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The Crystal and Molecular Structure of Calcium 1-Naphthyl Phosphate Trihydrate, $Ca(C_{10}H_7HPO_4)_2.3H_2O$*

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Crystals of $Ca(C_{10}H_7HPO_4)_2 . 3H_2O$ have symmetry $P\bar{1}$ with $a=7{\cdot}244 \pm 0{\cdot}002$, $b=8{\cdot}994 \pm 0{\cdot}003$, $c=18{\cdot}725 \pm 0{\cdot}004$ Å, $\alpha=95°41' \pm 4'$, $\beta=101°28' \pm 3'$, $\gamma=88°52' \pm 5'$, $Z=2$, $D_o=1{\cdot}503$, $D_c=1{\cdot}508$ g.cm^{-3}. 1750 intensities were estimated visually and corrected for size factor, Lorentz and polarization factors, and absorption. The structure was solved from a three-dimensional Patterson function, a minimum function, and a three-dimensional Fourier synthesis. Least-squares refinements including first isotropic, then the anisotropic temperature factors were carried out, giving the final R value of 0·097 for 1724 observed reflections. The four phosphate oxygen atoms are distributed in the following manner. One oxygen atom is bonded to the naphthyl group, another is bonded to a hydrogen atom, and the other two are coordinated to two calcium atoms which are related to one another by an inversion center. Neighboring phosphate groups are joined together by hydrogen bonding. Each calcium is coordinated to seven oxygen atoms, four of which are contributed from four nearby phosphate groups and the other three from water molecules. The oxygen atoms around the calcium are arranged in a distorted pentagonal bipyramid, the average girdle O–Ca–O bond angle being 72°. The bond distances and angles are as follows: P–O: 1·472–1·592, average 1·529 Å; O–P–O angle: 102·9°–116·8°; C–C: 1·272–1·477, average 1·376 Å; C–C–C angle: range 114·7°–126·8°. The molecules are held together by strong hydrogen bonding.

Introduction

Accurate structural knowledge of the organic phosphates is of interest and importance in understanding their behavior. Many biologically important substances are organic phosphates and the C–O–P linkage is of great importance, since hydrolysis at this bond is frequently involved in their metabolism. Many studies on the rates of hydrolysis have been made (*e.g.* Haake, 1960), but a correlation of the results with structures to establish reasons for different rates has not been possible since there is a lack of accurate structural knowledge. Furthermore, details of the bonding between phosphorus and oxygen, as for example, the amount of π character or the effect of different organic groups on the bond distances, have been only speculative.

Up to the present time, few accurate structures have been determined for organic phosphates and, to our knowledge, none involving naphthyl groups. The structure of dibenzyl phosphate was solved by Dunitz & Rollett (1956), calcium thymidylate by Trueblood, Horn & Luzzati (1961), 2-aminoethanol phosphate by Kraut (1961), adenosine-5′-phosphate by Kraut & Jensen (1963). A refinement of cytidylic acid has been completed by Sundaralingam & Jensen (1964).

Calcium 1-naphthyl phosphate was chosen for this study because we are interested in the effect of mono-, di-, and tri-aromatic esterification on the P–O bond lengths and rates of hydrolysis. Furthermore, we had just completed an indexing and checking method for triclinic crystals and welcomed the opportunity to try it out on this triclinic crystal. At the time this study was started, we were not concerned with the calcium coordination or hydrogen bonding, but these have proved to be interesting aspects of the study.

Experimental

Calcium naphthyl phosphate was purchased as a powder from Aldrich Chemical Company. Chemical analysis of the compound showed that it was $Ca(C_{10}H_7HPO_4)_2 . 3H_2O$. Since it was considered possible that the crystals used for the structural analysis might be some other calcium naphthyl phosphate, inasmuch as there was some uncertainty in the composition of the original compound*, it was established by infrared spectra that the two were the same substance.

Good single crystals were obtained by slow evaporation at room temperature of a saturated aqueous solution of $Ca(C_{10}H_7HPO_4)_2 . 3H_2O$. The crystal used for this X-ray work was a parallelepiped 1·3 mm long and with a cross section of 0·22 by 0·13 mm. Unit-cell parameters were determined from zero level precession, rotation, and zero level Weissenberg photographs. The Weissenberg camera diameter was calibrated with sodium chloride. The unit cell was triclinic with param-

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* The compound was purchased from the Aldrich Chemical Company as $CaC_{10}H_7PO_4$. Subsequent analysis and the solution of the structure has shown it to be $Ca(C_{10}H_7HPO_4)_2.3H_2O$.

