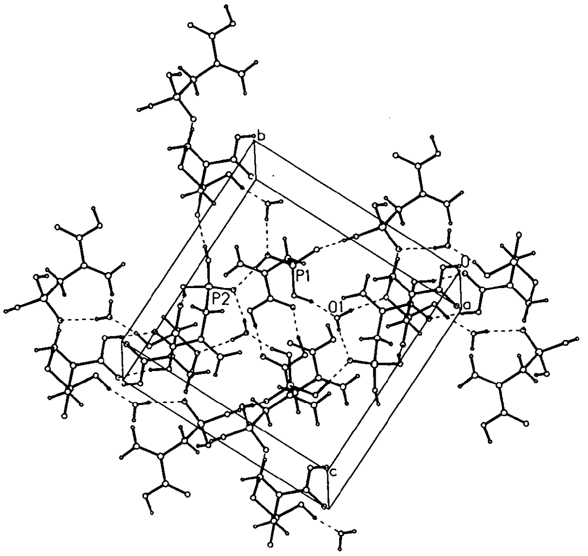
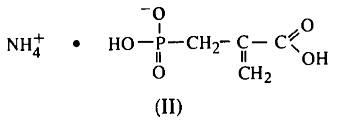


Fig. 2. Packing and hydrogen bonds in the crystal of 2-(phosphonomethyl)acrylic acid hemihydrate.

Crystals of (II) consist of 2-(phosphonomethyl)acrylate monoanions and ammonium cations. The molecular structure and numbering scheme for the anion are illustrated in Fig. 3. The overall structure of the monoanion is similar to those of acid molecules *A* and *B*. The anion differs from the acid in the orientation of the carboxylic hydroxyl group to the terminal $=CH_2$ group and in the distances and angles involving the P atom (Tables 2 and 4). It should be noted that the carboxylic hydroxyl groups in PEP acid and its monoammonium salt have the same orientation (Weichsel & Lis, 1994).



$$\mathrm{NH_4^+} \;\bullet\; \mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{^{-}O}{|}}{P}}{-}CH_2{-}\underset{\underset{CH_2}{\|}}{C}{-}C}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix}$$

(II)

The crystal packing of (II) and the hydrogen-bonding scheme are shown in Fig. 4. The NH_4^+ cations bridge through carboxylic and phosphonate O atoms to four symmetry-related monoanions. A three-dimensional network of hydrogen bonds is completed by links between phosphinic groups and by carboxylic → phosphinate interactions (Table 5).

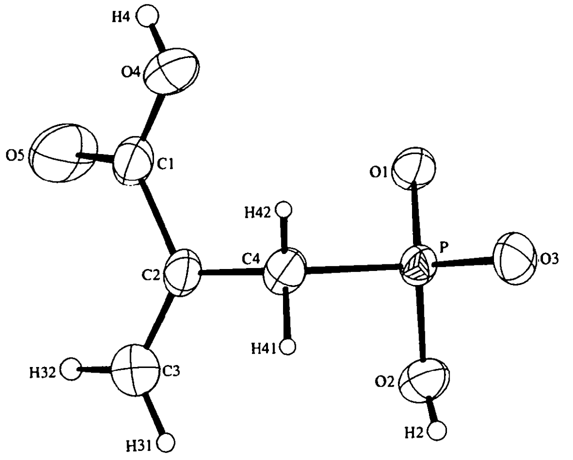


Fig. 3. Molecular geometry and numbering scheme of the 2-(phosphonomethyl)acrylate monoanion in the ammonium salt. Displacement ellipsoids are shown at the 50% probability level.

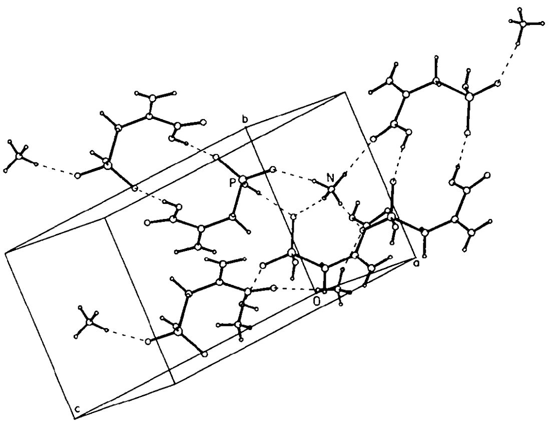


Fig. 4. Packing and hydrogen bonds in the crystal of ammonium 2-(phosphonomethyl)acrylate.

