Table 5. Compari	son of stri	uctural pa	rameter	s of the
dithiodiketopiperaz	in moiety	as found	in spor	idesmin,
gli	otoxin and	' chaetocin	-	

	Sporidesmin*	Gliotovin*	Chaetocin
	Spondeshim	Ghotoxin	chactoen
C–C(keto)	1·52 A	1.21 A	1·53 A
C(keto)-N	1.37	1.35	1.35
N–C	1.43	1.45	1.45
C=0	1.23	1.23	1.23
C-S	1.90	1.89	1.88
S - S	2.08	2.08	<b>2</b> ·077
C-C(keto)-N	11 <b>3</b> °	114°	113°
C=C(keto)-N	124	125	125
C-C(keto)=O	124	122	123
C(keto)-N-C	114	118	118
N-C-C(keto)	112	111	111
C(keto)-C-S	102	103	103
N-C-S	112	111	112
C(keto)-C-S	102	103	103
N-C-S	112	111	112
C-S-S	98	98	98
C-S-S-C	-10	-12	+11

\* Fridrichsons & Mathieson (1965).

† Fridrichsons & Mathieson (1967).

contacts. The shortest distances found are  $H \cdots H = 2\cdot 2$  (2),  $S \cdots H = 3\cdot 0$  (1),  $C \cdots N = 3\cdot 30$  (1),  $S \cdots C = 3\cdot 41$  (1) Å.

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# The Crystal Structure of Silver Diethyl Phosphate, AgPO<sub>2</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>

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The crystal structure of silver diethyl phosphate,  $AgPO_2(OC_2H_5)_2$ , was determined with 853 diffractometer-collected intensities. The space group is orthorhombic, *Pccn*, and the unit cell contains two formula units. The unit-cell dimensions at 23 °C are a=20.19 (1), b=14.35 (4) and c=5.86 (1) Å. The intensities were measured by the  $2\theta$ -scan method with Mo K $\alpha$  radiation and the structure was solved by Patterson methods and refined by block-diagonal least-squares calculations to an *R* value of 0.043. The silver ion is coordinated to four oxygen atoms in a distorted tetrahedral arrangement with a mean Ag-O distance of 2.36 Å. Thermal motion of the atoms in the diethyl phosphate anion is high and can be qualitatively explained as a rigid-body motion of the phosphate group coupled with a librational motion of the ester groups about the P-O bonds. The ester conformation with respect to the phosphate group is *syn*-clinal, *anti*-clinal.

### Introduction

A study of the conformation of diester phosphates is of interest both for the light it might throw on bonding within the phosphate group (Collin, 1966, 1969) and for its implications to the structure of nucleic acids (Sundaralingam, 1969) and other molecules of biological interest.

Although the structures of a number of phosphate diesters have been determined, that of barium diethyl

phosphate (Kyogoku & Iitaka, 1966) is the only acyclic ester in which the ester groups contain no ionic species, or species capable of hydrogen-bond formation.

Many silver salts exhibit short silver-oxygen distances in which partial covalent character may occur, and it is of interest to examine the effects of such interactions on the bonding scheme within the diester anion and on the resulting conformation. We suspect that conformational differences such as those between the diethyl phosphate anion in the barium and silver salt, may be eventually correlated with cation-oxygen interactions.

Experimental

# Crystal data

AgPO<sub>2</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, M.W. 260·96, Space group: *Pccn*   $a=20\cdot19$  (1),  $b=14\cdot35$  (4),  $c=5\cdot86$  (1) Å  $V=1695\cdot1$  Å<sup>3</sup>,  $D_m=1\cdot997$  g.cm<sup>-3</sup> (flotation),  $D_c=1\cdot952$  g.cm<sup>-3</sup> Z=8 F(000)=1016, Mo K $\alpha$  ( $\lambda=0.70926$  Å for  $K\alpha_1$ )  $\mu=24\cdot4$  cm<sup>-1</sup>

Silver diethyl phosphate was prepared by adding excess silver oxide to diethyl chlorophosphate in aqueous solution. The mixture was stirred for five hours at room temperature. The precipitated silver chloride and unreacted silver oxide were filtered off and the solvent removed by vacuum distillation at room temperature.

The compound was recrystallized from 95% ethanol by addition of ethyl acetate, and analyzed for Ag (obs. 41·40%, calc. 41·33%), P (obs. 11·99%, calc. 11·87%), C (obs. 18·47%, calc. 18·41%) and H (obs. 3·91%, calc. 3·86%). The direct addition of ethyl acetate to the ethanol solution yields crystals which are no larger than 0·5 mm in two dimensions and up to several mm long. Single crystals of more suitable size and shape for the collection of diffractometer data were grown by allowing the ethyl acetate vapor to diffuse into an ethanol solution of silver diethyl phosphate. The crystal used in the experiment was a colorless rectangular prism with dimensions  $0.15 \times 0.13 \times 0.25$  mm which quickly darkened on standing.

The unit-cell dimensions were determined at 23 °C from a least-squares fit of angular settings for ten reflections in the range  $2\theta = 40-45^{\circ}$  where the  $\alpha_1-\alpha_2$  doublet is resolved. The systematic absences 0kl for l odd, h0l for l odd and hk0 for h+k odd, along with *mmm* reciprocal lattice symmetry, uniquely identify the space group as *Pccn*. The unit-cell dimensions and space group are in agreement with the results of Scanlon & Collin (1954).

Intensity data were collected on an automated Picker four-circle diffractometer with the  $c^*$  axis of the crystal offset approximately 2° from the  $\varphi$  axis of the instrument. Intensities were measured using the  $2\theta$ -scan method up to a maximum value of  $2\theta = 50^\circ$  with Zrfiltered Mo K $\alpha$  radiation, a target take-off angle of 2.5° and a scan speed of 1° per min. The base width of the scan was 1.5° and the actual range of each scan was adjusted for increasing dispersion as  $2\theta$  increased.

The intensities of three standard reflections were remeasured every 60 reflections and used to correct the data for variations caused by drift in incident beam intensity or by slow crystal decomposition. A 5% decline in the standard intensities was observed between the start and finish of data collection. Values of  $|F_a|$  were obtained from the intensity data by applying corrections for the decline in the standard intensities and for the Lorentz and polarization factors. Within the angular range over which data collection was undertaken, there were 853 observed and 647 unobserved reflections by the criterion that a reflection was unobserved if its net count was less than 2.5standard deviations above background. The intensities were corrected for absorption by an analytical method based on the actual shape of the crystal measured under a microscope.