eters $a=7{\cdot}244 \pm 0{\cdot}002$, $b=8{\cdot}994 \pm 0{\cdot}003$, $c=18{\cdot}725 \pm 0{\cdot}004$ Å°, $\alpha=95°41' \pm 4'$, $\beta=101°28' \pm 3'$, $\gamma=88°52' \pm 5'$, where the uncertainty represents the standard deviation. The density was determined by flotation, carbon tetrachloride diluted with ether being used as the substrate. The observed density was 1·530 g.cm^{-3}, while the calculated density was 1·508 g.cm^{-3} on the basis of two molecules per unit cell. Integrated precession photographs and multiple film equi-inclination Weissenberg photographs ($k=0$ to $k=5$) were taken with Cu $K\alpha$ radiation. All intensities were estimated visually by comparing with a standard intensity scale. The Weissenberg intensities were corrected for size factor (Phillips, 1954, 1956), Lorentz and polarization factors, and absorption (the linear absorption factor for Cu $K\alpha$ is 39·6 cm^{-1}). There were 1750 unique observed reflections and 1024 unobserved reflections. Precession intensities, corrected by Lorentz and polarization factors, were used chiefly to scale the different Weissenberg levels to a common base. Final adjustments of the scale factor for each level were made from the Wilson plots, where the individual level Wilson plots were adjusted with a scale factor to fit the overall Wilson plot. After all Weissenberg levels were scaled to a common base, the overall Wilson plot was calculated again and is shown in Fig. 1. This was used to obtain the overall temperature factor and scale constant. The intensity distributions for the $h0l$ and the $0kl$ zones were examined by the method of Howells, Phillips & Rogers (1953). The results (Fig. 2) indicate that the crystal has the symmetry $P\bar{1}$.

Determination of structure

The positions of the calcium and phosphorus atoms were found by interpretation of a three-dimensional $|F|^2$ synthesis. Both sharpened and unsharpened three-dimensional Patterson maps were calculated and used in the solution. Three heavy atoms, not related by symmetry, and their symmetric equivalent should produce three single-weight peaks and six double-weight peaks in the three-dimensional $|F|^2$ map. Since more peaks appeared than were indicated by the three heavy atoms, the correct heavy atom positions were checked in a systematic way by an addition method which is discussed in detail by Li (1964).

The oxygen atoms were located in three different ways by further examination of the three-dimensional Patterson map. First, the vicinity around each peak resulting from a vector point involving the phosphorus –phosphorus interaction was examined for peaks of about the expected weight and distance from the phosphorus. Secondly, large peaks in the three-dimensional Patterson map, other than those due to the heavy atom interactions were suspected as being due to the superposition of many smaller peaks. Ca–O and P–O appeared the most likely. Finally, a minimum function was computed from the three-dimensional Patterson function using heavy atom vectors as search vectors. From these methods, all the oxygen atoms in the phosphate groups and the water oxygen atoms were found.

The remaining carbon atoms were found from a three-dimensional Fourier synthesis using phases determined by the calcium, phosphorus and oxygen atoms. Also the minimum function calculated from the sharpened Patterson function showed all the carbon atoms, although some were not present in the minimum function from the unsharpened Patterson function. Al-

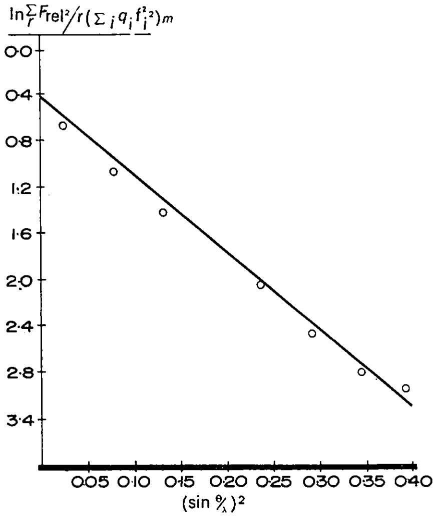

Fig. 1. Wilson plot for calcium 1-naphthyl phosphate trihydrate.

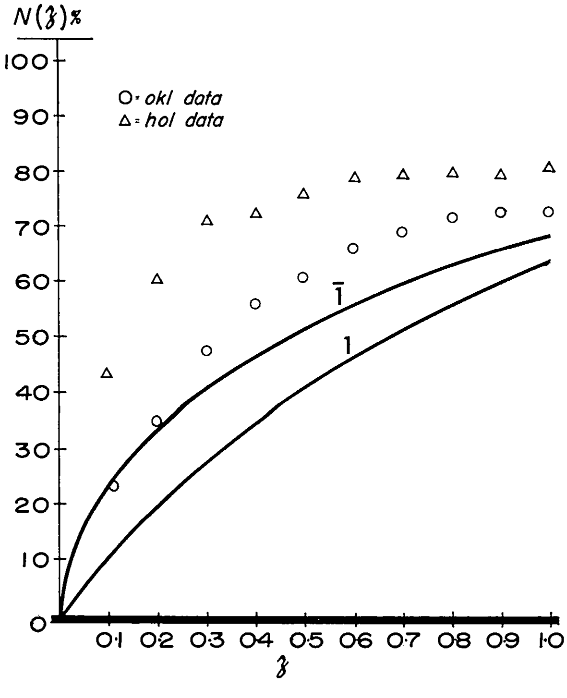

Fig. 2. Statistical distribution of intensities. Solid lines indicate theoretical distribution.

though we failed to recognize the whole structure, the first minimum function calculated from a sharpened Patterson function showed all the oxygen and carbon atoms in the cell.

