

Fig. 1. Projection of the structure along the *a* axis. The O...H contacts listed in Table 2 are indicated by broken lines.

benzene ring. The mean value of 1.352 Å for these bond distances is significantly shorter than the value 1.397 Å expected from neutron diffraction (Bacon, Curry & Wilson, 1964). The C—S distances of 1.779 and 1.759 Å can be considered as pure single bonds (if the shortening of the bonds due to hybridization is taken into account); this cannot be said of the C(1)—N [1.388 (10) Å] and C(2)—N [1.385 (9) Å] distances. These lengths suggest delocalization along the system C(1)—N—C(2). The C(1)—S—C(7) angle (92.1°) is typical of S-containing five-membered heterocyclic molecules (Chesick & Donohue, 1971; Prout & Miao, 1982). Corresponding bond distances and angles found here and by Prout & Miao (1982) for free benzothiazole (bttz) molecules differ from those in coordinated bttz ligands. The free bttz mol-

ecule involves elongation of the C—N bond of the N—C—S system, in comparison with 1.320 (8) Å (Kubiak, 1985) and 1.309 (7) Å (Oughtred, Raper, Nowell & March, 1982) in bttz ligands (see Table 2). This change may be related to a strong metal–ligand interaction (Jeannin, Jeannin & Lavigne, 1979). Electron donation from the *X_{exo}* atom to the metal (*X* = O or S) may induce a decrease in the π -electron density along the C—*X_{exo}* bond and this would result in a charge displacement from the N lone pair to the C—N bond, in agreement with the observed C—N shortening in coordinated bttz molecules. The bond angles in the bttz ligand are distorted because of steric hindrance arising from coordination. The coordination alters the bttz ring geometry by decreasing the C—N—C angle and opening up the S—C—N angle.

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Structure of Bis(cyclohexylammonium) Phosphoenolpyruvate Methanol Solvate (1/0.5)

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Abstract. 2C₆H₁₄N⁺·C₃H₃O₆P²⁻·0.5CH₃OH, *M_r* = 382.42, monoclinic, *C2/c*, *a* = 27.065 (15), *b* = 15.405 (6), *c* = 21.291 (16) Å, β = 112.30 (6)°, *V* = 8213 (10) Å³, *Z* = 16, *D_m* = 1.239, *D_x* = 1.237 (2) g cm⁻³, *Mo K α* , λ = 0.71069 Å, μ =

1.73 cm⁻¹, *F*(000) = 3312, *T* = 299 (1) K, final *R* = 0.066 for 4845 non-zero reflections. The crystal contains two crystallographically independent phosphoenolpyruvate dianions (*A* and *B*). In *B* the acidic H atom is attached to the phosphate group whereas

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in *A* it is disordered, being statistically shared between pairs of centrosymmetrically related phosphate O atoms and between pairs of diad-related carboxyl O atoms. These O atoms are involved in very short hydrogen bonds [2.440 (4) and 2.432 (5) Å, respectively] connecting the *A* dianions into infinite chains. Thus in *A* the phosphate group has a negative charge of -1.5 and the carboxyl group bears a negative charge of -0.5 . The ester phosphate bonds [1.627 (3) (in *A*) and 1.634 (3) Å (in *B*)] are longer than those found in phosphoenolpyruvic acid and phosphoenolpyruvate monoanion structures. The P atoms in *A* and *B* lie approximately in the enolpyruvate plane.

Introduction. This work is a continuation of our investigations on phosphate esters (Weichsel & Lis, 1989*a*) and relates to the geometric changes which occur on protonation. Phosphoenolpyruvate (PEP), a very important 'high-energy' intermediate, may exist in four forms: tribasic acid, monoanion, dianion and trianion; the crystal structures of the last two are not known. Provision of detailed structural information is aimed at elucidation of the mode of PEP hydrolysis, a reaction which depends on the pH (O'Neal, Bild & Smith, 1983). The hydrolysis of the phosphate ester bond in PEP and transfer of the phosphate group are fundamental to a variety of biochemical reactions (Stryer, 1986).

