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

–0.016 Å
0.013
-0.005
-0.002
0.002
0.009
0.065
0.059
0.003
-0.035
0.017
0.104
0.042

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The Crystal Structure of Magnesium Diethyl Phosphate, $Mg[PO_2(OC_2H_5)_2]_2$

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The crystal structure of magnesium diethyl phosphate, Mg[PO2(OC2H5)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 phosphodiesters 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 & litaka, 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-tocarbon 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 fourcircle diffractometer with the c^* axis aligned along the φ 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. ω scans of several peaks (in the $2\theta = 40-45^\circ$ range) showed the mosaic spread to be 0.13°.

Table I. Crystal a	lata
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Molecular formula	$[(C_2H_5O)_2PO_2]_2Mg$ 330.50
Molecular weight	C2/c or Cc
Space group	$a=22\cdot137$ (23) Å
Unit-cell dimensions:	$b=7\cdot998$ (5)
25°C	$c=9\cdot300$ (3)
Unit cell volume Density (calc.) Density (obs.) Z Absorption coefficient Wavelength	$\beta = 96.72 (5)^{\circ}$ 1635.0 Å^{3} 1.34 g cm^{-3} 1.34 g cm^{-3} 4 3.4 cm^{-1} Mo $K\alpha_{1}, \lambda = 0.70926 \text{ Å}$

Intensities of all unique reflections, in the range $0^{\circ} < 2\theta \le 50^{\circ}$, 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° target take-off angle, a minimum scan range of $1\cdot 2^{\circ}$ and a 1°/min scan speed. Two stationary-crystal stationary-counter background counts of 36 sec were taken, at the upper and lower 2θ 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 2θ 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

	Exper- imental	ī	1
$\langle E \rangle$	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 %
<i>E</i> > 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: Mg²⁺, 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 $|F_{calc}|$ was greater than $|F_{thresh}|$ (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

Ζ	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) T	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	0.421	0.551	0.632	0 ·777	0.865	0.950	0.982



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

 $P_2/P_1]^4\}^{-1}$, with $P_1 = 40$ and $P_2 = 50$, was used. Anisotropic temperature factors on all atoms were then included and the refinement was continued for another seven cycles until the shifts were less than 0.25 times the standard deviation of the parameter. The *R* index at this stage was 0.063. Attempts to locate hydrogen atoms by examining difference electron density maps before and after anisotropic refinement were unsuccessful, presumably because of the high thermal motion of the carbon atoms. The r.m.s. radial displacement of the carbon atoms ranged from 0.62 to 0.80 Å.

Revised values of P_1 and P_2 , chosen to minimize the variation in $w(|F_o| - |F_c|)^2$ over the range of F_o , were found to be 40 and 30 respectively. Three final cycles of a full-matrix least-squares refinement were computed, using only the observed reflections, and allowing for an isotropic extinction correction. The *R* index was reduced to the final value of 0.061.

The final structure parameters and errors, as calculated in the last full-matrix least-squares cycle, are listed in Tables 4 and 5. Table 6 is a list of the observed versus calculated structure factors. Of the 713 unobserved reflections, there are 658 with $|F_{calc}| \le 1.0|F_{thresh}|$ and 55 with $|F_{calc}| \le |1.5F_{thresh}|$.

Table 4. Fractional atomic coordinates and their standard deviations

	x	У	Z
Mg	0	-149 (4)	2500
Р	800 (1)	1883 (2)	262 (2)
O(1)	842 (3)	3793 (7)	524 (5)
O(2)	1467 (3)	1173 (8)	320 (6)
O(3)	514 (2)	1518 (6)	-1217 (4)
O(4)	506 (2)	1222 (6)	1468 (4)
C(1)	877 (5)	5032 (12)	- 587 (11)
C(2)	1057 (5)	6622 (10)	120 (11)
C(3)	1830 (5)	926 (17)	1712 (13)
C(4)	2415 (7)	306 (21)	1509 (19)

Results and discussion

Fig. 1 shows the contents of one unit cell. Each magnesium ion is tetrahedrally coordinated to four non-ester oxygen atoms from four different diethyl phosphate anions, and each anion in turn is bound to

two magnesium ions. A chain of magnesium ions, that are surrounded and linked together by the anions, runs

Table 6. Observed and calculated structure factors ($\times 10$)