Refinement

Refinement of the structure was carried out on an IBM 1620 Model I data processing machine using the least-squares refinement program of van der Helm (1960) modified for card input and output by Svetich (1964). Since the block-diagonal approximation was used in solution of the normal equations matrix, the convergence in the refinement process was very slow. Twenty-two cycles of isotropic and 14 cycles of anisotropic refinement were carried out. The weighting scheme of Hughes (1941) was used. In the process of refinement, 16 strong and low angle reflections which appeared to be affected most by primary extinctions were removed. Also, a re-check of some of intensities indicated apparent reading errors in ten reflections, most of which were close to an edge of the films, and these were rejected. During the process, a three-dimensional electron density map was calculated and used to speed the refinement by adjusting the atom locations according to these maps. At the end of the isotropic refinement, the R index had dropped from 33·80% to 13·63%. At this point, anisotropic temperature factors were included. They were initially calculated according to the following equation:

$$B(\sin\theta/\lambda)^2 = b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2$$

The following six high-order reflections were used to calculate the b_{ij}'s, based on the technique used by Cruickshank (1956):

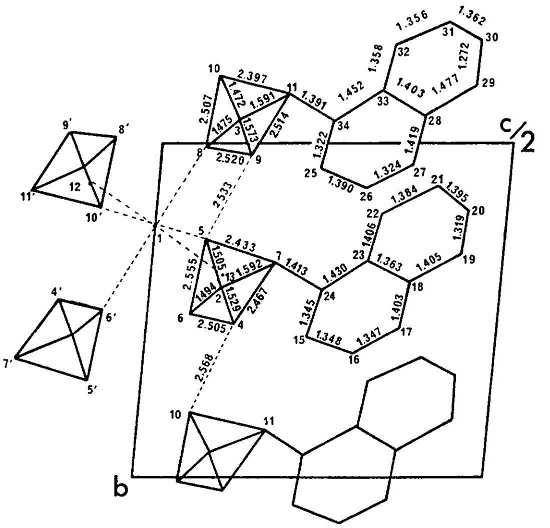

Fig. 3. The projection of the structure of calcium 1-naphthyl phosphate trihydrate down the a axis.

Table 1. *Positional parameters for non-hydrogen atoms*

Atom and number	x/a	σ	y/b	σ	z/c	σ
Ca(1)	0·2309	0·0002	0·2500	0·0003	−0·0001	0·0001
P(2)	0·5257	0·0003	0·4336	0·0004	0·8905	0·0001
P(3)	0·3651	0·0003	−0·0661	0·0004	0·8905	0·0001
O(4)	0·3618	0·0009	0·5410	0·0009	0·8697	0·0004
O(5)	0·4548	0·0008	0·3056	0·0009	0·9236	0·0004
O(6)	0·6969	0·0009	0·5133	0·0009	0·9339	0·0004
O(7)	0·5642	0·0010	0·3592	0·0009	0·8141	0·0004
O(8)	0·2364	0·0008	0·0152	0·0009	−0·0675	0·0004
O(9)	0·5068	0·0008	0·0431	0·0008	0·8685	0·0004
O(10)	0·4678	0·0009	−0·1934	0·0009	0·9233	0·0004
O(11)	0·2481	0·0009	−0·1414	0·0010	0·8149	0·0004
O(12)	0·1538	0·0010	0·1140	0·0012	0·0960	0·0005
O(13)	0·0600	0·0010	0·3880	0·0012	−0·0970	0·0005
O(14)	−0·1061	0·0011	0·2490	0·0014	−0·0012	0·0006
C(15)	0·6826	0·0021	0·5747	0·0027	0·7661	0·0008
C(16)	0·7187	0·0023	0·6339	0·0024	0·7069	0·0012
C(17)	0·6870	0·0029	0·5580	0·0033	0·6399	0·0012
C(18)	0·6044	0·0023	0·4157	0·0027	0·6288	0·0009
C(19)	0·5664	0·0032	0·3370	0·0035	0·5588	0·0012
C(20)	0·4840	0·0032	0·2050	0·0038	0·5487	0·0009
C(21)	0·4427	0·0024	0·1336	0·0029	0·6061	0·0009
C(22)	0·4782	0·0017	0·2116	0·0023	0·6749	0·0007
C(23)	0·5625	0·0018	0·3537	0·0022	0·6872	0·0007
C(24)	0·6056	0·0016	0·4376	0·0021	0·7574	0·0007
C(25)	0·0874	0·0019	0·0746	0·0022	0·7672	0·0008
C(26)	−0·0126	0·0021	0·1366	0·0025	0·7059	0.0011
C(27)	−0·0478	0·0024	0·0639	0·0032	0·6396	0·0012
C(28)	0 0217	0·0021	−0·0837	0·0029	0·6292	0·0008
C(29)	−0·0053	0·0028	−0·1739	0·0035	0·5576	0·0009
C(30)	0·0657	0·0037	−0·3027	0·0034	0·5477	0·0009
C(31)	0·1627	0·0023	−0·3661	0·0025	0·6071	0·0008
C(32)	0·1955	0·0020	−0·2923	0·0022	0·6751	0·0008
C(33)	0·1264	0·0017	−0·1530	0·0021	0·6882	0·0007
C(34)	0·1517	0·0014	−0·0633	0·0017	0·7574	0·0007

Reflection	800	0010	506	810	$\bar{5}10$	026
sinθ	0·860	0·418	0·545	0·864	0·544	0·289

The first structure factor calculation using anisotropic temperature factors gave a slight increase in the *R* value from 13·63% to 13·72%, but it dropped to 13·12% in the next cycle. After 14 such cycles, a final *R* of 10·30% was obtained. Two cycles using Busing & Levy's full-matrix least-squares refinement program on the University of Washington Research Computing Center's IBM 709 machine reduced *R* to 9·7%. The final positional parameters for non-hydrogen atoms are listed in Table 1. The individual anisotropic temperature factors are listed in Table 2, and the observed and calculated structure factors are listed in Table 3.

