

squares plane through the pyrimidine ring, the hydroxyuracil moiety is significantly nonplanar.

Table 8. *Deviations from a least-squares plane through the 6 atoms of the pyrimidine ring*

N(1)	-0.016 Å
C(2)	0.013
N(3)	-0.002
C(4)	-0.005
C(5)	0.002
C(6)	0.009
C(1')	0.065
O(2)	0.059
O(4)	0.003
O(5)	-0.035
H(N3)	0.017
H(O5)	0.104
H(C6)	0.042

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## The Crystal Structure of Magnesium Diethyl Phosphate, $\text{Mg}[\text{PO}_2(\text{OC}_2\text{H}_5)_2]_2$

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The crystal structure of magnesium diethyl phosphate,  $\text{Mg}[\text{PO}_2(\text{OC}_2\text{H}_5)_2]_2$ , has been determined from three-dimensional X-ray diffraction data. The crystal is monoclinic, space group  $C2/c$ , with  $a = 22.14$  (2),  $b = 7.998$  (4),  $c = 9.300$  (3) Å,  $\beta = 96.72$  (5)° and  $Z = 4$ . The intensities were measured using the  $\theta$ - $2\theta$  scan method with a Picker automatic 4-circle diffractometer and filtered Mo  $K$  radiation. The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares. The final  $R$  value was 0.061 for 732 observed reflections. Magnesium ions are located on a twofold symmetry axis and coordinated in a nearly regular tetrahedral arrangement to four oxygen atoms with a mean O-Mg-O angle of 109.14° and a mean Mg-O distance of 1.091 Å. The ester conformation with respect to the phosphate group is *synclinal-synclinal*.

### Introduction

Single-crystal X-ray diffraction analysis of phosphodiester has provided information on the possible conformations of the sugar-phosphate backbone in polynucleotides and nucleic acids (Shefter, Barlow, Sparks & Trueblood, 1969; Sundaralingam, 1969).

The conformation of the diester phosphate ion shows a range of allowable values and, in particular, the diethyl phosphate anion conformation is different in the two crystal structures which have been determined, barium diethyl phosphate (Kyogoku & Iitaka, 1966) and silver diethyl phosphate (Hazel & Collin, 1972). The present study was carried out to determine the

structure of the diethyl phosphate ion in a third crystal environment.

The crystal structure of magnesium diethyl phosphate was previously determined with precession camera data (Collin, 1961). Refinement yielded a final  $R$  index ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) of 0.13. High apparent motion of the carbon and oxygen atoms and short carbon-to-carbon bond lengths, of 1.41 and 1.45 Å, were observed. Since the reliability of the precession camera data was uncertain, we decided to obtain new diffractometer data and to redetermine the crystal structure.

### Experimental

Magnesium diethyl phosphate was prepared by dissolving silver diethyl phosphate (Hazel & Collin, 1971) in water and titrating the solution with a standard aqueous solution of magnesium chloride until no silver chloride precipitate formed. The mixture was stirred for one hour, silver chloride filtered off, and the solvent removed by vacuum distillation at room temperature.

Magnesium diethyl phosphate was recrystallized several times from 95% ethanol by addition of ethyl acetate and was then analyzed for the following elements: Mg, 7.45; P, 18.61; C, 29.19; H, 6.25% (Calculated: Mg, 7.36; P, 18.74; C, 29.07; H, 6.10%). Single crystals were grown by allowing ethyl acetate vapor to diffuse into an ethanol solution of magnesium diethyl phosphate. The density, of the colorless rectangular prism-shaped crystals, was measured using the sink-or-float method, in a mixture of carbon tetrachloride and diethyl ether. One crystal was selected and reduced to about  $0.1 \times 0.13 \times 0.20$  mm by dissolving the edges uniformly with a 95% ethanol solution and was used for the diffractometer data collection.

A preliminary survey of the reciprocal lattice with a Buerger precession camera showed monoclinic Laue

symmetry and the following systematic absences:  $hkl$ ,  $h+k=2n+1$ ;  $h0l$ ,  $l=2n+1$ . The unit-cell dimensions and possible space group assignment,  $C2/c$  or  $Cc$ , reported by Scanlon & Collin (1954), were confirmed.