Experimental. Bis(cyclohexylammonium) phosphoenolpyruvate was prepared by combining an equivalent quantity of commercially available cyclohexylammonium phosphoenolpyruvate and cyclohexylamine. Crystals were obtained as well developed prisms from methanol solution by diffusion of ethyl ether through the vapour phase in the desiccator. D_m by flotation in $\text{CH}_2\text{Cl}_2/1,1$ -dichloroethane; preliminary examination by rotation and Weissenberg photographs. A specimen $0.3 \times 0.65 \times 0.65$ mm was cut from a large crystal and coated with lacquer. Syntex $P2_1$ diffractometer, graphite monochromator, Mo $K\alpha$ radiation for lattice parameters (15 reflections in range $21 < 2\theta < 23^\circ$) and intensity measurements. Intensities were recorded in shells by the ω - 2θ scan technique up to $2\theta = 66^\circ$, $0 \leq h \leq 38$, $0 \leq k \leq 23$, $-28 \leq l \leq 28$. Two standards ($28\bar{2}$ and $15,1,\bar{5}$) which were monitored after each group of 50 reflections exhibited crystal decay from reflection number 4500. The measurements were ended when the intensities of check reflections declined to 77% of their initial value. 7358 data were recorded and reflections from 4500 to 7358 were scaled according to the intensities of the check reflections. After averaging 4845 data with $I > 3\sigma(I)$ were used in calculations. Neutral-atom scattering factors from *International Tables for*

X-ray Crystallography (1974). Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986); C-bonded H atoms of cyclohexyl rings positioned geometrically [$d(\text{C}-\text{H}) = 1.08$ Å] and not subsequently refined; other H atoms were located from difference syntheses and their positional parameters were refined with constraints $d(\text{C}-\text{H}) = 1.08$, $d(\text{N}-\text{H}) = 1.00$ and $d(\text{O}-\text{H}) = 0.96$ Å, except for H(12) and H(15) which lie in special positions. Blocked full-matrix least-squares refinement, based on *F* values, with $w^{-1} = \sigma^2(F)$, was performed with *SHELX76* (Sheldrick, 1976) (P, N, C, O anisotropic, H isotropic). In the final cycle of refinement no parameter shifted more than 0.18 of its standard deviation. Final $R = 0.0660$ and $wR = 0.0639$. Residual electron density between -0.44 and 0.45 e \AA^{-3} .

The final atomic parameters are given in Table 1.*

Discussion. The asymmetric unit comprises two crystallographically independent dianions of PEP, four cyclohexylammonium cations and one methanol molecule. Selected bond lengths, bond angles and torsion angles are listed in Table 2. Fig. 1 shows the geometry and atom-numbering scheme of the *A* and *B* dianions.

In phosphoenolpyruvate dianion *B* the acidic H atom is attached to the phosphate group. In dianion *A* this hydrogen is statistically shared between pairs of centrosymmetrically related O atoms of phosphate groups and pairs of diad-related O atoms of carboxyl groups. The symmetrically related pairs of O atoms are thereby involved in very short hydrogen bonds [of 2.440 (4) and 2.432 (5) Å, respectively] which form infinite chains (Table 3 and Fig. 2). Similar short hydrogen bonds lying across centres of inversion and similar proton coordination to the phosphate groups were observed in crystals of *O*-DL-serine phosphate monohydrate (Putkey & Sundaralingam, 1970). Short hydrogen bonds involving A carboxylic O atoms have also been previously observed, e.g. in sodium hydrogen acetate (Speakman & Mills, 1961). Thus, in *A*, the phosphate group has a formal negative charge of -1.5 and the carboxyl group bears a charge of -0.5 . The above-mentioned acidic hydrogen coordination pattern in *A* and *B* dianions is interesting as far as the proton-donor properties of the carboxyl group and mono-ionized phosphate group in PEP are concerned. It indicates that in PEP the carboxylate group and mono-ionized phosphate group have comparable acidity.