Discussion of the structure

The distances and angles for covalent bonds and for pairs of atoms not covalently linked are listed in Tables 4, 5, 6, and 7, where the atom identification numbers refer to those assigned in Fig. 3. Figs. 3 and 4 show the packing arrangement for the *bc* and *ab* projections.

The phosphate group

There are two independent phosphate groups. In each group one oxygen atom is bonded to the naphthyl group, another to a hydrogen atom, and the other two are coordinated to two calcium atoms which are related to each other by an inversion center. As seen in Table 4, the $P-OC_{10}H_7$ ester bond is the longest [P(2)–O(7),1·592 Å; P(3)–O(11),1·591 Å], the P–OH bond is the next longest [P(2)–O(4),1·529 Å; P(3)–O(9), 1·573 Å], whereas the bond distances between phosphorus and the two oxygen atoms coordinated with calcium ions are considerably shorter and are essentially the same length (1·47 and 1·50 Å). The maximum O–P–O angle is the one subtended by the two oxygen atoms involved in short P–O bonds, while the minimum O–P–O angle involves oxygen atoms with the longest and one of the short P–O bonds. These distortions from tetrahedral arrangement appear owing to (1) the hydrogen bonding network, (2) the effect of the calcium coordination and (3) packing considerations. These will be discussed briefly in later paragraphs.

The two phosphate groups do not appear equivalent, although the average P–O bond distance is very nearly the same for the two groups. The P–OR distances are identical, but the P(2)–O(4)H bond is significantly shorter than the P(3)–O(9)H bond whereas the P(2)–O(5) and P(2)–O(6) bonds seem significantly longer than the P(3)–O(8) and the P(3)–O(10) bonds.

The general features of the phosphate groups in $Ca(C_{10}H_7HPO_4)_2 . 3H_2O$ agree well with others that have been determined. A comparison of the results is shown in Table 8. Table 8 shows that calcium 1-naph-

Table 2. *Anisotropic thermal parameters*

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Ca(1)	0·01157	0·00123	+0·00105	0·01056	−0·00025	0·00262
P(2)	0·01214	0·00100	+0·00133	0·00881	−0·00020	0·00279
P(3)	0·01239	0·00111	+0·00150	0·01038	+0·00016	0·00253
O(4)	0·01837	0·00190	+0·00234	0·00428	+0·00133	0·00500
O(5)	0·01498	−0·00197	+0·00130	0·00218	0·00000	0·00373
O(6)	0·01428	0·00109	+0·00173	0·01070	+0·00036	0·00368
O(7)	0·02578	0·00025	+0·00294	0·01416	+0·00045	0·00296
O(8)	0·01484	0·00188	+0·00316	0·00970	+0·00008	0·00436
O(9)	0·01868	0·00342	+0·00278	0·00533	+0·00069	0·00445
O(10)	0·01905	0·00397	+0·00208	0·00238	+0·00103	0·00394
O(11)	0·02197	−0·00061	+0·00054	0·01502	+0·00108	0·00334
O(12)	0·01438	0·00291	+0·00192	0·02191	+0·00264	0·00600
O(13)	0·01598	0·00504	+0·00134	0·02334	+0·00340	0·00557
O(14)	0·01760	0·00350	+0·00410	0·02950	+0·00820	0·00660
C(15)	0·02823	−0·01039	+0·00490	0·03495	+0·00253	0·00445
C(16)	0·03543	−0·00179	+0·00589	0·02774	+0·00886	0·00696
C(17)	0·04265	0·00779	+0·00939	0·03782	+0·00580	0·00557
C(18)	0·03430	0·00099	+0·00366	0·02697	+0·00191	0·00441
C(19)	0·04550	0·01007	+0·01038	0·05028	+0·00168	0·00574
C(20)	0·04702	0·01568	+0·00306	0·05411	+0·00035	0·00252
C(21)	0·03797	0·00122	+0·00316	0·05401	−0·00556	0·00338
C(22)	0·02736	0·00167	+0·00249	0·02761	−0·00308	0·00388
C(23)	0·02676	0·00673	+0·00308	0·02192	+0·00011	0·00357
C(24)	0·01976	0·00069	+0·00463	0·02250	+0·00063	0·00407
C(25)	0·03140	0·01110	+0·00170	0·01810	+0·00330	0·00480
C(26)	0·02650	0·00820	+0·00070	0·03880	+0·00600	0·00600
C(27)	0·03050	0·00170	−0·00280	0·04250	+0·00570	0·00640
C(28)	0·02680	0·00360	−0·00120	0·04400	+0·00280	0·00360
C(29)	0·04020	−0·01580	−0·00310	0·04160	+0·00310	0·00370
C(30)	0·06100	−0·01420	+0·00270	0·03360	+0·00350	0·00330
C(31)	0·03590	−0·00310	+0·00040	0·04200	−0·00160	0·00290
C(32)	0·03060	−0·00810	+0·00340	0·01890	+0·00050	0·00410
C(33)	0·02380	−0·00590	−0·00110	0·02030	+0·00170	0·00340
C(34)	0·01950	−0·00050	−0·00130	0·01150	+0·00250	0·00410