Intensity data were collected on a Picker automatic four-circle diffractometer with the  $c^*$  axis aligned along the  $\varphi$  axis of the instrument. Lattice constants were refined by a least-squares fit of the calculated settings against the measured values for eleven high angle  $Mo K\alpha_1$  reflections centered in the detector. The crystal data are listed in Table 1.  $\omega$  scans of several peaks (in the  $2\theta=40-45^\circ$  range) showed the mosaic spread to be  $0.13^\circ$ .

Table 1. *Crystal data*

Molecular formula	$[(C_2H_5O)_2PO_2]_2Mg$
Molecular weight	330.50
Space group	$C2/c$ or $Cc$
Unit-cell dimensions: 25°C	$a = 22.137 (23) \text{ \AA}$ $b = 7.998 (5)$ $c = 9.300 (3)$ $\beta = 96.72 (5)^\circ$
Unit cell volume	$1635.0 \text{ \AA}^3$
Density (calc.)	$1.34 \text{ g cm}^{-3}$
Density (obs.)	$1.34 \text{ g cm}^{-3}$
Z	4
Absorption coefficient	$3.4 \text{ cm}^{-1}$
Wavelength	$Mo K\alpha_1, \lambda = 0.70926 \text{ \AA}$

Intensities of all unique reflections, in the range  $0^\circ < 2\theta \leq 50^\circ$ , including space-group extinctions of the type  $h0l$ ,  $l=2n+1$ , were measured using the  $\theta-2\theta$  scan mode of an automated diffractometer and Zr-filtered  $Mo K$  radiation, with a  $3^\circ$  target take-off angle, a minimum scan range of  $1.2^\circ$  and a  $1^\circ/\text{min}$  scan speed. Two stationary-crystal stationary-counter background counts of 36 sec were taken, at the upper and lower  $2\theta$  limits of each scan, for all reflections. Of the 1445 intensities measured, 732 were classified as observed by the criterion that the net intensity was greater than

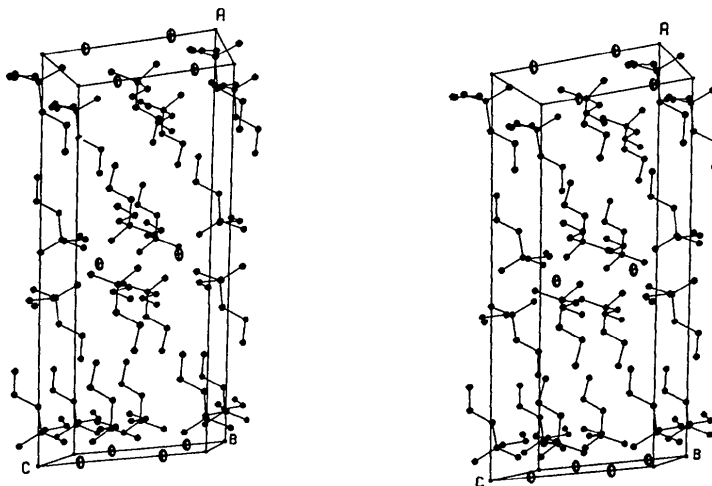


Fig. 1. Stereoscopic view of the unit-cell contents. Magnesium ions are indicated by ellipsoids.

2.5 times its standard deviation. All unobserved reflections were assigned a uniform threshold value based on an estimate of the minimum observable intensity in the high  $2\theta$  range.

The 602, 402 and 600 reflections, which were monitored every 60 reflections, showed a 3–4% decline in intensity over the data collection period and the final data were normalized accordingly. The net intensities were then corrected for Lorentz and polarization factors, but an absorption correction was not applied since the differences in transmission due to absorption were not significant ( $I_{\min}/I_{\max} = 0.97$ ).

To test for a center of symmetry, Giebe Scheibe's piezoelectric test and a variation of Kundt's method for the pyroelectric test (Buerger, 1965) were applied and gave negative results.