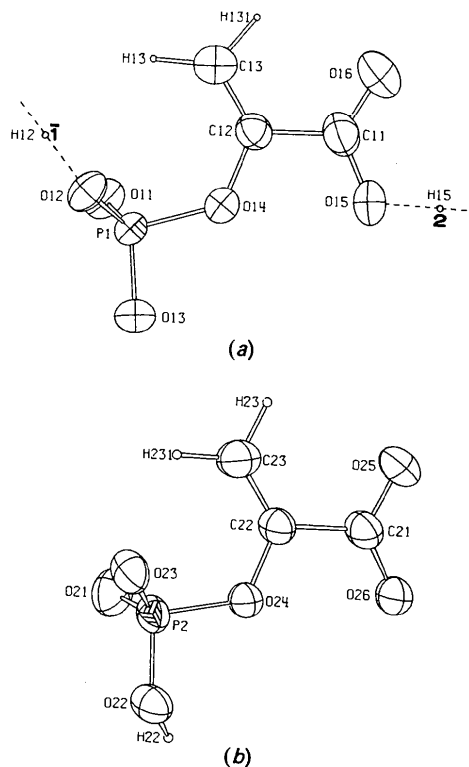
* Lists of structure factors, anisotropic thermal parameters, additional bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52361 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic temperature factors with *e.s.d.*'s in parentheses
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_{ij}$$

| | x | y | z | U_{eq} (Å ² × 10 ³) |
|-------|-------------|-------------|-------------|--|
| P(1) | 0.29057 (4) | 0.67069 (7) | 0.10416 (5) | 32 (1) |
| P(2) | 0.28108 (5) | 0.82416 (8) | 0.28896 (6) | 43 (1) |
| O(11) | 0.2762 (2) | 0.5897 (2) | 0.0625 (2) | 44 (1) |
| O(12) | 0.2691 (2) | 0.7523 (2) | 0.0619 (2) | 43 (1) |
| O(13) | 0.2791 (2) | 0.6715 (2) | 0.1676 (2) | 42 (1) |
| O(14) | 0.3553 (2) | 0.6793 (2) | 0.1360 (2) | 46 (1) |
| O(15) | 0.4540 (2) | 0.6648 (3) | 0.2096 (2) | 83 (2) |
| O(16) | 0.4818 (2) | 0.6890 (3) | 0.1261 (2) | 89 (2) |
| O(21) | 0.3396 (2) | 0.8194 (3) | 0.3081 (2) | 60 (1) |
| O(22) | 0.2497 (2) | 0.8092 (2) | 0.2116 (2) | 52 (1) |
| O(23) | 0.2592 (2) | 0.9020 (2) | 0.3107 (2) | 54 (1) |
| O(24) | 0.2635 (2) | 0.7378 (2) | 0.3199 (2) | 46 (1) |
| O(25) | 0.2638 (2) | 0.6246 (3) | 0.4633 (2) | 77 (2) |
| O(26) | 0.2398 (2) | 0.5843 (2) | 0.3566 (2) | 60 (2) |
| C(11) | 0.4465 (2) | 0.6790 (4) | 0.1478 (3) | 55 (2) |
| C(12) | 0.3888 (2) | 0.6842 (3) | 0.1010 (2) | 42 (2) |
| C(13) | 0.3742 (3) | 0.6932 (4) | 0.0345 (3) | 65 (2) |
| C(21) | 0.2588 (2) | 0.6377 (3) | 0.4040 (3) | 48 (2) |
| C(22) | 0.2790 (2) | 0.7237 (3) | 0.3888 (3) | 42 (2) |
| C(23) | 0.3084 (3) | 0.7765 (4) | 0.4372 (3) | 64 (2) |
| C(1) | 0.4549 (6) | 0.8645 (9) | 0.4275 (5) | 219 (6) |