Table 3. *Observed and calculated structure factors*

Within each group the columns reading from left to right contain the values of *h*, $10F_o$ and $10F_c$

	h00	
2	544	457
3	331	-305
4	259	280
7	164	-139
8	103	113
	h01	
1	352	-282
3	257	-272
4	173	182
5	178	-166
7	250	-242
	h0$\bar{1}$	
2	891	-877
3	274	-257
4	131	137
6	181	-185
7	116	-106
8	127	125
	h02	
1	397	305
2	498	-535
4	407	435
6	116	158
7	207	-218
	h0$\bar{2}$	
1	367	-293
2	535	451
3	274	-262
6	302	-332
	h03	
1	790	748
2	803	-781
3	105	112
4	165	169
	h0$\bar{3}$	
	478	452
1	388	290
3	320	-281
4	131	136
6	317	-334
	h04	
1	604	575
2	668	-717
3	150	166
6	141	-159
	h0$\bar{4}$	
	607	-636
1	815	743
2	512	-520
3	271	-252
4	278	275
6	315	-308
	h05	
1	342	350
2	304	-281
3	156	156
4	41	-41
5	260	296
6	257	-285
	h0$\bar{5}$	
	481	-398
1	612	585
2	753	-751
4	180	209
6	167	-176
	h06	
1	139	109
2	65	-94
3	171	-180
5	243	288
6	263	-278
	h0$\bar{6}$	
	335	-309
1	342	382
3	89	90
4	403	427
5	153	-148
7	116	-111
	h07	
2	79	90
3	223	-252
5	170	163
6	116	-152
	h0$\bar{7}$	
1	139	125
2	301	-257
3	142	152
4	164	166
7	129	-144
8	103	115
	h08	
4	119	-161
7	98	-105
	h0$\bar{8}$	
	239	217
2	77	-105
3	160	160
6	121	134
7	257	-221
8	103	96
	h09	
1	167	-166
2	98	109
7	124	-120
	h0$\bar{9}$	
2	85	92
3	184	-164
7	213	-198
	h,0,10	
3	69	-111
4	120	155
5	116	-122
7	124	-110
	h,0,$\overline{10}$	
	474	424
1	164	-151
3	218	-229
5	294	270
6	123	-142
	h,0,11	
1	139	132
2	107	-123
4	301	297
7	114	-97
	h,0,$\overline{11}$	
	389	399
2	99	104
5	284	268
6	284	-246
	h,0,12	
2	340	-329
3	231	-221
4	213	215
	h,0,$\overline{12}$	
	79	89
1	103	97
4	151	-136
5	166	157
6	267	-248
	h,0,13	
1	232	230
	h,0,$\overline{13}$	
	201	220
2	105	-115
6	116	-122
	h,0,14	
4	114	124
6	79	-99
	h,0,$\overline{14}$	
	79	-86
1	201	203
2	294	-290
4	116	153
	h,0,15	
1	116	-120
2	227	-198
5	71	90
	h,0,$\overline{15}$	
3	203	-184
4	257	242
5	119	-102
7	98	-76
	h,0,16	
5	120	113
	h,0,$\overline{16}$	
	353	291
1	98	-96
4	208	187
7	101	-96
	h,0,17	
	201	168
2	213	-190
7	116	-85
	h,0,$\overline{17}$	
	177	164
7	80	-72
	h10	
1	874	814
3	292	325
8	115	120
-1	708	644
-2	152	91
-3	603	-624
-4	56	44
-5	228	252
-6	81	88
-7	62	-74
-8	70	77
	h11	
1	316	-269
-1	779	-802
2	411	-452
3	131	133
-3	498	-529
-4	45	-63
-5	177	186
6	263	-238
-6	123	119
-7	77	-67
	h1$\bar{1}$	
1	741	-644
3	128	108
-3	179	-186
4	70	-65
-4	320	-389
5	52	-49
-5	291	300
-6	62	74
-7	62	-79
8	112	131
-8	38	50
	h12	
1	195	-199
-1	330	265
2	114	-138
3	136	143
-3	122	-112
4	235	243
-4	143	-149
-5	162	158
6	101	-129
-6	60	74
7	72	61
-7	73	-73
	h1$\bar{2}$	
-1	345	-242
2	231	-108
-2	231	-231
3	511	537
-3	296	-264
4	135	145
-4	302	-354
5	66	-76
-5	314	351
6	134	-126
-6	62	79
8	151	151
-8	27	-52
	h13	
1	462	-492
-1	201	195
2	148	168
-2	436	461
-3	306	-326
4	217	246
-4	66	67
5	177	-196
-5	45	56
6	106	-116
7	77	71
-7	69	-69
	h1$\bar{3}$	
1	287	258
-1	710	732
-2	524	-468
3	573	634
-3	271	-300
-4	222	-234
5	160	-160
-5	287	337
-6	83	104
8	187	173
-8	137	-131
	h14	
1	143	137
-1	487	499
2	162	130
-2	116	137
3	134	126
-3	141	-147
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6	145	-146
-6	95	116
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-9	49	52
	h1$\bar{4}$	
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2	223	243
-2	418	-411
3	157	159
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5	164	-186
6	83	-78
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7	69	59
8	94	92
-8	137	-147
	h15	
1	127	117
-1	138	-130
2	145	142
-2	152	-156
3	66	81
-3	129	-165
4	243	314
5	134	-167
6	123	-135
8	52	56
-8	150	-164
-9	91	82
	h1$\bar{5}$	
1	282	-310
-1	452	443
2	454	451
-2	172	178
3	260	263
-3	258	-282
4	310	341
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5	217	-231
-5	93	-110
6	134	-118
-6	63	88
7	69	68
-8	129	-122
	h16	
1	248	237
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2	121	142
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3	259	290
-3	38	-39
4	92	119
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5	73	-81
6	64	-88
8	77	83
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-9	84	88
	h1$\bar{6}$	
1	450	-434
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2	395	376
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3	254	281
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4	291	329
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5	266	-281
-5	60	-74
6	78	-83
-6	115	125
7	69	71
-8	57	-45
	h17	
-1	234	-234
2	254	301
-2	145	-132
3	160	188
-3	119	-116
-4	222	-220
5	79	-76
-6	216	232
8	65	68
-8	143	-120
-9	81	73
	h1$\bar{7}$	
1	64	-66
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-3	295	-335
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5	309	-310
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6	52	-74
	h18	
1	241	-297
2	121	124
-2	116	-118
3	246	269
-3	81	-68
-4	277	-294
5	59	-41
-5	181	179
-6	119	123
7	66	66
-8	110	-96
	h1$\bar{8}$	
1	171	-175
-1	51	58
-3	230	-249
4	144	108
-4	81	-94
5	279	-283
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	h19	
1	81	-93
-1	242	291
2	208	-237
-2	246	-266
3	280	303
-3	242	-259
4	123	-147
-4	242	-297
5	99	-124
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-7	59	-61
	h1$\bar{9}$	
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	h,1,10	
1	246	-235
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2	152	-177
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3	323	381
-3	152	-169
-4	110	-109
5	91	-101
-5	144	155
6	74	-74
-6	120	120
7	37	44
-7	60	-71
-8	51	48
	h,1,$\overline{10}$	
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	h,1,11	
1	134	-112