### Structure determination and refinement

The silver and phosphorus atom positions were determined from the highest peaks on a Patterson map. The resulting z coordinate of the silver atom was close to zero and that of the phosphorus atom was close to  $\frac{1}{2}$ . After two cycles of least-squares refinement on the position and isotropic thermal parameters of silver and phosphorus, the z coordinates of the two atoms had shifted somewhat, but were still close enough to their original positions so that the calculated magnitudes of structure factors with h+k=2n+1 were very small. As a result, the phases of most structure factors in this class were poorly determined at this stage. A three-dimensional Fourier synthesis was prepared, using as coefficients only those observed structure factors for which  $|F_c| \ge 0.25 |F_o|$  in an effort to limit the number of incorrectly phased reflections. If all reflections of the class h+k=2n+1 had been excluded from the Fourier synthesis, a false mirror plane would have been introduced at  $z = \frac{1}{2}$ . Because only a small number of reflections of this class were allowed to contribute to the first Fourier synthesis, vestiges of the false mirror remained. The electron density map yielded five peaks as possible oxygen atoms, two pairs of which were approximately mirror images, while a single peak appeared near  $z=\frac{1}{2}$ . The latter and a member of one pair, both with maximum densities of about  $6 \text{ e.} \text{Å}^{-3}$ , were chosen as oxygen atoms O(1) and O(3) respectively. The other three peaks had densities of less than 4 e.Å<sup>-3</sup>. The position and isotropic thermal parameters of silver, phosphorus and the two newly located oxygen atoms were refined by three cycles of blockdiagonal least-squares calculations. A second Fourier synthesis was prepared imposing the previous restrictions on the magnitudes of coefficients. The false mirror symmetry now vanished completely, and the two remaining oxygen atoms and one carbon atom, C(1), were located. Two more structure factor-Fourier map calculations with all observed reflections resulted in the location of all atoms except one carbon, C(3).

The shapes of the peaks in the electron density maps suggested that the carbon atoms and three of the oxygen atoms were undergoing large thermal motion. The structure at this stage was refined by three cycles of block-diagonal least-squares calculations on position and isotropic thermal parameters, and a set of  $F_c$  was obtained and used in a difference Fourier synthesis

# Table 1. Observed and calculated structure factors $\times 10$

Unobserved reflections are indicated by an asterisk and the value of  $F_0$  is replaced by the estimated threshold value.