H L 10FU 10FC	M L 10FO 10FC	M L 10FU 10FC	M L 10FO 10FC	H L 10FU 10+C	M L 1050 10FL
***** E. 0****	-3 2 551 -357	10 1 302 280	-7 2 64 -39	6 3 202 -200	yer. cEE 4 C
-14 0 101 98	3 2 241 -299 5 2 299 -300	10 1 117 -102 -10 2 204 -208	-3 2 90 -124	10 3 240 -233	-7 7 147 -157
-12 0 844 845 2 0 1707 1767	9 2 381 -342 11 2 196 -164	-14 2 325 -334 -12 2 420 -448	1 2 750 -751 3 2 322 -280	14 3 202 183 -18 4 109 133	-13 8 100 90
4 0 775 -690 4 0 1496 -1409 8 0 712 -205	-23 3 87 -80	-10 2 169 -166 -0 2 135 176	5 2 158 -167 7 2 139 147	-6 4 241 259	-1 8 106 127
10 0 201 -141	-15 3 339 367	-4 2 375 -398	11 2 315 -298	0 4 273 285	V U 134 144
-20 2 197 -186 -18 2 269 -291	-11 3 518 -506 -9 3 415 -401	0 2 900 -857 2 2 309 -327	15 2 112 -73	4 4 376 381 6 4 97 -65	-12 0 145 142
-16 2 157 -210 -14 2 356 348	-7 3 305 -275	6 2 78 74	-9 3 160 155 -7 3 192 -234	8 4 219 -214 14 4 142 143	0 0 505 501 2 0 317 315
-10 2 254 -233	-1 3 331 -308	1C 2 403 -399	-3 3 221 -206	-12 5 205 198	-1e 1 122 128
-6 2 1377 -1307 -4 2 2132 -1798	3 3 175 -200	14 2 199 -193 -18 3 76 70	1 3 75 -39 3 3 165 169	-0 > 213 -196 -4 5 217 -214	-10 1 207 -192 -8 1 177 -169
-2 2 1492 1307 0 2 1769 1668	7 3 554 559 9 3 310 328	-16 3 284 296 -14 3 226 196	5 3 320 331 9 3 205 -196	0 5 421 427 2 5 410 424	-0 1 149 194 -0 1 337 320
4 2 1630 -1583	13 3 294 -315	-12 3 44 -112	-21 4 97 119	6 5 238 -262	-2 1 220 214 2 1 116 -99
8 2 272 -289 10 2 174 172	-13 + 37+ 370 -11 + 316 305	-6 3 915 -873 -4 3 108 -97	-17 4 119 111 -15 4 101 -108	10 5 94 -82	6 1 90 108 8 1 269 279
12 2 360 338	-7 + 395 376	-2 3 277 281 0 3 75 -70	-13 4 221 -199 -9 4 124 116	14 5 165 176	10 1 194 203
18 2 336 -323	1 4 80 71	6 3 460 459 6 3 135 130	-7 4 298 285	-2 6 306 -327	-8 2 204 -189
-18 4 95 -134 -16 4 217 208	5 4 360 354 7 4 550 531	12 3 85 -79	-1 4 263 265	6 6 196 -154 8 6 111 -119	U 2 188 185 2 210 -213
-12 4 495 535	9 4 271 277	16 3 181 -195 -20 4 150 142	3 4 351 350 5 4 356 340	-12 7 93 89 -8 7 121 -137	6 2 255 -226 -12 3 185 -183
-8 4 202 187	-19 5 99 87	-16 4 118 104	11 4 217 -226	-6 7 218 -225	-10 3 247 -257
-4 4 201 -191 -2 4 666 703	-15 5 125 143	-8 - 586 586	15 4 161 137	2 7 244 234	-4 3 325 302
2 4 275 -250	-11 5 326 -334 -9 5 143 -150	-4 4 145 130 -2 4 178 -166	19 4 125 136	8 7 197 -195 -12 8 93 108	4 3 349 -361 4 3 275 -283
6 4 280 287 8 4 002 000	-> > 422 394	2 4 539 559	-9 5 95 77	-10 8 109 112	8 3 154 145 -12 4 180 178
10 4 743 720	-1 5 287 -293	10 4 127 -121	3 5 297 310	-12 9 121 125	-0 4 99 -84
16 4 251 -254	7 5 389 374	15 4 147 119	7 5 91 -109 9 5 124 -116	-6 9 132 -120 0 9 177 166	0 4 217 200
18 4 98 -97 -20 6 116 -118 -16 6 126 95	9 5 256 269	18 4 142 162 -18 5 113 117 -18 5 227 208	-13 6 201 -200	2 9 117 121	10 4 146 197
-12 6 233 -202 -10 6 509 -507	-19 6 106 -94 -17 6 98 -59	-12 5 84 -83	-3 6 404 -413	-11 0 270 267	-4 5 210 216
-# 6 530 -537 -6 6 368 -372	-11 6 145 -208	-8 5 255 -248 -6 5 198 -184	1 6 241 -227 5 6 117 110	1 0 347 339 3 0 265 286	2 5 148 -161 6 5 135 124
-6 6 113 94 -2 6 523 512	-7 6 362 -348 -5 6 339 -351	-4 5 224 238 -2 5 334 368	9 6 114 -133 11 6 261 -266	7 0 178 -191 9 0 96 113	8 5 210 184 -10 6 85 -72