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2	202	-232
-2	206	201
3	265	314
-3	215	-232
4	85	70
-5	72	71
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7	46	50
	h,1,$\overline{11}$	
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-2	236	-244
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-4	192	-208
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-6	45	53
	h,1,12	
1	173	-160
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2	158	-168
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3	52	-41
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5	153	-136
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	h,1,$\overline{12}$	
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-6	43	56
	h,1,13	
1	152	-152
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2	207	202
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3	70	63
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-4	124	123
5	168	-147
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	h,1,$\overline{13}$	
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-2	137	-130
-3	195	-186
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	h,1,14	
1	282	-236
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2	79	108
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-3	280	-276
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5	72	-81
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6	34	-50
-7	45	-36
-8	85	-69
	h,1,$\overline{14}$	
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-3	165	-176
-4	65	53
-6	70	48
	h,1,15	
1	135	-136
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-2	192	-184
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4	149	125
-4	92	-65
5	45	-72
-5	88	65
-7	63	-42
-8	85	-58
	h,1,$\overline{15}$	
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-3	261	-258
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	h,1,16	
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-3	77	-56
-6	77	59
-7	52	-33
	h,1,$\overline{16}$	
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	h,1,17	
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4	41	-50
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	h,1,$\overline{17}$	
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-3	112	-111
	h,1,18	
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-4	180	-142
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	h,1,$\overline{18}$	
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	h,1,19	
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3	139	119
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	h,1,$\overline{19}$	
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	h,1,20	
3	80	73
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	h,1,$\overline{20}$	
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	h,1,21	
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-3	139	-91
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	h,1,22	
-2	87	59
-3	143	-102
-4	51	33
	h,1,23	
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-3	96	-63
	h20	
2	50	49
3	170	188
4	120	121
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	h21	
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2	156	-127
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4	67	57
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5	209	-221
6	306	351
7	78	-93
	h2$\bar{1}$	
2	153	133
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3	153	126
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4	241	-241
5	112	120
-5	164	-174
6	91	93
-6	162	192
9	94	-90
	h22	
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-1	50	-14
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3	466	499
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4	52	-64
-4	208	-166
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-5	119	115
6	227	261
-6	170	-180
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	h2$\bar{2}$	
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2	127	-99
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3	159	149
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-7	73	-92
9	103	-92
	h23	
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3	221	-199
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6	85	82
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8	62	-72
	h2$\bar{3}$	
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3	603	621
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7	249	243
8	73	-79
9	52	-55
	h24	
	863	-909
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4	92	-107
-4	96	114
-5	119	116
7	130	140
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8	70	-79
	h2$\bar{4}$	
	794	-702
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2	294	261
-2	338	331
3	166	-162
-3	185	-197
4	544	-555
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-5	120	-113
6	174	-182
-6	258	298
7	288	279
8	127	-114
-8	73	-84
9	55	-46
	h25	
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2	451	530
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3	192	-207
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4	179	-215
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-5	120	-126
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8	69	-81
	h2$\bar{5}$	
	431	-513
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3	192	-227
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4	73	-90
-6	146	147
7	231	205
8	119	-107
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9	57	-49
	h26	
	451	-498
1	143	-181
3	71	-92
4	237	-271