| O(1) | 0.4356 (4) | 0.8963 (7) | 0.3658 (6) | 262 (5) |
| N(6) | 0.4024 (2) | 0.6811 (3) | 0.3009 (3) | 64 (2) |
| C(16) | 0.3878 (6) | 0.5990 (5) | 0.3253 (4) | 98 (3) |
| C(26) | 0.4067 (4) | 0.5983 (5) | 0.4006 (4) | 132 (4) |
| C(36) | 0.3871 (6) | 0.5082 (7) | 0.4206 (6) | 239 (8) |
| C(46) | 0.4012 (5) | 0.4359 (7) | 0.3951 (5) | 183 (5) |
| C(56) | 0.3815 (6) | 0.4420 (6) | 0.3206 (5) | 208 (6) |
| C(66) | 0.3991 (6) | 0.5294 (6) | 0.2975 (5) | 221 (7) |
| N(7) | 0.2162 (2) | 0.5719 (3) | 0.2174 (2) | 45 (1) |
| C(17) | 0.1597 (3) | 0.5918 (6) | 0.1811 (3) | 97 (3) |
| C(27) | 0.1454 (3) | 0.5973 (5) | 0.1062 (3) | 95 (3) |
| C(37) | 0.0878 (4) | 0.6211 (8) | 0.0687 (4) | 179 (6) |
| C(47) | 0.0603 (4) | 0.6657 (8) | 0.0965 (4) | 176 (5) |
| C(57) | 0.0758 (3) | 0.6626 (6) | 0.1721 (4) | 111 (3) |
| C(67) | 0.1355 (3) | 0.6451 (7) | 0.2094 (4) | 160 (4) |
| N(8) | 0.2948 (2) | 0.4191 (3) | 0.0996 (2) | 47 (2) |
| C(18) | 0.3522 (2) | 0.3995 (3) | 0.1316 (3) | 55 (2) |
| C(28) | 0.3814 (3) | 0.4353 (4) | 0.0892 (4) | 88 (3) |
| C(38) | 0.4409 (3) | 0.4162 (6) | 0.1217 (5) | 135 (4) |
| C(48) | 0.4489 (3) | 0.3185 (6) | 0.1288 (5) | 132 (4) |
| C(58) | 0.4198 (4) | 0.2810 (5) | 0.1718 (4) | 118 (3) |
| C(68) | 0.3608 (3) | 0.3019 (4) | 0.1424 (3) | 78 (2) |
| N(9) | 0.2201 (2) | 0.4345 (3) | 0.4221 (2) | 51 (2) |
| C(19) | 0.1619 (2) | 0.4346 (3) | 0.4084 (3) | 56 (2) |
| C(29) | 0.1308 (3) | 0.4179 (4) | 0.3337 (3) | 75 (2) |
| C(39) | 0.0715 (3) | 0.4198 (5) | 0.3168 (4) | 106 (3) |
| C(49) | 0.0547 (3) | 0.5055 (5) | 0.3391 (4) | 104 (3) |
| C(59) | 0.0864 (3) | 0.5231 (5) | 0.4135 (4) | 100 (3) |
| C(69) | 0.1461 (3) | 0.5200 (4) | 0.4311 (3) | 76 (2) |