L FO FC	L FO FC	L FO FC	L FU FC	L FU FC	L FO FC	L FO FC	L FU FC	L FU FC	L FU FL	L FU FC	LFU
2 2439 2626 4 1690 1725 6 652 649	4 126 -130 5 80 -87 6 710 -70 H= 9, K= 1	5 206 232 6 226 232 H= 9, K= 2 1 440 17	0 762 -762 1 458 472 2 540 -537 3 291 309	2 217 222 3 RY TO 6 76 36 5 67 52	1 186 -161 2 212 -195 3 58° 48 4 121 -133	4 664 74 5 724 -9 He 124 Ke 6 0 159 -125	H= 14, K= 7 1 610 8 2 95 -104 3 67	1 710 -12 2 145 135 3 750 -13	4 143 -132 5 275 -279 H= 5, K= 10	4 764 -10 H= 13, K= 11 0 674 77	0 205
2 1106 1085 4 523 543 6 163 185	0 1661 1639 1 114 90 2 1134 1141	2 203 195 3 534 -64 4 153 171 5 89 -31	4 463 -680 5 142 124 6 127 -145	6 740 -4 He 10, Ke 4 0 362 -340	5 690 -25 6 760 -47 H+ 11, K+ 5	1 201 -206 2 83 -99 3 83 -97	4 714 -63 He 15, Ke 7 0 487 484	1 730 9 2 740 7 H= 20, K= 8	2 58* -26 3 62* -60 4 67* -47	2 70+ 45 3 235 -230 H= 14+ K= 11	H= 10, K= 1 69 2 71
0 2766 -2892 2 2198 -2234 4 1051 -1027	4 428 416 5 650 -47 6 216 229	6 73* 65 H= 10, K= 2 0 1149 -1169	1 175 -159 2 510 16 3 173 153	2 145 -155 3 404 -402 4 62* 45	1 330 328 2 377 386 3 171 192	5 73* -61 H= 13, K= 6 1 58* 28	1 634 88 2 381 378 3 99 80 4 190 192	1 117 113 2 76* -40 H* U, K* 9	5 104 -93 H= 6+ K= 10 U 84 91 1 596 593	1 70° -19 2 71° 35 3 74° -23 H• 15, K• 11	H= 11, K= U 134 ~ 1 71=
6 371 -378 H= 3, K= 0 2 132 125 4 127 -114	He 10, Re 1 1 365 407 2 247 237 3 143 -135	1 839 848 2 847 -849 3 642 637 4 442 -414	6 610 -76 5 134 130 6 740 -49 He 11, Ke 3	5 213 -146 6 75* 4 H= 11, K= 4 1 51* -73	6 194 219 5 92 94 H# 12, K# 5	2 60* 35 3 63* -12 4 69* 70 5 76* 10	H= 16, K= 7 1 640 -21 2 94 72 3 700 23	2 530 -10 4 620 -70 He I, Ke 9 0 871 916	2 241 219 3 460 434 4 100 112 5 205 223	0 71= -73 1 71= 79 2 73= -58	2 94 3 750 He 12, Ke
6 670 -37 He 4. Ke 0 0 1172 -1243 2 201 -217	4 79 98 5 660 -67 6 730 24	5 328 333 6 157 -174 He 11, Ke 2 1 79 -89	0 288 284 1 1041 -1034 2 222 232 3 829 -819	2 91 -110 3 58° -8 4 93 -69 5 70° -85	2 570 48 3 610 -21 4 90 28 5 720 13	H= 14, K= 6 0 613 -602 1 232 210 2 378 -366	4 744 44 H= 17, K= 7 0 223 -238 1 674 -7/	1 521 -538 2 550 558 3 370 -353 5 500 527	H= 7, K= 10 1 58* 26 2 60* -80 5 87 49	He 16, Ke 11 1 734 4 2 744 -36	2 730 H= 13, H= U 720
4 437 -412 6 101 -86 H- 5, K- 0	0 747 -767 1 734 728 2 514 -524	2 133 -146 3 172 142 4 105 -87 5 202 182	4 120 113 5 395 -390 6 75* 69	H= 12, K= 4 0 321 313 1 658 631	HT 13, K+ 5 0 74 79 1 387 -404	3 125 145 4 226 -237 5 75* 79	2 233 -236 3 720 -55 4 105 -99	5 197 -184 H= 2, K= 9 1 514 69	4 680 -38 5 740 47 H- 8 K- 10	0 74+ 40 1 74+ 69 2 76+ 32	2 75+ H= 14, K+ 1 74+
4 385 -395 6 111 -116 H= 6, K= 0	6 275 -275 5 308 301 6 740 -105	6 75* -26 H= 12, K= 2 0 327 315	1 510 -17 2 500 71 3 580 -40	3 510 528 4 141 130 5 251 243	3 342 -335 4 670 44 5 124 -149	1 61° -5 2 153 -119 3 67° 41	1 69 2 71 -27 3 74 -2	3 196 -206 6 30 37 5 132 -128	1 195 -186 2 61* 32 5 110 -130	1 76* 8 H= 0, K= 12 0 652 646	0 101 1 760 Me 0. Ke
2 1651 1664 4 899 888 6 335 324	1 50+ -35 2 53+ 10 3 151 170	2 175 154 3 936 -928 4 63* 55	5 166 -153 H= 13, K= 3 U 406 399	1 75 -65 2 57• -19 3 61• 17	1 78 66 2 99 66 3 644 -80	H= 16, K= 6 0 458 459 1 111 -124	0 115 110 1 710 -5 2 730 68	0 107 -105 1 1035 1045 2 91 -95	> 7>* -64 H* 9, K* 10 1 AU* -1	4 253 240 He 1, Ke 12 1 590 2	2 308 - 4 217 H= 1, K=
2 640 648 4 258 241 6 115 116	5 114 110 6 758 -2 H= 13, K= 1	6 76° 27 H= 13, K= 2 1 87 -63	2 204 204 3 640 663 4 189 179	5 108 84 H= 14, K= 4 0 94 -82	> 84 -34 Hr 15, Kr 5 U 495 -469	3 69° -44 4 190 180 H= 17, X= 6	H= 20, K= 7 1 730 9 2 750 8	4 94 -83 5 378 371 H= 4, K= 9	3 66° -17 4 100 93 5 76° 20	2 190 199 3 650 1 4 690 108 He 2, Ke 12	2 67• 3 70• H= 2, K=
0 2294 -2293 2 1445 -1431 4 571 -532	0 128 107 1 678 -690 2 540 -21 3 444 -432	2 55 -20 3 89 -88 4 64 -52 5 152 -132	5 330 340 He 14, K# 3 1 55* -5 2 91 97	1 533 -543 2 81 -94 3 471 -459 4 68* -58	2 277 -277 3 271 272 4 186 -163	1 65* -43 2 68* 63 3 71* 13 - 75* 36	H= 21, K= 7 0 754 -30 1 754 45 H= 0, K= 8	1 64 -87 2 55• 55 3 158 153 4 64• 53	H= 10, K= 10 0 234 -256 1 251 -235 2 124 -121	0 406 -419 1 169 -152 2 3/4 -332 3 89 -62	0 242 1 60* 2 194 3 71*
6 307 -282 H= 9, K= 0 2 370 -354 4 91 -86	4 86 49 5 242 -221 H= 14, K* 1 1 88 -90	H= 14, K= 2 0 427 457 1 542 537 2 299 301	3 62° -22 4 67° 51 5 73° 89 H= 15, K= 3	5 223 -225 H= 15, K= 4 1 599 18 2 619 -3	5 145 154 HI 16, KI 5 1 620 36 2 96 -107	H= 18, K= 6 0 173 -169 1 68* -79 2 136 -151	0 872 -894 2 902 -949 4 494 -526 6 192 -231	5 152 160 H= 5, K= 9 0 515 -539 1 659 -671	3 205 -197 4 7L0 -47 He 11, Ke 10 1 630 9	4 159 -149 Me 3, Ke 12 1 600 -7 2 620 -40	He 3, Ka 1 66* 2 68* 3 71*
6 93 -28 H= 10, K= 0 0 1060 1091 2 759 765	2 56* -26 3 60* -8 4 66* -37 5 71* -57	3 361 375 4 174 166 5 197 214	0 361 -359 1 273 -274 2 211 -202 3 261 -270	3 64* -55 4 70* 49 5 75* -48	3 68° 48 4 72° -64 H= 17, K± 5	3 73° -33 H= 19, K= 6 1 70° -21 2 72° -30	He 1, KE 8 1 470 63 2 66 -54 3 127 107	2 318 -292 3 596 -588 4 234 -227 5 245 -261	2 65* -81 3 65* -44 4 73* -38 H= 12, 5* 10	3 66* -29 4 70* -31 H* 4, K# 12 0 76 -75	H= 4, K= 0 66 <sup>0</sup> 1 67 <sup>0</sup> 2 69 <sup>0</sup>
4 252 280 6 143 155 H= 11; K= 0	H= 15, X= 1 0 472 469 1 564 34	1 56* 7 2 119 110 3 62* -87	4 145 -141 5 121 -143 H* 16; K* 3	0 221 -235 1 298 283 2 164 -153	1 98 -93 2 238 248 3 70* -65	3 75* -10 H* 20, K* 6 0 71* 45	4 610 -51 5 670 88 6 730 -56	H= 6, K= 9 1 54# 18 2 57# -8 3 51# 6	U 62* -24 1 428 425 2 66* 6 1 326 319	1 346 342 2 79 -69 3 187 199 6 718 -28	3 72+ H= 5, K= 1 67+ 2 69+