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7	45	48
8	56	-52
	h2$\bar{6}$	
	813	-763
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2	324	314
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-3	181	181
4	193	160
5	160	-146
-5	91	117
6	67	89
-7	162	163
8	24	-42
-8	79	-90
9	53	-34
	h27	
	264	-269
1	437	-491
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2	403	486
-2	447	502
3	62	-96
4	193	-226
	h2$\bar{7}$	
	608	-626
1	301	-269
-1	404	-436
2	496	447
3	200	-181
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5	271	-252
-5	128	125
6	180	169
-7	155	160
	h28	
1	372	-434
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2	437	521
4	119	-133
6	158	172
	h2$\bar{8}$	
	65	-54
1	395	-357
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2	428	408
-2	327	357
3	78	72
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5	203	-194
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6	327	280
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9	78	-59
	h29	
	130	159
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2	248	282
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4	91	-106
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6	79	115
	h2$\bar{9}$	
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-1	88	-96
2	43	97
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3	160	157
-3	124	139
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-5	107	94
6	332	303
7	87	-86
-7	72	82
9	110	-86
	h,2,10	
	96	-122
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3	50	78
4	102	122
5	95	-115
6	144	-145
	h,2,$\overline{10}$	
	306	-300
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2	316	350
-2	142	155
-3	121	140
-4	170	-191
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6	270	247
	h,2,11	
	330	-355
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6	129	113
	h,2,$\overline{11}$	
	205	-186
2	195	212
-3	124	140
4	152	-153
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-5	120	-136
6	146	120
-6	38	57
7	62	-22
	h,2,12	
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3	98	116
4	106	-111
	h,2,$\overline{12}$	
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3	101	112
-3	53	75
4	165	-158
5	117	105
-5	95	-107
-6	107	105
7	62	71
8	71	-59
	h,2,13	
	419	-423
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3	123	126
6	63	-55
	h,2,$\overline{13}$	
	108	-105
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3	115	114
4	246	-208
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-5	78	-106
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7	153	131
8	98	-67
	h,2,14	
	211	-191
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3	85	88
4	98	-92
	h,2,$\overline{14}$	
	122	-112
1	127	117
-1	86	69
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3	121	117
4	198	-154
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7	141	133
8	87	-65
	h,2,15	
1	77	-90
4	87	-91
	h,2,$\overline{15}$	
	392	-336
4	67	-72
7	63	66
8	56	-60
	h,2,16	
1	128	-129
2	149	144
4	71	-63
	h,2,$\overline{16}$	
	162	-187
1	67	87
3	92	81
-3	87	80
5	132	-107
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	h,2,17	
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2	114	100
	h,2,$\overline{17}$	
	92	85
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-2	155	143
5	87	-96
	h,2,18	
2	64	61
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	h,2,$\overline{18}$	
	87	-86
1	92	-104
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-2	117	118
5	62	-77
6	78	78
	h,2,$\overline{19}$	
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-1	83	-91
2	120	130
-2	107	119
3	87	70
5	58	-57
6	71	68
	h,2,$\overline{20}$	
2	80	98
6	62	48
	h,2,$\overline{21}$	
2	110	109
	h30	
2	435	-388
4	267	-286
5	185	187
8	109	-122
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-3	116	-133
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	h31	
1	208	214
2	320	334
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3	393	-395
-3	80	64
4	101	97
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-6	259	-223
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8	114	-115
-8	102	109
	h3$\bar{1}$	
2	777	-731
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3	44	27
-3	364	299
4	309	-310
-4	114	101
5	237	231
6	53	62
7	55	-62
-8	164	165
	h32	
1	392	308
-1	208	-218
2	209	173
-2	446	358
3	469	-469
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4	260	271
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-5	302	-296
-6	65	-70
8	56	-79
-8	87	92
	h3$\bar{2}$	
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2	458	-448
-2	407	-328
3	72	-56
-3	661	659
4	351	-369
-4	301	-278
5	285	295
-5	188	162
6	71	69
-6	194	-172
7	86	-76
-8	124	123
	h33	
1	354	339
-1	394	-325
2	236	194
-2	347	-308
3	435	-419
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4	281	274
-4	371	333
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-5	284	-285
-6	89	-88
	h3$\bar{3}$	
1	220	-208
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2	241	-234
-2	619	-530
3	96	116
-3	380	349
4	265	-293
-4	139	-154
5	297	286
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6	87	94
-6	121	-141
7	63	-70
	h34	
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2	87	92
-2	217	-191
3	504	-499
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-4	277	243
5	120	129
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7	63	-60
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-8	53	-50
	h3$\bar{4}$	
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-1	165	122
2	351	362
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3	300	-263
-3	338	318