Table 2. Principal interatomic distances (Å), bond angles (°) and torsion angles (°) in the phosphoenolpyruvate dianions

| Anion A | | Anion B | |
|-------------------------|-------------|-------------------------|------------|
| P(1)—O(11) | 1.494 (3) | P(2)—O(21) | 1.481 (4) |
| P(1)—O(12) | 1.527 (3) | P(2)—O(22) | 1.558 (3) |
| P(1)—O(13) | 1.496 (3) | P(2)—O(23) | 1.487 (3) |
| P(1)—O(14) | 1.627 (3) | P(2)—O(24) | 1.634 (3) |
| O(14)—C(12) | 1.375 (6) | O(24)—C(22) | 1.382 (5) |
| C(12)—C(11) | 1.504 (7) | C(22)—C(21) | 1.515 (6) |
| C(12)—C(13) | 1.324 (7) | C(22)—C(23) | 1.316 (7) |
| C(11)—O(15) | 1.273 (6) | C(21)—O(25) | 1.233 (6) |
| C(11)—O(16) | 1.217 (7) | C(21)—O(26) | 1.252 (5) |
| C(1)—O(1) | 1.312 (14) | | |
| O(11)—P(1)—O(12) | 112.5 (2) | O(21)—P(2)—O(22) | 112.4 (2) |
| O(11)—P(1)—O(13) | 116.5 (2) | O(21)—P(2)—O(23) | 117.7 (2) |
| O(11)—P(1)—O(14) | 108.1 (2) | O(21)—P(2)—O(24) | 107.1 (2) |
| O(12)—P(1)—O(13) | 111.2 (2) | O(22)—P(2)—O(23) | 109.0 (2) |
| O(12)—P(1)—O(14) | 106.7 (2) | O(22)—P(2)—O(24) | 100.4 (2) |
| O(13)—P(1)—O(14) | 100.6 (2) | O(23)—P(2)—O(24) | 108.6 (2) |
| P(1)—O(14)—C(12) | 127.3 (3) | P(2)—O(24)—C(22) | 122.6 (3) |
| C(11)—C(12)—O(14) | 111.7 (4) | C(21)—C(22)—O(24) | 112.1 (4) |
| C(11)—C(12)—C(13) | 121.8 (5) | C(21)—C(22)—C(23) | 122.2 (5) |
| C(13)—C(12)—O(14) | 126.5 (5) | C(23)—C(22)—O(24) | 125.7 (5) |
| C(12)—C(11)—O(15) | 114.3 (5) | C(22)—C(21)—O(25) | 116.9 (5) |
| C(12)—C(11)—O(16) | 120.6 (5) | C(22)—C(21)—O(26) | 118.2 (5) |
| O(15)—C(11)—O(16) | 125.0 (6) | O(25)—C(21)—O(26) | 124.8 (5) |
| O(11)—P(1)—O(14)—C(12) | 59.2 (10) | O(21)—P(2)—O(24)—C(22) | 66.5 (8) |
| O(12)—P(1)—O(14)—C(12) | -62.0 (9) | O(22)—P(2)—O(24)—C(22) | -176.0 (6) |
| O(13)—P(1)—O(14)—C(12) | -178.2 (8) | O(23)—P(2)—O(24)—C(22) | -61.6 (9) |
| P(1)—O(14)—C(12)—C(11) | -172.0 (7) | P(2)—O(24)—C(22)—C(21) | -178.2 (8) |
| P(1)—O(14)—C(12)—C(13) | 8.5 (10) | P(2)—O(24)—C(22)—C(23) | 0.9 (10) |
| C(13)—C(12)—C(11)—O(15) | -175.6 (11) | C(23)—C(22)—C(21)—O(25) | 11.0 (9) |
| C(13)—C(12)—C(11)—O(16) | 5.2 (11) | C(23)—C(22)—C(21)—O(26) | -166.9 (9) |

Fig. 1. Molecular geometry and numbering scheme of phosphoenolpyruvate dianions (a) *A* and (b) *B*.

The enolpyruvate systems in *A* and *B* are not quite planar. Significant deviation from planarity of the enolpyruvate system in *B* is revealed by the angle between the plane of the carboxyl group and the plane formed by the atoms C(22), C(23) and O(24). However, this angle, 11.8 (8)°, is smaller than the analogous angle in orthorhombic monocyclohexylammonium PEP (Weichsel & Lis, 1989*b*). The enolpyruvate system in *A* is less deformed. The angle between the carboxyl group and the plane formed by the C(12), C(13) and O(14) atoms is 5.1 (8)°.

The conformations about the enolic C—O bonds are such that the P atoms are *trans* with respect to the carboxyl groups in both *A* and *B*. The variable phosphate-group orientations with respect to the enolpyruvate moiety found in phosphoenolpyruvic acid (Weichsel, Lis & Kuczek, 1989), its monopotassium salt (Lis, 1987), monosodium salt (Katti,

Hosur & Viswamitra, 1981), and in two forms of the monocyclohexylammonium salt (Weichsel & Lis, 1989*b*) betray the considerable conformational flexibility about the enolic bond.

The conformation about the phosphate ester bond is different in *A* and *B*. The hydroxyl phosphate O atom is *gauche* to the C atom in *A* and *trans* in *B* (see the O—P—O—C torsion angles in Table 2). In both *A* and *B* the smallest O(ester)—P—O(terminal) bond angles occur when the C—O—P—O torsion angles are *ca* 180°. Such deformations of the phosphate-group tetrahedra are observed in all known PEP structures. The phosphate ester bonds in *A* [1.627 (3) Å] and *B* [1.634 (3) Å] are equal to within 3σ and are slightly long than the P—O(ester) bonds in the monoanions of PEP [1.622 (2) Å in the potassium, 1.595 (5) and 1.610 (6) Å in the sodium and 1.604 (5), 1.610 (2) Å in the cyclohexylammonium salts] and markedly longer than the P—O(ester) bond in PEP acid [1.578 (3) and 1.583 (3) Å]. They are, however, significantly shorter than the value in AgBa(C₃H₂O₆P)₃H₂O (Weichsel & Lis, 1989*c*) which contains a phosphoenolpyruvate trianion. This suggests that the length of the so-called 'high-energy phosphate ester bond' in PEP strongly depends on the degree of ionization of the phosphate group and confirms earlier doubts about interdependence of the free energy of hydrolysis and the P—O(ester) bond length (Watson & Kennard, 1973).