4 59+ 40 6 74+ 4 H= 12, R= 0	3 62 95 6 203 161 5 73 27	5 73* 38 H= 16, K= 2 0 440 -443	2 61* 7 3 66* 18 4 70* 9	4 88 -52 H= 17, K= 4 1 62* 2	H= 18, K= 5 1 67* 2 2 104 71	2 74# 23 H# 21, K# 6 1 74# 0	0 908 942 1 855 -883 2 621 634	4 56* -59 5 102 -82 H= 7, K= 9	4 740 -45 H= 13+ K= 10 1 000 -11	H# 5, K# 12 1 62* 12 2 85 -80	3 720 H= 6. K= 0 167
2 216 -239 4 206 -228 6 754 -65	2 116 121 3 640 -63	2 3+3 - 3+1 3 64* -19 4 169 -167	H= 17, K= 3 U 87 -98 1 61+ -50	2 121 -121 3 69* 11 4 73* -48 H= 18, K= 4	4 766 29 H= 19, K= 5 0 125 -125	2 76 3 H= 22, K= 6 0 75 3 1 76 -43	3 657 -648 4 395 399 5 337 -326 6 167 172	1 135 134 2 300 287 3 140 153	3 714 62 4 754 -26 H= 14, K= 10	4 71+ -48 H= 6, K= 12 0 381 362	2 155 3 87 H= 7, K+
2 84 80 4 620 -49 H+ 14, X+ 0	5 740 -3 H= 17, K= 1 0 041 -663	H= 17, K= 2 1 104 102 2 63* -51	3 68° -39 4 72° 3 H* 18, K* 3	1 94 96 2 174 159 3 71• 72	2 120 -102 3 137 -126 H= 20, K= 5	H 0, K 7 2 190 194 4 97 91 6 72* 58	1 110 -111 2 52 83 3 123 -121	4 223 243 5 720 73 H= 8, K= 9 1 570 2	1 300 -296 2 69* 54 3 210 -221	2 293 288 3 226 -222 4 131 134	2 710 3 740 H= 8, K=
0 213 ~196 2 55* -79 4 65* -61 H= 15, K= 0	1 146 157 2 428 -441 3 107 89 4 229 -230	3 67* 13 4 88 -36 H* 18, K= 2 0 202 196	1 63• -1 2 66• -45 3 70• 2 4 74• -20	4 750 90 H3 19, K 4 1 680 -5 2 700 30	1 71° -3 2 73° -12 3 76° -28 H <sup>10</sup> 21, K* 5	H= 1, K= 7 0 1076 -1094 1 44* 82 2 1155 -1212	4 61* 45 5 213 -199 6 74* 23	2 59* -54 3 53* -50 4 58* 1 5 73* -13	H= 15, K= 10 1 690 -10 2 710 49 3 740 -20	H# 7, K\$ 12 1 63° -3 2 133 97 3 69° -31	0 178 1 70• 2 165 3 75•
2 57* 16 4 123 -84 H* 16+ K* 0 0 655 653	H= 18, K= 1 1 62* -2 2 111 -107 3 68* 11	1 131 -132 2 154 169 3 154 -161 4 73* 75	H 19, K 3 0 66* 93 1 144 160 2 69* 69	3 73+ 32 H= 20, K= 4 0 69+ -23 1 231 -247	0 72* -10 1 201 190 2 74* -5 H# 22* K* 5	3 116 137 4 419 -436 5 96 82 6 219 -228	0 275 -259 1 740 756 2 83 -101 3 680 678	H= 9, K= 9 0 155 -127 1 138 153 2 140 -156	H= 16, K= 10 0 700 -19 L 710 50 2 720 -1	4 110 74 H= 8, K= 12 0 305 -313 1 95 81	H= 9, K= 1 71* 2 73* 3 76*
2 486 498 4 245 245 H+ 17, K+ 0 2 61+ 191	4 73+ -52 H= 19, K+ 1 0 302 320	H= 19, K+ 2 1 66* 44 2 68* 14 3 71* -3	3 163 161 4 764 51 H= 20, K= 3	2 72 -74 3 202 -195 H= 21, K	1 75+ 1 H+ 0, X+ 6 0 2027 2023	н= 2, К= 7 1 184 -156 2 200 -216 3 53 10	4 62* -80 5 303 311 6 75* -18 H= 5, K= 8	3 105 104 4 680 -95 5 740 33 Hx 10, Kn 9	3 750 35 He 17, Ke 10 1 720 16 2 740 -30	2 246 -250 3 70° 56 4 108 -107 H* 9, K* 12	H= 10, K= 0 164 1 720 2 128
4 710 78 H= 16, K= 0 0 665 -692 2 508 -516	2 226 241 3 700 -84 4 132 137 H= 20, K= 1	4 75+ 7 H= 20+ K= 2 0 67+ -35 1 109 94	2 71 * 1 3 74 * 15 H= 21, K * 3	2 73* 3 H= 22. K= 4 0 73* -49	4 497 469 6 213 217 H= 1, K= 6	4 117 -113 5 65* 93 6 72* -56 He 3 K= 7	1 50• 48 2 53• 30 3 56• 8 4 63• -15	1 590 25 2 610 52 3 650 18 4 590 45	H= 18, K= 10 0 740 -53 1 740 95 2 117 -43	1 65° 12 2 68° -65 3 71° -24 4 75° -43	H. 11, K 1 730 2 750 H. 12, K
4 252 -249 H= 19, K= 0 2 674 -61	1 68* 12 2 69* 10 3 72* -3	2 70+ -23 3 73+ 96 H= 21, K= 2 70+ 5	1 140 -167 2 720 -10 3 129 -136	2 75 -50 H= 23, K= 4 1 76 -6	2 414 429 3 86 95 4 209 219	0 1113 1142 1 101 -105 2 662 663	5 149 147 6 750 17 H= 6, K= 8	5 75# 49 H= 11, K= 9 D 59# -28	H= 19, K= 10 1 76* 4 H= 0, K= 11 2 173 =149	He 10, Ke 12 0 144 141 1 214 204 2 127 124	0 740 1 740 H= 13, K=
H= 20, K= 0 0 674 128 2 184 174	0 69 21 1 70 23 2 71 -4	2 720 6 3 750 2 Ha 22, Ka 2	1 73* 4 2 75* 1 H= 23; K= 3	2 516 -522 4 268 -271 6 89 -74	6 71+ 63 H= 2, K= 6 0 1760 -1759	4 409 397 5 161 -154 6 155 170	1 146 -152 2 408 -425 3 202 -212	2 19 57 3 204 -215 4 714 39	4 123 -102 H= 1, K= 11 0 328 355	3 148 138 4 764 44 H= 11, K# 12	H= 0, K= 2 700 H= 1, K=
2 71* -5 H= 22+ K= 0 0 71* 116	H* 22. K 1 1 721 2 73. 16	1 95 -72 2 744 -28 H= 23, K= 2	1 100 88 H 0, K 4 0 2582 -2514	0 1952 2013 1 980 959 2 1187 1174	2 1111 -1137 3 362 -356 4 440 -445	1 222 216 2 72 76 3 55* -29	5 70= -75 H= 7, K= 8 1 71 -29	H= 12, K= 9 1 78 45 2 649 -34	2 246 253 3 62° 74 4 67° 55	2 700 19 3 730 44 He 12, Kr 12	1 69* 2 138 3 73*
H= 23, K= 0 2 759 21 H= 24, K= 0	0 113 -126 1 740 -32 H= 0, K= 2	H- 0, K- 3 2 293 303 4 116 130	6 215 -214 H= 1, K= 4	5 328 536 5 323 344 5 208 213	5 232 -238 6 220 -212 H= 3, K= 6 1 43* 59	5 112 -106 6 73* 33 H= 5, K= 7	2 55 -44 3 107 83 4 65 -80 5 71 -24	4 72+ -17 H= 13, K= 9 0 01+ 2	H= 2, K= 11 1 570 60 2 99 123	1 227 -237 2 71e -34 3 146 -155	1 69+ 2 71+ 3 73+
0 152 -155 H= 0, K= 1 2 852 876 4 379 412	0 .04 -794 2 1225 -1209 4 481 -493 6 232 -247	6 68° 45 H= 1, K= 3 O 336 -382 1 905 -925	1 138 116 2 336 -316 3 208 -216 4 180 -169	H= 2, K= 5 1 225 -188 2 405 391 3 237 236	2 250 -245 3 106 -108 4 114 -132 5 64* -32	0 46° -58 1 47° 28 2 157 156 3 126 107	H 8, K 8 0 955 933 1 137 -161 2 648 662	1 291 276 2 65* -26 3 272 268 4 73* -33	3 63° -53 4 67° 81 5 73° 11 H= 3, K= 11	Ha 13, Ka 12 1 70° -17 2 72° 10 3 75° -11	H* 3, K 0 69* 1 81 2 111
6 143 151 H= 1, K= 1 0 3398 -3900 1 620 -596	H 1, K 2 1 451 -394 2 134 -98 3 242 -233	2 39• -35 3 702 -736 4 104 -88 5 245 -245	5 61* -98 6 69* -73 H# 2, K# 4 0 241 266	4 183 176 5 83 98 6 70* 65 H= 3, K= 5	6 85 -58 H= 4, K= 6 0 580 583 1 690 704	4 78 -59 5 113 82 6 74* 10 H= 6, K= 7	3 92 -99 4 424 424 5 710 -41 H= 9; K= 8	H= 14, K= 9 1 81 -46 2 67= -9 3 70= 42	0 233 -255 1 324 -324 2 146 -139 3 241 -255	He 14, Ke 12 0 710 -15 1 93 81 2 740 -27	H= 4, K= 1 70* 2 72*
2 2512 -2519 3 156 157 4 1156 -1157 5 60* -11	6 530 -55 5 120 129 6 680 -63 H= 2, K= 2	6 68° -30 H= 2, K= 3 1 62 -48 2 39° 55	1 2042 2039 2 564 592 3 1284 1339 4 213 220	0 838 -836 1 1650 -1647 2 601 -627 3 1150 -1181	2 288 287 3 472 492 4 285 304 5 159 188	1 49° -39 2 167 173 3 57° -5 4 62° 39	1 73 -75 2 102 98 3 61* -28 4 91 76	4 740 -16 H= 15, K= 9 0 060 -22 1 237 -229	4 87 -73 5 123 -129 H= 4, K= 11 1 100 -103	H= 15, K# 12 1 730 15 2 750 -27 H= 16, K# 12	H= 5, K= 0 70* 1 153