### Solution and refinement of the structure

An overall temperature factor (4.52) and scale factor (1.55) were calculated by the method of Wilson (1942). The statistical averages and distributions of the normalized structure factors, listed in Table 2, are

Table 2. Statistical averages and distributions for normalized structure factors

	Experimental	$\bar{I}$	$\bar{I}$
$\langle  E  \rangle$	0.811	0.798	0.886
$\langle  E^2  \rangle$	0.982	1.000	1.000
$\langle  E^2 - 1  \rangle$	0.936	0.968	0.736
$ E  > 3$	0.0%	0.3%	0.01%
$ E  > 2$	4.04	5.0	1.8
$ E  > 1$	33.14	32.0	37.0

close to the theoretical distribution for a centrosymmetric space group (Karle, Dragonette & Brenner, 1965). The results of the modified  $N(z)$  test (Hargreaves & Gogoi, 1966) shown in Table 3, also indicate a centrosymmetric structure. The structure was, therefore, solved and refined in the space group  $C2/c$ .

The magnesium atom must lie on a special position since there are only four magnesium atoms per unit cell. A three-dimensional Patterson map revealed the peaks due to magnesium and phosphorus interactions and an analysis of these peaks showed the magnesium atom to lie on the twofold axis with coordinates  $(0, y, \frac{1}{4})$  with  $y$  close to zero. The Patterson map also clearly revealed the positions of the phosphorus atom and one oxygen atom.

A Fourier map, phased by the known positions of these three atoms, showed the locations of all other oxygen and carbon atoms, and a subsequent structure factor calculation yielded an  $R$  index of 0.27. Atomic scattering factors and anomalous-dispersion corrections for magnesium ( $f' = 0.05$ ,  $f'' = 0.05$ ) and phosphorus ( $f' = 0.11$ ,  $f'' = 0.12$ ) tabulated by Cromer (1965), Cromer & Waber (1965) and Cromer & Liberman (1970), were used in all structure factor calculations. The following ionization states of the atoms were assumed:  $Mg^{2+}$ , P, C,  $O^-$  for the two non-ester oxygen atoms and O for the two ester oxygen atoms.

Five cycles of block-diagonal least-squares refinement of atomic positions, isotropic temperature factors and scale factor reduced the  $R$  index to 0.145. Unobserved reflections were included in the refinement only if  $|F_{\text{calc}}|$  was greater than  $|F_{\text{thresh}}|$  (an estimate of the maximum possible value of the observed structure factor) and a weighting scheme,  $w = \{1 + [(|F_o| -$

Table 3. Modified  $N(z)$  test

$Z$	0.1	0.2	0.3	0.4	0.6	0.8	1.0	1.5	2.0	3.0	4.0
$N(z)$ Experimental	0.249	0.362	0.447	0.511	0.585	0.648	0.693	0.791	0.846	0.922	0.952
$N(z)$ $\bar{I}$	0.248	0.345	0.416	0.473	0.561	0.629	0.683	0.779	0.843	0.917	0.955
$N(z)$ 1	0.095	0.181	0.259	0.330	0.451	0.551	0.632	0.777	0.865	0.950	0.982

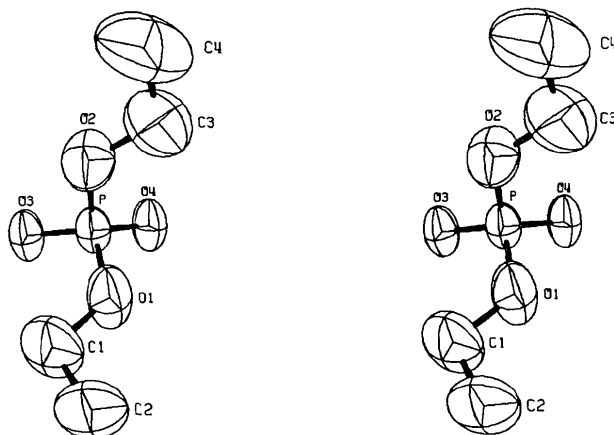


Fig. 2. A stereoscopic view of the diethyl phosphate anion.



along the *c* axis with a Mg–Mg separation of 4.66 Å. A second identical chain can be found parallel to, but displaced from the first by a translation of  $\frac{1}{2}(\mathbf{a} + \mathbf{b})$ . These chains, with the ethyl groups turned outward, are stacked and held together through van der Waals interaction between the ethyl groups. The short carbon–carbon intermolecular distances are 3.98 and 4.05 Å.