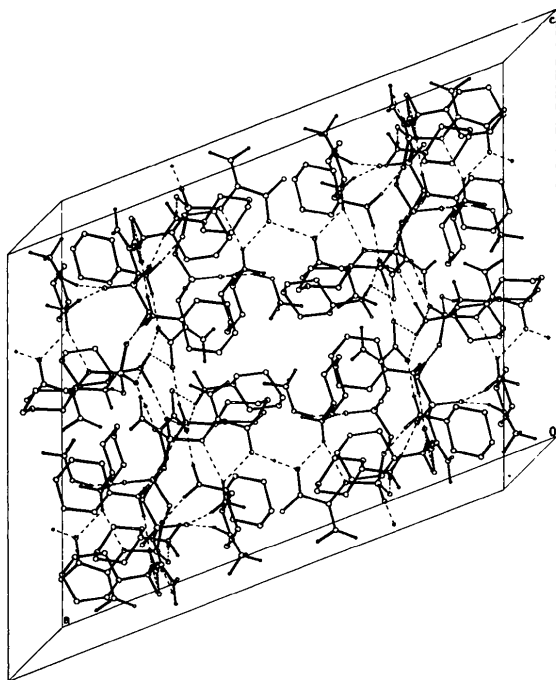


Fig. 2. The packing arrangement. Dashed lines show hydrogen bonds. (C-bonded H atoms in cyclohexyl rings are omitted for clarity.)

Table 3. Probable hydrogen bonds in bis(cyclohexylammonium) phosphoenolpyruvate methanol solvate (1/0.5)

| X—H...O | X...O (Å) | H...O (Å) | ∠X—H...O (°) |
|-----------------------------------|------------|-----------|--------------|
| O(12)—H(12)...O(12) | 2.440 (4) | 1.22 (1) | 180 |
| O(15)—H(15)...O(15 ^m) | 2.432 (5) | 1.22 (1) | 178 (5) |
| O(22)—H(22)...O(13) | 2.565 (4) | 1.60 (4) | 173 (5) |
| N(6)—H(61)...O(14) | 3.250 (5) | 2.31 (2) | 157 (3) |
| N(6)—H(61)...O(15) | 2.800 (6) | 2.05 (4) | 130 (3) |
| N(6)—H(62)...O(16 ⁿ) | 2.925 (6) | 1.94 (3) | 166 (3) |
| N(6)—H(63)...O(21) | 2.766 (6) | 1.78 (4) | 171 (4) |
| N(7)—H(71)...O(26) | 2.791 (5) | 1.80 (2) | 172 (3) |
| N(7)—H(72)...O(23 ^m) | 2.821 (5) | 1.83 (3) | 172 (3) |
| N(7)—H(73)...O(13) | 2.784 (5) | 1.79 (4) | 172 (3) |
| N(8)—H(81)...O(25 ⁿ) | 2.781 (5) | 1.84 (2) | 156 (3) |
| N(8)—H(82)...O(11) | 2.736 (4) | 1.74 (2) | 170 (3) |
| N(8)—H(83)...O(23 ^m) | 2.824 (5) | 1.86 (4) | 160 (3) |
| N(9)—H(91)...O(12 ^m) | 2.829 (4) | 2.07 (3) | 131 (3) |
| N(9)—H(92)...O(26) | 2.848 (5) | 1.87 (3) | 166 (3) |
| N(9)—H(92)...O(25) | 3.155 (5) | 2.52 (3) | 121 (3) |
| N(9)—H(93)...O(11 ⁿ) | 2.818 (5) | 1.85 (2) | 161 (3) |
| O(1)—H(1)...O(21) | 2.690 (11) | 1.76 (9) | 160 (8) |

Symmetry code: (i) 0.5 - x, 1.5 - y, - z; (ii) 1 - x, y, 0.5 - z; (iii) 0.5 - x, y - 0.5, 0.5 - z; (iv) x, 1 - y, z - 0.5; (v) x, 1 - y, 0.5 + z.