6 485 -481 H= 2+ K* 1 1 688 -563 2 408 -376	0 1155 1112 1 281 -295 2 1091 1074 3 898 -891	3 116 -106 4 540 -29 5 241 -251 6 690 -13	5 676 670 6 69* 94 H* 3, K* 4 1 249 -244	4 243 -240 5 625 -653 6 90 -112 H= 4, K= 5	6 98 113 H= 5, K= 6 1 215 221 2 188 -191	5 68° 64 6 75° 29 He 7, K= 7 0 1305 -1237	5 720 -42 H= 10, K= 8 0 591 -595 1 122 109	2 69* -49 3 180 -178 4 76* -27 H= 16: K= 9	2 60° -13 3 64° 11 9 68° -18 5 74° -42	0 74* 86 1 75* 28 H= 0, X* 13 2 64* 84	2 72* 3 126 H* 6* K* 1 71*
3 334 -307 4 252 -244 5 61* 64 6 108 -101	4 392 405 5 169 -176 6 216 204 H= 3, K= 2	H= 3, K= 3 0 1262 -1204 1 2368 2366 2 205 -184	2 42* -27 3 237 255 4 55* 55 5 234 240	1 206 209 2 45° -46 3 51° -75 4 57° -7	3 540 -46 4 600 -26 5 660 11 6 730 11	1 79 57 2 891 -912 3 58* 16 6 507 -481	2 400 -480 3 113 98 4 255 -248 5 730 28	1 690 -13 2 700 21 3 730 -13	H= 5. K= 11 0 570 -62 1 576 575 2 82 -48	4 96 81 H= 1, K= 13 0 542 -546 1 86 -73	2 73* H= 7, K= 0 104 1 150
He 3, Ke 1 0 632 580 1 30e 34 2 1051 1049	1 1283 -1033 2 254 237 3 227 222 4 92 97	3 1634 1638 4 276 -278 5 679 647 6 109 -98	6 70 10 H# 4, K# 4 0 312 321 1 2125 -2132	5 132 -143 6 710 -17 H= 5, K= 5 0 382 -606	H: 6, K: 6 0 1141 1145 1 306 -321 2 006 651	5 69* 34 6 223 -218 H= 8, K= 7	H= 11, K= 8 1 100 84 2 608 -44 3 668 -63	0 135 120 1 70• 27 2 91 104 3 75• 19	3 425 409 4 69* 16 5 193 207 He 6, 5* 11	2 396 -398 3 68 -26 4 253 -259 H= 2, K+ 13	2 209 H= 8, K+ 1 73+ 2 75+
3 388 -369 4 298 302 5 114 -135 6 122 145	5 204 -212 6 69% 37 H= 4, K= 2 0 996 -927	H= 4, K= 3 1 36* 15 2 85 -86 3 223 226	2 43° 21 3 1639 -1649 4 276 286 5 776 -766	1 975 996 2 282 -275 3 8+3 855	3 121 -107 4 237 206 5 67* -40	2 179 -176 3 58* 17 4 196 -191 5 70* -8	6 699 -14 5 749 58 H= 12, X= 8 0 589 56	H= 18, K= 9 1 72 15 2 74 -9 H= 19, K= 9	1 60° 52 2 62° -98 3 65° 71 4 70° -61	1 63° -25 2 106 -49 3 68° -17 4 72° -48	H= 9, K= 0 148 1 74= 2 141
H• 4, K• 1 1 411 345 2 39• -15 3 46• -53	1 2046 1949 2 344 -321 3 1178 1131 4 217 -199	4 97 -100 5 282 293 6 704 -52	6 71+ 72 H= 5, K= 4 1 192 205 2 151 -180	5 323 347 6 72* -38 H* 6, K* 5	H 7, K 6 1 144 -130 2 329 337	H= 9, K= 7 0 1332 1369 1 53* 12	1 60° -67 2 103 88 3 125 -126	0 740 -97 1 123 114 2 95 -77	5 750 55 H= 7, K= 11 0 369 351 1 470 -458	H= 3, K= 13 0 131 131 1 168 162 2 93 102	He 10, Ke 1 750 He 11, Ke 0 99
4 17 -59 5 61* -69 6 68* -27	5 606 581 6 87 -63 H= 5, K= 2	0 489 498 1 2297 -2263 2 283 313 3 1543 -1543	3 116 -115 4 137 125 5 169 -196	2 247 -237 3 53* -52 4 166 -140	+ 200 188 5 68+ 31 • 74+ 76	3 60° -32 4 614 609 5 71° -32	5 750 -46 H= 13, K= 8 1 614 38	1 76* -5 H= 0, K= 10 0 214 212	2 197 205 3 297 -294 4 105 85	3 91 60 4 87 55 H= 4, K= 13	H= 0. K= 0 71+ 2 73+
0 1154 1147 1 1270 1192 2 873 905	2 414 -35 3 168 171 4 85 -63 5 314 330	4 362 346 5 787 -754 6 114 95	H= 6, K= 4 0 505 -493 1 1085 1065	6 73* -45 H• 7, K= 5 0 1181 1202	0 1838 -1845 1 72 -73 2 1228 -1193	H= 10, K= 7 1 81 76 2 144 154 3 61* -21	2 63 - 23 3 67 12 4 71 - 26 H= 14, K= 8	4 202 216 H= 1, K= 10 1 544 23	1 620 11 2 131 114 3 670 -61	2 664 -7 3 699 21 4 739 -16	1 720 2 730 H= 2, K
4 536 529 5 453 436 6 189 185	6 70* -7 H* 6, K* 2 0 441 -416	1 238 234 2 100 -103 3 117 -93	3 841 856 4 199 -226 5 375 357	2 920 902 3 544 -57 4 344 323	+ 671 -657 5 690 -16 6 260 -276	+ 154 143 5 724 -27 H= 11, K= 7 0 617 -610	0 231 220 1 175 175 2 167 183 3 165 186	6 360 -68 3 600 -27 4 650 -9 5 704 -29	H= 9, K= 11 0 286 -319 1 63* -23	0 237 240 1 149 -130 2 177 167	1 72 2 74 H• 3, K•
1 411 -390 2 230 216 3 270 282	2 521 -533 3 1387 -1422 4 211 -208	5 197 -202 6 710 40 H= 7, K= 3	H= 7, K= 4 1 61 96 2 232 -249	7 67* 9 6 179 162 H= 8, K= 5 1 182 -181	1 111 -111 2 246 -217 3 58* 31	1 92 -58 2 466 -471 3 629 -23 4 219 -212	4 94 85 He 15, K= 8 1 640 -39 2 670 58	H4 2, K= 10 0 524 55 1 478 482 2 117 -122	2 232 -209 3 68* -43 4 100 -35 H= 10, K= 11	4 104 123 H= 6, K= 13 1 650 3	2 740 H= 4, K 0 720
5 140 132 6 96 100 H 7, K 1	6 149 -129 H= 7, K= 2 1 429 397	1 811 806 2 94 62 3 784 794	3 530 -59 4 594 -33 5 650 43 6 730 -41	2 396 388 3 55* 28 4 152 155 5 83 39	4 225 -233 5 690 -24 6 760 -98 H= 10, K+ 6	5 73* -16 H= 12, R= 7 1 58* 35 2 40* -55	5 /0* 37 4 74* 18 H= 16, K= 8 0 248 -239	3 350 345 4 650 -82 5 212 200 H= 3, K= 10	2 B1 -77 3 690 -16 4 730 -52	3 700 -6 4 740 44 He 7, Ke 13	2 740 He 5, Ki 1 730
0 1770 -1722 1 1076 -1083 2 1662 -1686 3 813 -828	2 170 -174 3 240 -234 4 576 -71 5 138 -163	4 219 218 5 357 385 6 720 60 H= 8, K= 3	H= 8, K= 4 0 335 307 1 45* 5 2 270 264	6 740 74 H= 9, K= 5 0 1341 -1323 1 100 -165	0 1191 1214 1 159 136 2 894 883 3 59* 88	3 630 -27 4 680 17 5 740 44 H= 13, K= 7	1 171 -172 2 194 -207 3 132 -128 4 124 -105	1 540 -73 2 76 104 3 610 59 4 650 56	H= 11, K= 11 0 63# 89 1 389 386 2 67# 72	0 320 -304 1 66• 9 2 201 -215 3 71• -2	0 740 1 118 Ha 7, Kr
4 678 -600 5 358 -361 6 299 -297 H= 8, K= 1	6 714 -49 H# 8, K= 2 0 1468 1421 1 625 600	1 107 -93 2 84 -100 3 76 -71 4 89 107	3 54* 30 4 60* -70 5 66* 26 6 73* 31	2 806 -780 3 181 -174 4 410 -396 5 96 -84	4 506 512 5 709 15 H= 11+ K+ 6 1 97 82	0 279 -275 1 59° 34 2 208 -197 3 79 -22	H= 17, X= 8 1 690 7 2 700 -13 3 730 -15	5 87 84 He 4, K= 10 0 336 -341 1 716 -701	3 280 282 4 75* 12 H= 12, K= 11 1 67* 21	4 150 -137 He 8, Ke 13 1 67e -3 2 69e -43	1 754 H 8, K 0 754 H 1, K
1 41° 41 2 513 -501	2 1066 1071 3 459 436	5 650 22 6 730 39	H= 9, K+ +	6 190 -175	2 125 118	4 143 -134	H= 18, K= 8	2 226 -213	2 690 15	3 72• -16	0 740