The Mg–O bond lengths and O–Mg–O bond angles are listed in Table 7. The angles, 107.7°, 109.6° and 111.1° are close to those of a regular tetrahedron. The magnesium atom is usually found in an octahedral coordination (Vijayan & Viswamitra, 1967; Nyborg & Danielson, 1970; Khan & Baur, 1972) and occasionally in fivefold coordination (Calvo, 1967; Nord & Kierkegaard, 1968; Vallino, 1969; Toney & Stucky, 1971) or eightfold coordination (Zeman & Zeman, 1961; Gibbs & Smith, 1965). The existence of four-coordinated magnesium ions has been observed in the crystal structures of spinel oxides (MgAl<sub>2</sub>O<sub>4</sub>: Bacon, 1952; MgV<sub>2</sub>O<sub>4</sub>: Reuter & Riedel, 1969), melilite (Smith, 1953) and several Grignard reagents: phenyl magnesium bromide dietherate (Stucky & Rundle, 1964), ethyl magnesium bromide dietherate (Guggenberger & Rundle, 1968), and magnesium bromide diethyl etherate (Schibilla & LeBihan, 1967). In the Grignard reagent structures, the magnesium ion is coordinated in a distorted tetrahedral arrangement to two bromine and two oxygen atoms, or one bromine, two oxygen and one carbon atom. The coordination angles about the magnesium ion vary from 62.9° to a maximum of 133.0° and the distortion of the tetrahedron presumably arises from the steric requirements of the different atoms coordinated to magnesium. In magnesium diethyl phosphate, spinel oxides and melilite, the magnesium atom is coordinated to four chemically similar oxygen atoms and distortion from tetrahedral symmetry is minimized.

Table 7. *Coordination distances and angles within the coordination tetrahedron of magnesium and their standard deviations*

Mg–O(3')	1.897 (5) Å	O(3')–Mg–O(3'')	109.5 (3)°
Mg–O(3'')	1.897 (5)	O(4)–Mg–O(4''')	109.7 (4)
Mg–O(4)	1.905 (5)	O(3'')–Mg–O(4)	107.7 (2)
Mg–O(4''')	1.905 (5)	O(3')–Mg–O(4''')	107.7 (2)
		O(3')–Mg–O(4)	111.1 (2)
		O(3'')–Mg–O(4''')	111.1 (2)

O(3') is related to O(3) by  $(-x, -y, -z)$ , O(3'') is related to O(3) by  $(x, -y, \frac{1}{2} + z)$  and O(4''') is related to O(4) by  $(-x, y, \frac{1}{2} - z)$ .

For those structures in which the magnesium ion is coordinated only to oxygen atoms, the average Mg–O bond lengths increase with increasing coordination number from 1.91 Å for four-coordinated to 2.27 Å for eight-coordinated magnesium (Shannon & Prewitt, 1969). The Mg–O bond distances in magnesium diethyl phosphate are 1.90 and 1.91 Å. These are comparable

to the Mg–O distances observed in melilite (1.88 Å), MgAl<sub>2</sub>O<sub>4</sub> (1.91 Å), and MgV<sub>2</sub>O<sub>4</sub> (1.96 Å).

In barium diethyl phosphate (Kyogoku & Iitaka, 1966) there are close approaches of barium ions to the ester oxygen atoms. This situation does not hold in magnesium diethyl phosphate where the closest magnesium ester oxygen approach is 3.83 Å, between Mg and O(4).