Experimental

Crystals of 2-(phosphonomethyl)acrylic acid hemihydrate, (I), were obtained by slow evaporation in a refrigerator of aqueous solution of the commercially available compound (Fluka). Ammonium 2-(phosphonomethyl)acrylate, (II), was obtained from aqueous solution by mixing equimolar amounts of 2-(phosphonomethyl)acrylic acid and NH_4HCO_3. The density D_m of (I) was measured by flotation in $C_2H_4Br_2/CCl_4$ and that of (II) by flotation in $CHCl_3/CCl_4$.

Compound (I)

Crystal data

$C_4H_7O_5P.0.5H_2O$
$M_r = 175.07$
Monoclinic
$P2_1/c$
$a = 9.461\,(4)$ Å
$b = 12.298\,(6)$ Å
$c = 12.603\,(6)$ Å
$\beta = 98.60\,(3)°$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}12°$
$\mu = 0.353$ mm^{-1}
$T = 295\,(2)$ K
Platy

$V = 1449.9\ (12)$ Å^3
$Z = 8$
$D_x = 1.604\ (2)$ Mg m^{-3}
$D_m = 1.60$ Mg m^{-3}

0.4 × 0.4 × 0.25 mm
Colourless

Data collection

Syntex $P2_1$ four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2695 measured reflections
2574 independent reflections
2511 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0419$
$\theta_{\rm max} = 27°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 15$
$l = -12 \rightarrow 12$
2 standard reflections monitored every 50 reflections intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0377$
$wR(F^2) = 0.1041$
$S = 1.090$
2574 reflections
254 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.073P)^2 + 0.48P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.134$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.47$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for compound* (I)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P1	0.42511 (4)	0.62552 (4)	0.29546 (4)	0.0257 (2)
P2	0.71534 (4)	0.89212 (3)	0.51799 (4)	0.0254 (2)
O11	0.4993 (2)	0.55878 (12)	0.39031 (12)	0.0395 (4)
O12	0.4949 (2)	0.73967 (12)	0.30800 (12)	0.0360 (4)
O13	0.4340 (2)	0.57958 (13)	0.18711 (12)	0.0404 (4)
O14	0.1826 (2)	0.50604 (12)	0.47547 (13)	0.0429 (4)
O15	0.1576 (3)	0.64377 (15)	0.58551 (15)	0.0515 (5)
O21	0.7548 (2)	0.95692 (13)	0.42167 (13)	0.0406 (4)
O22	0.6416 (2)	0.97298 (12)	0.58605 (13)	0.0375 (4)
O23	0.6272 (2)	0.79319 (11)	0.48820 (12)	0.0383 (4)
O24	0.8890 (2)	0.99070 (13)	0.77460 (13)	0.0477 (4)
O25	0.8432 (2)	0.85327 (14)	0.87956 (14)	0.0480 (4)
O1	0.4747 (3)	0.3591 (2)	0.3776 (2)	0.0696 (7)
C11	0.1841 (2)	0.6040 (2)	0.4950 (2)	0.0330 (5)
C12	0.2125 (2)	0.6848 (2)	0.4136 (2)	0.0336 (4)
C13	0.2135 (4)	0.7900 (2)	0.4355 (3)	0.0551 (7)
C14	0.2393 (2)	0.6413 (2)	0.3065 (2)	0.0337 (5)
C21	0.8686 (2)	0.8932 (2)	0.7888 (2)	0.0319 (4)
C22	0.8744 (2)	0.8133 (2)	0.7010 (2)	0.0312 (4)
C23	0.8676 (3)	0.7076 (2)	0.7204 (3)	0.0447 (6)
C24	0.8866 (2)	0.8587 (2)	0.5919 (2)	0.0321 (4)

Table 2. *Selected geometric parameters (Å, °) for compound* (I)