which yielded the position of the remaining carbon atom. Because of the large thermal motion of the ester carbon atoms, no attempt was made to locate hydrogen atoms. In this and subsequent least-squares calculations, the quantity minimized was  $\sum w |F_o - F_c|^2$ .

The position and anisotropic thermal parameters were refined by successive cycles of block-diagonal least-squares calculations with a weighting scheme  $w = \{1 + [(|F_0| - 40)/50]^4\}^{-1}$  until all parameter shifts were less than 0.25 times the standard deviation of the parameter. After this refinement, the R index (R = $\sum |F_o - F_c| / \sum |F_o|$  based on observed reflections only was 0.043. The mean value of the final  $w(|F_o| - |F_c|)^2$ showed little variation over the range of  $|F_{a}|$ . In all structure factor calculations, the atomic scattering factors were taken from International Tables for X-ray Crystallography (1952) and corrections for anomalous dispersion by silver and phosphorus were made using the values given by Cromer & Liberman (1970). The observed and calculated structure factors are listed in Table 1. The final atomic positions are listed in Table 2 and the final thermal parameters are listed in Table 3.

# Table 2. Fractional coordinates and estimated standard deviations

	x	У	z
Ag	0.19051 (4)	0.17558 (5)	-0.01017 (11)
P	0.14186 (12)	0.09508 (18)	0.48733 (37)
<b>O(</b> 1)	0.1600 (5)	-0.0084(5)	0.4458 (16)
O(2)	0.0780 (4)	0.1067 (8)	0.3438 (16)
O(3)	0.1917 (3)	0.1589 (4)	0.3806 (9)
O(4)	0.1297 (4)	0.1061 (7)	0.7312 (11)
C(1)	0.1809 (8)	<i>−</i> 0·0426 (9)	0.2412 (26)
C(2)	0.1734 (9)	<i>−</i> 0·1458 (10)	0.2377 (38)
C(3)	0.0237 (10)	0.1280 (21)	0.3398 (45)
C(4)	-0.0262 (8)	0.1302 (14)	0.1860 (33)

#### **Results and discussion**

The overall structure is composed of independent columns, centered on the  $2_1$  axes parallel to c. Each column has four silver ions per repeat unit inside, close to the column axis, and four diethyl phosphate anions per repeat unit on the outside. Fig. 1 shows the packing of these columns within the unit cell.