A stereoscopic drawing of the diethyl phosphate anion is shown in Fig. 2 and bond lengths and angles are given in Table 8. All O–P–O angles range from 105.0 to 110.1°, except for the O–P–O angle involving the non-ester oxygen atoms, which is opened up to 117.6°. The C–O–P angles (119.8, 125.0°) and C–C–O angles (110.3, 108.1°) are close to the expected values (120 and 110° respectively).

Table 8. *Bond distances and angles within the diethyl phosphate anion and their standard deviations*

P—O(1)	1.548 (6) Å	O(1)–P—O(2)	108.2 (4)°
P—O(2)	1.577 (6)	O(1)–P—O(3)	110.7 (3)
P—O(3)	1.475 (4)	O(1)–P—O(4)	105.1 (3)
P—O(4)	1.461 (4)	O(2)–P—O(3)	105.0 (3)
C(1)–O(1)	1.44 (1)	O(2)–P—O(4)	110.1 (3)
C(3)–O(2)	1.46 (1)	O(3)–P—O(4)	117.6 (3)
C(1)–C(2)	1.47 (1)	C(1)–O(1)–P	125.0 (6)
C(3)–C(4)	1.42 (2)	C(3)–O(2)–P	119.8 (6)
		C(4)–C(3)–O(2)	110.3 (9)
		C(2)–C(1)–O(1)	108.1 (8)

The bonds between phosphorus and esterified oxygen atoms are longer (1.548, 1.577 Å) than those to the non-esterified oxygen atoms (1.475, 1.461 Å). The two carbon–oxygen bond lengths are 1.44 and 1.46 Å.

Carbon–carbon bonds in diethyl phosphates appear consistently shortened below the 1.54 Å single-bond length found in diamond and this must, to some extent at least, be an apparent shortening brought about by the high thermal motion of the ester group. For magnesium diethyl phosphate, the carbon–carbon bond lengths are 1.47 and 1.42 Å. The corrected carbon–carbon distances, averaged over the thermal motion and assuming a riding motion of the first atom on the second, are C(4)–C(3), 1.48; C(2)–C(1), 1.47 Å.

Important conformational parameters are the torsion angles about the P–O(C) bonds. These two angles,  $\omega$  and  $\omega'$ , as defined by Sundaralingam (1969), are the dihedral angles between the C–O–P and O–P–O planes. They are calculated by considering the sequence of atoms C → O → P → O' → C' and applying the right-hand-rule convention of Klyne & Prelog (1960). In magnesium diethyl phosphate, these angles are 77.6° for C(3) → O(2) → P → O(1) and 87.4° for O(2) → P → O(1) → C(1).

The conformation of the anion is similar to that in the barium salt (Kyogoku & Iitaka, 1966), where the corresponding dihedral angles are 68.2 and 71.6°. The conformation of the silver salt (Hazel & Collin, 1972) is quite different in that these angles are 68.3 and 124.9°.

Bond lengths and bond angles in the magnesium diethyl phosphate structure, determined by Collin (1961), are within the standard deviation of the values reported in this work; however, significant differences in the positions of carbon and oxygen atoms were observed and a maximum shift of 0.14 Å occurred in the position of C(2).

#### Computer programs used

Fourier and block-diagonal least-squares calculations were carried out with the NRC crystallographic programs of Ahmed, Hall, Pippy & Saunderson (1966). The full-matrix least squares and final bond distances, angles and errors were computed with *ORXFLS3* and *ORFFE3* (Busing, Martin & Levy, 1971) and crystal structure illustrations were made with *ORTEP* (Johnson, 1965).

The construction and programming of the computer-controlled diffractometer used in this work was partly supported by Biotechnology Resource Grant RR-220 from the National Institute of Health. We are indebted to Dr David A. Goldstein of our department for the supervision of this effort and to Dr William R. Busing for supplying us with paper tapes of the programs used on the Oak Ridge computer-controlled X-ray diffractometer. This paper is based on work performed under contract with the U.S. Atomic Energy Commission at the University of Rochester Atomic Energy Project and has been assigned Report No. UR-3490-263.

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