P1—O13	1.492 (2)	O15—C11	1.300 (3)
P1—O11	1.531 (2)	O24—C21	1.232 (3)
P1—O12	1.549 (2)	O25—C21	1.300 (3)
P1—C14	1.795 (2)	C11—C12	1.481 (3)
P2—O23	1.491 (2)	C12—C13	1.322 (3)
P2—O21	1.544 (2)	C12—C14	1.508 (3)
P2—O22	1.546 (2)	C21—C22	1.487 (3)
P2—C24	1.791 (2)	C22—C23	1.325 (3)
O14—C11	1.229 (3)	C22—C24	1.505 (3)
O13—P1—O11	115.4 (2)	O14—C11—C12	121.1 (2)
O13—P1—O12	110.8 (1)	O15—C11—C12	115.7 (2)
O11—P1—O12	105.5 (1)	C13—C12—C11	120.6 (3)
O13—P1—C14	107.6 (2)	C13—C12—C14	122.4 (3)
O11—P1—C14	109.7 (1)	C11—C12—C14	117.0 (2)
O12—P1—C14	107.5 (2)	C12—C14—P1	113.9 (2)
O23—P2—O21	114.5 (1)	O24—C21—O25	123.3 (2)
O23—P2—O22	112.5 (1)	O24—C21—C22	120.7 (2)
O21—P2—O22	106.7 (2)	O25—C21—C22	116.0 (2)
O23—P2—C24	111.8 (2)	C23—C22—C21	120.2 (2)
O21—P2—C24	102.7 (2)	C23—C22—C24	123.0 (2)
O22—P2—C24	107.9 (1)	C21—C22—C24	116.8 (2)
O14—C11—O15	123.1 (2)	C22—C24—P2	111.9 (2)
O11—P1—C14—C12	52.2 (2)	C21—C22—C24—P2	−85.6 (2)
O12—P1—C14—C12	−62.0 (2)	O14—C11—C12—C13	179.8 (3)
O13—P1—C14—C12	178.6 (2)	O15—C11—C12—C13	1.6 (4)
O21—P2—C24—C22	169.1 (2)	O14—C11—C12—C14	0.0 (3)
O22—P2—C24—C22	56.7 (2)	O15—C11—C12—C14	−178.2 (2)
O23—P2—C24—C22	−67.6 (2)	O24—C21—C22—C23	172.7 (2)
C13—C12—C14—P1	84.7 (3)	O25—C21—C22—C23	−6.4 (3)
C11—C12—C14—P1	−95.5 (2)	O24—C21—C22—C24	−7.8 (3)
C23—C22—C24—P2	93.9 (3)	O25—C21—C22—C24	173.1 (2)

Compound (II)

Crystal data

$NH_4^+.C_4H_6O_5P^-$
$M_r = 183.10$
Monoclinic
$P2_1/c$
$a = 6.324\ (3)$ Å
$b = 7.710\ (3)$ Å
$c = 16.444\ (6)$ Å
$\beta = 91.52\ (3)°$
$V = 801.5\ (6)$ Å^3
$Z = 4$
$D_x = 1.517\ (2)$ Mg m^{-3}
$D_m = 1.52$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 33 reflections
$\theta = 10$–$14°$
$\mu = 0.322$ mm^{-1}
$T = 296\ (2)$ K
Irregular
0.6 × 0.4 × 0.3 mm
Colourless

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
3935 measured reflections
2874 independent reflections
1996 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0374$
$\theta_{\rm max} = 32.5°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = -24 \rightarrow 24$
3 standard reflections monitored every 50 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0380$
$wR(F^2) = 0.1017$
$S = 1.092$
2874 reflections
141 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.074P)^2 + 0.065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.115$

$\Delta\rho_{\rm max} = 0.60$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0031 (33)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($\mathring{A}^2$) *for compound* (II)

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

	x	y	z	U_{eq}
P	0.57852 (5)	0.79756 (4)	0.31188 (2)	0.02374 (11)
O1	0.5135 (2)	0.97347 (12)	0.34408 (6)	0.0293 (2)
O2	0.4068 (2)	0.75279 (15)	0.24391 (6)	0.0325 (2)
O3	0.7976 (2)	0.78828 (14)	0.28002 (7)	0.0362 (2)
O4	0.4832 (2)	0.8200 (2)	0.53022 (7)	0.0415 (3)
O5	0.1346 (2)	0.7934 (3)	0.52529 (11)	0.0705 (5)
C1	0.3062 (3)	0.7584 (2)	0.49913 (9)	0.0339 (3)
C2	0.3369 (2)	0.6411 (2)	0.42869 (8)	0.0298 (3)
C3	0.1735 (3)	0.5479 (3)	0.40176 (11)	0.0482 (4)
C4	0.5499 (2)	0.6362 (2)	0.39025 (8)	0.0291 (3)
N	0.9380 (2)	0.5515 (2)	0.16453 (9)	0.0364 (3)

Table 4. *Selected geometric parameters* (Å, °) *for compound* (II)