The enolic bond lengths in *A* [1.375 (6)] and *B* [1.382 (5) Å] are in agreement with those in other PEP salts and with C—O(ester) bonds in other phosphate esters where the C atom is linked to an O atom (*e.g.* anomeric C atom in carbohydrates) or doubly bonded to another C atom. Consideration of 24 monoionized and 34 doubly ionized phosphate groups in phosphate esters (excluding phosphate groups bound to an aromatic carbon) gives respective mean values for the C—O(ester) bond lengths of 1.432 and 1.438 Å (Starynowicz, 1986).

The hydroxyl oxygen in the carboxyl group in *A* is *cis* planar to the ester oxygen O(14). Only in the monoclinic form of monocyclohexylammonium PEP was the same *cis* position of the hydroxyl oxygen observed. These two crystals were obtained from alcohol solution in contrast to other PEP crystals which were obtained from aqueous solutions.

All four cyclohexyl rings have chair conformations. Some of the C—C bond lengths and C—C—C bond angles [especially in the N(5) and N(7) rings] differ from those found in other salts of this cation [see Table 2*a* of Weichsel & Lis (1989*a*)]. This is probably because of partial disorder of these cyclohexyl rings shown by very high temperature factors of some ring atoms.

The crystal packing and hydrogen-bonding scheme are shown in Fig. 2. Hydrogen-bonding parameters are listed in Table 3. All the N- and O-bonded H atoms participate in hydrogen bonds, forming a three-dimensional network. The methanol molecule forms a hydrogen bond with carboxyl oxygen O(21).

The C—O distance in the methanol molecule is shorter than values for other methanol solvates (Küppers, Kvick & Olovsson, 1981). The large thermal motion of the methanol C and O atoms suggests some disorder but it is also possible that decompo-

sition of the crystal observed during data collection is the effect of methanol loss. Fig. 2 shows that methanol molecules are placed in relatively large cavities.

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Structure of Methyl (*E*)-2-Cyano-2-(1-phenyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-acetate

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Abstract. $C_{11}H_9N_5O_2$, $M_r = 243.23$, monoclinic, $C2/c$, $a = 18.198$ (7), $b = 5.790$ (2), $c = 22.457$ (8) Å, $\beta = 109.11$ (5)°, $V = 2235.9$ (4) Å³, $Z = 8$, $D_x = 1.445$ g cm⁻³, $\lambda(Mo K\alpha) = 0.70926$ Å, $\mu = 0.987$ cm⁻¹, $F(000) = 1008$, room temperature, final $R = 0.046$ for 2593 reflections. The molecule is planar except for the phenyl ring which is rotated about the N—C bond to form an angle of 59.5° with the plane defined by the rest of the molecule.

Introduction. Vinylazides (1)† ($R/R^1 \neq H$) substituted with donor groups in the 4-position can undergo

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† The (unsystematic) numbering of compound (1) assists in discussing the substituent effects and in assigning the type of ring-closure reaction.

both 1,5 and 3,5 ring-closure reactions. Depending on the substituents R/R^1 and the reaction conditions, either stable 1,2,3-triazoles are formed *via* the 4*H*-1,2,3-triazoles (2) or 2*H*-azirines (3) are generated with elimination of nitrogen (Saalfrank, Ackermann, Fischer & Wirth, 1987).

A detailed investigation of the vinyl azides (1) ($R \neq H$; $R^1 = H$) revealed that, for suitable substituents in the 4-position, these compounds could undergo a novel intramolecular 1,5' ring-closure reaction to give (4) (Saalfrank, Fischer, Wirth & Zimmermann 1987).

The constitution of the heterocycles (4) could not be firmly established from the spectroscopic data. These data would also be in agreement with the methyl *N*-alkyl/aryl-*N*-(5-cyano-1*H*-1,2,3-triazol-4-