2 6 672 -690	-1 6 131 146 1 6 91 -71	4 5 193 200 6 5 231 229	-1 7 76 -67 7 7 169 -141	-19 1 85 66	-6 6 97 -93
6 6 348 -321 8 6 124 -131	3 6 336 -343 5 6 212 -218	8 5 171 166 10 5 163 165	15 7 94 43 -13 8 82 61	-9 1 198 189 -5 1 163 -159	2 117 -127
12 6 106 113	9 6 155 -166	-16 6 123 -133 -16 6 225 -215	-11 8 220 210 -9 8 298 277 -7 8 198 196	-3 1 254 -252	6 6 109 -129 -10 7 100 -84 -10 7 113 -101
10 0 148 -104 -10 8 208 178	-17 7 91 71 -15 7 89 -67	-12 6 190 -167 -10 6 71 -19	-3 8 176 -176 -1 8 136 -146	3 1 377 370 5 1 241 219	0 7 114 -117 -4 8 109 113
-14 8 126 145	-13 7 250 -247 -11 7 204 -192	-8 6 96 91	3 8 265 260	7 1 91 118	-2 8 149 140 U 8 101 89
-6 8 181 103	-7 7 389 386	0 6 375 -381	7 8 140 144	-9 2 368 -388	-11 0 100 -71
-2 8 670 687 0 8 272 276	-3 7 143 151 -1 7 362 -386	8 6 217 -199 10 6 299 -282	-5 10 108 -98 -3 10 176 -163	-5 2 308 -278 -3 2 78 105	9 0 214 212 7 0 120 136
4 8 125 -136	3 7 201 -206	-14 7 107 -126	-1 10 125 -107	-1 2 176 192 1 2 85 95	-15 1 92 89 -5 1 141 132
10 8 192 175	9 7 147 145 13 7 117 -101	-6 7 220 229 -6 7 368 376	-12 0 218 206	5 2 404 -424 7 2 282 -295	-1 1 141 113
-10 10 169 -157 -8 10 148 -146	-15 8 97 106 -13 8 87 70	-2 7 145 134 0 7 368 -375	-6 0 274 248	11 2 126 137	7 1 88 76 9 1 97 100
0 10 191 -195	-3 8 350 357	6 7 196 -212 8 7 143 137	4 0 446 440	19 2 109 -121	-1 2 247 -234
4 10 168 -156 8 10 103 75	1 8 186 200 9 8 93 75	10 7 116 105	-16 1 148 -149 -12 1 150 140	-15 3 157 -185 -13 3 89 -86	5 2 95 44 13 2 97 -85
-15 0 177 183	-13 9 112 -123 -7 9 215 195	-8 8 286 272 -6 8 183 159 -2 8 86 -82	-10 1 422 427	-11 3 93 100 -9 3 131 142	-11 3 139 -148 -9 3 159 -157
-9 0 370 -372 1 0 960 1040	-5 9 180 194 -1 9 193 -207	2 8 211 210	-4 1 641 -652	-1 3 92 -71 3 3 108 -134	s 3 141 -140 5 3 99 -82
3 0 153 187 5 0 1180 990	1 9 171 -174	6 8 182 171 -6 9 151 145	2 1 693 702	5 3 243 -231 7 3 216 -203	-7 - 110 130
11 0 165 -183	-7 10 133 -120	0 9 173 -162	8 1 252 -245	-15 4 173 164	-1 - 118 - 42
21 0 119 108 -21 1 100 -84	1 10 110 -122 3 10 126 -131	-6 10 86 -77	14 1 230 220	-9 4 230 -253 -7 4 238 -233	7 - 115 119
-17 1 190 178 -15 1 250 251	-16 0 150 146	-2 10 164 -165	-14 2 138 -129 -12 2 166 -184	-5 4 176 167	-> > 140 138 > 5 145 133
-11 1 669 -669 -9 1 243 -275	-10 0 112 107	-17 0 211 199 -13 0 83 -74	-8 2 244 -260	1 4 210 218	-3 6 94 -73
-7 1 411 305 -5 1 852 892	2 0 337 -348	-11 0 179 183	-4 2 87 -88	5 4 266 -273 7 4 100 -102	4 0 80 69 6 0 103 115
-3 1 1721 1727 -1 1 754 752 1 1 1378 -1344	8 0 533 544 18 0 151 154	7 0 521 550 7 0 778 743 9 0 754 749	2 2 116 120	4 205 205 11 4 267 265	-2 1 100 102 -4 2 86 -33
3 1 1066 -1213 5 1 722 -712	20 0 119 122	-17 1 96 -72 -9 1 342 364	6 2 192 -186 8 2 324 -314	-11 5 129 126	0 2 120 -135
7 03 -44 9 1 458 479	-14 1 94 71 -12 1 239 -260	-7 1 2+1 272 -3 1 368 328	10 2 213 -208	-1 5 157 160 1 5 173 157	-6 4 108 109
15 1 236 -238	-8 1 336 318	1 1 547 -529	-14 3 96 -81 -12 3 142 143	7 5 88 -80	U 4 84 -78
19 1 127 117	-4 1 589 581 -2 1 1638 1547	11 1 92 113	-10 3 370 358 -0 3 101 100	-13 6 94 31	6 4 122 138 -2 6 120 -110
-17 2 183 -196 -15 2 84 -61	2 1 1019 -365	15 1 105 103 21 1 95 -58	-6 3 251 -237	-9 6 238 -245	1 99 97
-9 2 293 -323	6 1 278 -244	-13 2 464 -461	2 3 373 393	-	-, , 12, -100