A drawing of the diethyl phosphate anion in the

silver diethyl phosphate crystal is shown in Fig. 2. Table 3 shows that all atoms in the anion have moderate to large thermal motion (or disorder) which reaches a maximum r.m.s. radial displacement for C(3) of 0.95 Å. A marked apparent distortion of bond lengths and angles is expected to arise from such large thermal motion and, indeed, the C(4)-C(3) and C(3)–O(2) bonds of 1.35 and 1.14 Å are unreasonably short and the C(3)–O(2)–P angle of  $147^{\circ}$  is unreasonably large (Tables 4 and 5). A similar situation exists in the one other diethyl phosphate structure reported. barium diethyl phosphate (Kyogoku & litaka, 1966). where thermal motion in the ester groups is high and a carbon-carbon bond length of 1.37 Å is reported. Corrections for thermal motion can only be made if a specific model for the relative motion of the various atoms is assumed. Such assumptions and their derived bond lengths are fraught with considerable uncertainty in this particular structure.

# Table 4. Bond distances within the anion with thermal motion corrections

Estimated standard deviations are given in parentheses.

	Un-		Corrected	
	corrected ]	Rigid PO <sub>4</sub>	Lower limit	Upper limit
PO(1)	1·549 (8) Å	1•57 Å	1·55 Å	1·78 Å
P—–O(2)	1.548 (9)	1.58	1.57	1.87
PO(3)	1.497 (6)	1.51	1.20	1.69
PO(4)	1.459 (7)	1.49	1.47	1.80
C(1)-O(1)	1.363 (17)		1.36	1.77
C(3) - O(2)	1.138 (22)		1.18	2.12
C(2) - C(1)	1.488 (19)		1.48	2.01
C(4) - C(3)	1.353 (29)		1.37	2.26

#### Table 5. Bond angles within the anion

Estimated standard deviations are given in parentheses.

	Angle
O(1)-PO(2)	102.4 (5)
O(1)-PO(3)	111.1 (4)
O(1)-PO(4)	107.4 (5)
O(2)-PO(3)	105.4 (4)
O(2)-PO(4)	112.4 (5)
O(3)-PO(4)	117.2 (4)
C(1) - O(1) - P	124 (1)
C(3)-O(2)-P	147 (2)
C(2)-C(1)-O(1)	110 (1)
C(4) - C(3) - O(2)	137 (2)

Table 3. Thermal	parameters and	their estimated	l standard d	leviations (	$(\times 10^{4})$	)
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Temperature factor = exp  $\left[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\right]$ 

	$U_{11}$	U <sub>22</sub>	U <sub>33</sub>	$U_{12}$	$U_{13}$	$U_{23}$	R.m.s. radial displacement (Å)
Ag	0.0953 (4)	0.0899 (4)	0.0577 (4)	-0.0026 (6)	0.0019 (4)	0.0077 (4)	0.493
P	0.079 (1)	0.088 (1)	0.045 (1)	-0.019(2)	0.000 (1)	0.000 (1)	0.461
<b>O(</b> 1)	0.150 (7)	0.084(5)	0.140 (8)	-0.026(7)	0.025 (6)	0.006 (5)	0.612
O(2)	0.088 (5)	0.254 (12)	0.127 (7)	-0.028(10)	-0.031(6)	-0.021(8)	0.686
O(3)	0.073 (4)	0.075 (4)	0.049(3)	-0.012(5)	0.004 (3)	0.000 (3)	0.444
O(4)	0.148 (7)	0.189 (9)	0.059 (4)	0·091 (10)	0.012(5)	-0·014 (5)	0.630
C(1)	0.192 (15)	0.084 (8)	0.140(12)	-0.004(13)	0.035 (12)	-0.028(8)	0.645
C(2)	0.194 (17)	0.091 (9)	0.250 (23)	-0.012(15)	-0.023(17)	-0.014(17)	0.731
C(3)	0.144 (16)	0.499 (40)	0.257(25)	0.134 (31)	-0.104(18)	-0.112(30)	0.950
C(4)	0.123 (12)	0.241 (20)	0.181 (16)	0.001 (19)	-0.046(12)	-0.051 (16)	0.739

An examination of the thermal ellipsoids in Fig. 2 and the r.m.s. radial thermal displacements in Table 3 rules out a rigid body motion of the whole molecule. The relatively small r.m.s. displacement of O(3) and the magnitudes and directions of the displacements of phosphorus and the other three oxygen atoms suggest that the PO<sub>4</sub> group itself may behave approximately as a rigid body with a major axis of rotation along the P-O(3) bond. The r.m.s. displacement of carbon atom C(3) is larger than that of the terminal carbon atom C(4) and this suggests the possibility of an additional librational motion of the ester group about the P-O bond.

An attempt to analyze the rigid body motion quantitatively was made with the computer program MGTLwritten by Schomaker & Trueblood (1968). It was impossible to obtain a satisfactory rigid body description in terms of all the heavy atoms of the anion, and this is in accord with the qualitative picture discussed above. With the PO<sub>4</sub> group alone as a rigid body an r.m.s. value of 0.0059 Å was obtained for the difference between the  $U_{ij}$ 's observed for the atoms in the PO<sub>4</sub> group and those calculated for rigid body motion. The model derived from these calculations has two main axes of librational motion. The first axis, associated with an r.m.s. amplitude of  $13.2^{\circ}$ , passes close to the phosphorus atom and makes an angle of 18.4° with the P-O(3) bond direction. The second axis, r.m.s. amplitude of 11.3°, is almost perpendicular to the first, but its intersection with it is displaced from the phosphorus atom by 0.80 Å in the direction of O(3). The third principal axis is associated with a small negative value for the mean square amplitude of libration. Phosphorus-oxygen bond distances corrected for the rigid body motion of the PO<sub>4</sub> group are given in Table 4. The corrected bond lengths are in accord with those found for bonds from phosphorus atoms to esterified and non-esterified oxygen atoms (Karle & Britts, 1966; Kyogoku & Iitaka, 1966; Li & Caughlan, 1965).

The carbon-oxygen and carbon-carbon bond



Fig. 1. A stereoscopic view of the unit-cell contents, looking down the column axes. Silver ions are indicated by the large open circles.



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

lengths are all smaller than would be expected and this is undoubtedly connected with the large thermal motion of these atoms. The bond lengths and angles involving C(3) are quite unreasonable, but the upper and lower limits of the corrected bond lengths (Table 4) calculated by the method of Busing & Levy (1964), span a range that includes the commonly accepted values. Both the C(3)–O(2)–P and C(4)–C(3)–O(2) angles are considerably larger than what would be expected (120 and 110° respectively) but an apparent opening out of the C(3)-O(2)-P would be anticipated if considerable rotational motion of C(3) about the O(2)-P bond occurred. If, as is likely, the C(4) atom was constrained by intermolecular forces so that it could not take on large excursions, librational motion of C(3) about O(2)-P would be expected to open up the apparent C(4)-C(3)-O(2) angle.