P—O1	1.517 (2)	O5—C1	1.209 (2)
P—O2	1.576 (2)	C1—C2	1.486 (2)
P—O3	1.496 (2)	C2—C3	1.325 (2)
P—C4	1.804 (2)	C2—C4	1.504 (2)
O4—C1	1.307 (2)		
O1—P—O2	104.8 (1)	O5—C1—O4	123.2 (2)
O1—P—O3	115.3 (1)	O5—C1—C2	123.4 (2)
O2—P—O3	111.6 (1)	O4—C1—C2	113.4 (2)
O1—P—C4	109.5 (1)	C3—C2—C1	118.3 (2)
O2—P—C4	106.0 (1)	C3—C2—C4	123.0 (2)
O3—P—C4	109.2 (1)	C1—C2—C4	118.7 (2)
C2—C4—P	113.0 (2)		
O1—P—C4—C2	50.3 (2)	O5—C1—C2—C3	−11.6 (3)
O2—P—C4—C2	−62.2 (2)	O4—C1—C2—C3	168.2 (2)
O3—P—C4—C2	177.4 (2)	O5—C1—C2—C4	167.2 (2)
C3—C2—C4—P	91.0 (2)	O4—C1—C2—C4	−13.0 (2)
C1—C2—C4—P	−87.7 (2)		

Table 5. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
Compound (I)				
O(11)—H(11)···O(1)	0.94 (5)	1.55 (5)	2.470 (3)	167 (5)
O(12)—H(12)···O(23)	0.91 (4)	1.60 (4)	2.511 (3)	176 (4)
O(15)—H(15)···O(24^{i})	0.84 (4)	1.83 (4)	2.661 (3)	172 (4)
O(21)—H(21)···O(13^{ii})	0.78 (4)	1.79 (4)	2.572 (3)	179 (4)
O(22)—H(22)···O(13^{iii})	0.83 (5)	1.76 (5)	2.578 (3)	164 (4)
O(25)—H(25)···O(14^{iv})	0.97 (5)	1.70 (4)	2.657 (3)	169 (4)
O(1)—H(1)···O(12^{v})	0.83 (4)	1.98 (4)	2.813 (4)	173 (4)
O(1)—H(2)···O(23^{vi})	0.82 (5)	1.98 (4)	2.790 (4)	166 (4)
Compound (II)				
O(2)—H(2)···O(1^{vii})	0.71 (3)	1.94 (3)	2.650 (3)	176 (3)
O(4)—H(4)···O(1^{viii})	0.75 (4)	1.88 (4)	2.609 (3)	165 (4)
N—H(11)···O(5^{ix})	0.89 (3)	2.00 (3)	2.893 (2)	176 (3)
N—H(12)···O(3^{x})	0.89 (3)	1.88 (3)	2.768 (3)	174 (3)
N—H(13)···O(3)	0.94 (3)	1.90 (3)	2.796 (3)	159 (3)
N—H(14)···O(1^{vii})	0.89 (3)	2.07 (3)	2.918 (3)	160 (3)

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vi) $1-x, 1-y, 1-z$; (vii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (viii) $1-x, 2-y, 1-z$; (ix) $1+x, \frac{3}{2}-y, z-\frac{1}{2}$; (x) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Data collection: *XTL/XTLE* system (Syntex, 1976) for (I); KM-4 software (Kuma, 1989) for (II). Cell refinement: *XTL/XTLE* system for (I); KM-4 software for (II). Data reduction: *XTL/XTLE* system for (I); KM-4 software for (II). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,4-Dihydro-3-methyl-6-nitro-2*H*-1,3-benzoxazin-2-one and *p*-Nitrophenyl Dimethylcarbamate

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(*Received 10 April 1995; accepted 5 August 1995*)

Abstract

In 3,4-dihydro-3-methyl-6-nitro-2*H*-1,3-benzoxazin-2-one ($C_9H_8N_2O_4$) (1), the plane of the *cis* carbamate group is 11.1 (2)° to that of the benzene ring, whereas, in the acyclic analogue, *p*-nitrophenyl dimethylcarbamate ($C_9H_{10}N_2O_4$) (2), the corresponding angle is 51.88 (9)° and the configuration is *transoid*. In (1), the O1—C7—O2 angle is 115.4 (3)° and the O1—C7—N1 angle is 117.3 (2)°; in (2), the corresponding angles are 122.8 (2) and 110.8 (2)°, respectively.

Comment

The title compounds have been used as modifiers of enzymes such as chymotrypsin (Kitson & Freeman,