Table 5. Thermal parameters and their estimated standard deviations $(\times 10^4)$

Temperature factor = exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})].$

				11	, 12	,	R.m.s. radial displacement
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	(Å)
Mg	34 (1)	204 (6)	74 (3)	0	9 (1)	0	0.425 (3)
P	35 (1)	200 (4)	111 (2)	-19(1)	4 (1)	0 (2)	0.445 (2)
O(1)	83 (3)	240 (11)	158 (7)	-48(5)	6 (4)	- 7(7)	0.593 (6)
O(2)	36 (2)	468 (17)	226 (9)	-6(43)	13 (3)	-16 (10)	0.581 (5)
O(3)	44 (2)	266 (11)	112 (5)	-28(5)	1 (3)	- 5 (6)	0.495 (5)
O(4)	43 (2)	302 (16)	117 (6)	- 32 (4)	17 (2)	13 (7)	0.502 (5)
C(1)	81 (4)	253 (19)	279 (17)	-27 (8)	17 (7)	60 (17)	0.663 (9)
C(2)	73 (4)	195 (18)	328 (19)	-22 (7)	10 (7)	10 (14)	0.621 (8)
C(3)	48 (4)	606 (38)	346 (22)	16 (10)	- 37 (7)	-45 (24)	0.689 (10)
C(4)	53 (4)	748 (51)	604 (40)	58 (13)	-35 (10)	52 (37)	0.804 (13)

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 (MgAl₂O₄: Bacon, 1952; MgV₂O₄: Reuter & Riedel, 1969), melilite (Smith, 1953) and several Grignard reagents: phenyl magnesium bromide dietherate (Stucky & Rundle, 1964), ethvl 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), $MgAl_2O_4$ (1.91 Å), and MgV_2O_4 (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

$\begin{array}{l} P &O(1) \\ P &O(2) \\ P &O(3) \\ P &O(4) \\ C(1)-O(1) \\ C(3)-O(2) \\ C(1)-C(2) \\ C(3)-C(4) \end{array}$	1.548 (6) Å 1.577 (6) 1.475 (4) 1.461 (4) 1.44 (1) 1.46 (1) 1.47 (1) 1.42 (2)	$\begin{array}{c} O(1)-P &O(2) \\ O(1)-P &O(3) \\ O(1)-P &O(4) \\ O(2)-P &O(4) \\ O(2)-P &O(4) \\ O(3)-P &O(4) \\ C(1)-O(1)-P \\ C(3)-O(2)-P \\ C(4)-C(3)-O(2) \end{array}$	108·2 (4)° 110·7 (3) 105·1 (3) 105·0 (3) 110·1 (3) 117·6 (3) 125·0 (6) 119·8 (6) 110·3 (9)
		C(4)-C(3)-O(2) C(2)-C(1)-O(1)	110·3 (9) 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, ω and ω' , 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 \rightarrow O \rightarrow P \rightarrow O' \rightarrow C' and applying the righthand-rule convention of Klyne & Prelog (1960). In magnesium diethyl phosphate, these angles are 77.6° for C(3) \rightarrow O(2) \rightarrow P \rightarrow O(1) and 87.4° for O(2) \rightarrow P \rightarrow O(1) \rightarrow 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).

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