This thermal-motion analysis and the bond-length corrections derived from it are consistent with a model for the diethyl phosphate anion which involves rigidbody motion of the PO<sub>4</sub> group, plus a rotational motion of each ester group about the P–O bonds. However, these two types of motion are correlated in such a manner as to prevent very large excursions of the terminal methyl groups. It is unlikely that any more stringent tests of the model can be applied to the  $U_{ij}$ 's because with the very large thermal motion present in the structure, the validity of fitting the motion with six  $U_{ij}$ 's is in itself questionable.

The silver ions are coordinated to four oxygen atoms in a distorted tetrahedral arrangement as shown in Fig. 3. Atom O(3) and atom O(4) are members of phosphate tetrahedra displaced one unit cell from each other along c. The Ag-O coordination distances and the O-Ag-O angles are listed in Table 6. The next closest Ag-O approach beyond the distorted tetrahedral coordination is at 3.64 Å.

# Table 6. Coordination distances and angles within the coordination tetrahedron of silver

Estimated standard deviations are given in parentheses.

	Uncor- rected	Cor- rected*		
Ag-O(3) Ag-O(3')	2·303 (5) Å 2·474 (6)	2·376 Å 2·530	O(3) - Ag - O(4') O(3) - Ag - O(3')	$130.4(3)^{\circ}$ 103.7(2)
Ag-O(3'')	2.460(6)	2·517	O(3)—Ag- $O(3'')O(3')$ —Ag- $O(4')$	$111 \cdot 1$ (2)
Ag-0(4)	2.191 (0)	2.303	O(3') - Ag - O(4') O(3') - Ag - O(3'')	90·9 (2)
			O(3'')-Ag- $O(4')$	105.3 (3)

\* Corrected for thermal motion assuming no correlation between the motions of the silver and oxygen atoms.

The Ag–O distances within the coordination sphere of silver average 2.36 Å with two approaches of 2.19 and 2.30 Å which are much shorter than the other two. Short approaches of 2.34 Å in Ag<sub>3</sub>PO<sub>4</sub> (Helmholtz, 1936) and 2.40 Å in AgCN 2AgNO<sub>3</sub> (Britton & Dunitz, 1965) have been attributed to partial Ag–O



Fig. 3. Bond distances in the coordination sphere of the silver ion. O(4') is related to O(4) by x, y, z-1. O(3') is related to O(3) by  $\frac{1}{2}-x$ , y,  $z-\frac{1}{2}$  and O(3'') is related to O(3) by  $x, \frac{1}{2}-y, z-\frac{1}{2}$ .

covalent bonding and it is likely that covalent interactions also exist in silver diethyl phosphate. However, in this case, effects of such partial covalent bonding on the phosphorus-oxygen bond lengths would be masked by the large thermal motion of the phosphate group.

The conformation of the ester groups with respect to the phosphate group can be described by the dihedral angle between the COP and OPO planes. Using the convention of Klyne & Prelog (1960) and the nomenclature of Sundaralingam (1969), these angles are  $\omega = 68^{\circ}$  for C(1)–O(1)–P–O(2) and  $\omega' = 125^{\circ}$  for C(3)–O(2)–P–O(1) and the conformation can be described as *syn*-clinal (sc), *anti*-clinal (ac). In barium diethyl phosphate (Kyogoku & Iitaka, 1966), these angles are  $\omega = 68\cdot2^{\circ}$  and  $\omega' = 71\cdot6^{\circ}$  and the conformation is sc, sc.

## Computer programs used

Fourier, least-squares and absorption calculations were carried out with the NRC crystallographic programs of Ahmed, Hall, Pippy & Saunderson (1966). The analyses of thermal motion were made with the ORFFE program of Busing, Martin & Levy (1964) and the program *MGTLS* written by Schomaker & Trueblood (1968). The drawings were made with the *ORTEP* program of Johnson (1965).

The construction and programming of the computercontrolled diffractometer used in this work was partly supported by Biotechnology Resource Grant RR-220 from the National Institutes 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 diffractometer.

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# Concerning Systems for the Generating and Coding of Layered, Tetrahedrally Close-Packed Structures of Intermetallic Compounds

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Planar, tetrahedrally close-packed structures containing pentagon-triangle primary nets are analyzed on the basis of their secondary-net tessellations and geometry. Included are: (1) the structures generated and coded by Pearson and Shoemaker containing secondary-net tessellations of  $4^4$ ,  $3^6$ ,  $3^34^2$ , and  $3^2434$ ; (2) the structures derived by Kripyakevich in which secondary-net tessellations of  $3^44$  and  $3^54$  occur; and (3) some structures, generated here for the first time, with some secondary-net tessellations of  $3^5$ . We have extended the coding scheme of Pearson and Shoemaker to describe the second group of structures. It becomes complicated for structures with secondary nets that are not based on two sets of parallel lines. However, the simpler code proposed by Kripyakevich does not uniquely define these structures. Neither coding scheme adequately describes the third group of structures.

### Introduction

'Tetrahedrally close-packed' (t.c.p.) structures are structures in which all atoms have interpenetrating triangulated coordination polyhedra with coordination numbers (C.N.) 12, 14, 15 or 16, and in which all interstices are tetrahedral. Many of the known examples of t.c.p. structures are 'planar'; that is, they are generated by the alternate stacking of main (primary) layers, in mirror planes, consisting of hexagon- and/or pentagon-triangle nets of atoms and subsidiary (secondary) layers which are less dense and consist of triangle, rectangle-triangle, or rectangle nets between the mirror planes. The pentagons and the hexagons of the primary nets are covered antisymmetrically by the pentagons and hexagons of the neighboring primary nets, and the atoms of the interleaving secondary nets center (in projection) all the pentagons and hexagons of the primary nets.

In Fig. 1, projections are shown of fragments of structures which have primary nets consisting in (a) of

hexagons and triangles and in (b) of pentagons and triangles. The secondary nets in these two cases differ in geometry. They consist in (a) of (approximate) squares and (approximately) equilateral triangles, and in (b) of rectangles (ratio of the two sides about  $\sqrt{3}/2$ ) and of isosceles triangles with two angles of about 55° and one angle of about 70° (Shoemaker & Shoemaker, 1969). The polyhedra surrounding the atoms of the secondary nets in (a) share triangular faces perpendicular to all edges of the squares and triangles in the secondary net, and in (b) share triangular faces perpendicular to the short edges of the triangles and rectangles, but share edges in the planes perpendicular to the long edges of the net. To emphasize this asymmetry in the secondary nets of pentagon structures we will indicate the long edges of the nets by full double lines and the short edges by full lines. (These lines connect second-nearest neighbors and do not represent bonded contacts.)

In analyzing possible t.c.p. structures it is convenient to consider the possible configurations of the secondary