4	245	-223
-4	55	-51
-5	44	-49
-7	102	108
-8	35	-39
	h35	
-1	333	-321
2	322	304
-2	244	-210
3	230	-231
-3	474	469
4	119	-144
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5	152	161
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6	69	92
-6	58	-55
-7	89	93
	h3$\bar{5}$	
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-3	96	92
4	113	-98
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-5	200	-189
6	237	220
-7	105	114
-8	51	-57
	h36	
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-2	87	-96
3	69	-95
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4	171	-180
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5	163	184
7	46	-54
-7	62	64
	h3$\bar{6}$	
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-2	137	75
3	331	-349
4	260	252
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6	218	190
-7	88	83
-8	35	-22
	h37	
1	116	113
-1	93	-87
2	213	-226
-2	336	-294
3	65	-102
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4	167	-163
-4	286	-270
5	102	93
6	116	135
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-8	63	62
	h3$\bar{7}$	
1	187	166
-2	232	232
3	280	-291
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4	123	128
-4	288	332
5	156	-146
-5	257	-287
-6	45	-41
	h38	
1	263	222
-1	121	-108
2	156	-166
-2	51	-52
-3	221	231
4	149	-152
-5	69	-66
6	127	157
-8	105	109
	h3$\bar{8}$	
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-4	206	200
5	66	-81
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-6	96	-88
	h39	
1	206	196
-1	230	-233
2	227	-237
-2	214	208
-3	64	84
4	156	-168
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-5	121	-114
-6	52	-40
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	h3$\bar{9}$	
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-1	122	-148
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-3	189	225
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3	95	-101
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	h,3,$\overline{10}$	
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-3	266	311
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	h,3,11	
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3	164	-146
-4	157	160
-5	159	-170
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	h,3,$\overline{11}$	
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	h,3,12	
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3	145	-133
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-4	139	149
-5	95	-93
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	h,3,$\overline{12}$	
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	h,3,13	
2	136	127
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-3	83	85
-4	141	151
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-8	55	-37
	h,3,$\overline{13}$	
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	h,3,14	
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-2	142	-130
3	122	-115
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-5	62	-56
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	h,3,$\overline{14}$	
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	h,3,15	
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4	57	-52
5	105	94
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	h,3,$\overline{15}$	
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	h,3,16	
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-3	144	129
4	93	-88
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	h,3,$\overline{16}$	
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	h,3,17	
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	h,3,18	
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2	41	-48
-3	85	69
-6	44	-29
	h,3,19	
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-1	141	-108
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-4	56	45
-5	70	-40
-6	35	-24
	h,3,20	
1	131	89
-1	107	-77
-2	48	38
-4	94	65
-5	110	-69
	h,3,21	
1	57	48
-1	134	-80
-2	66	44
-4	109	70
	h,3,22	
-1	57	-40
	h40	
2	310	-264
3	94	-103
4	309	335
5	156	-165
6	66	79
7	130	-131
-1	139	-137
-2	383	-347
-5	171	161
-6	191	-190
	h41	
	473	450
1	105	-98
-1	16	-27
2	400	-382
-2	155	-128
4	245	268
-4	179	169
5	194	-189
-5	158	145
-6	260	-255
7	72	-77
-8	34	-29
	h4$\bar{1}$	
1	200	-176
-1	71	83
2	136	-136
-2	382	-368
3	191	-192
-3	98	95
4	314	331
-4	172	-168
5	92	-91
-5	285	282
6	83	89
-6	168	-165
7	198	-181
-8	40	36
	h42	
1	103	-87
-1	99	-102
2	218	-194
-2	346	-291
3	62	-75
-3	202	-190
4	245	260
-4	332	296
-5	123	124
6	121	-103
-6	200	-217
-7	71	74
	h4$\bar{2}$	
1	87	82
-1	156	144
2	331	-321
-2	295	-261
-3	79	80
4	281	302
-4	198	-176
-6	160	-155
7	160	-139
-8	45	53
	h43	
	311	327
1	63	52
-1	91	-73
2	179	-172
-2	416	-370
3	236	-243
-3	99	-100
4	132	117
-4	322	347
5	132	117
6	136	-143
-6	116	-120
	h4$\bar{3}$	
1	184	140
-1	137	108
2	321	-330
-2	234	-218
-3	52	-32
4	156	159
5	114	94
-5	63	-51
6	132	-114
-6	59	-56
-7	194	-189
-8	63	59
	h44	
	216	269
1	196	185
-1	51	38
-2	229	-195
3	272	-267
-3	48	-51
4	112	-121
-4	307	337
5	144	150
-5	96	-91
6	209	-210
-7	57	-59
	h4$\bar{4}$	
	359	324
-1	367	342
2	256	-250
-2	132	-125
3	87	85
-3	160	-138
-4	106	78
5	142	136
-5	52	59
6	221	-208
-6	69	80
-7	170	-169
-8	69	66
	h45	
	192	207
1	92	121
-1	162	177
2	62	54
-2	182	-161
-3	63	-64
-4	243	271
5	163	171
-5	156	-155
6	143	-159
-6	86	83
-7	136	-135
-8	72	65
	h4$\bar{5}$	
	119	91
1	317	333
-1	388	368
-2	124	-111
3	77	87
-3	135	-139
4	164	-156
-4	46	60
5	146	137
-6	102	103
-7	139	-134
-8	58	58
	h46	
	357	386
1	98	-86
-1	92	128
-2	43	-31
-3	227	-234
4	74	-84
-4	244	243
5	158	153
-5	182	-188
6	60	-64
-6	70	72
7	67	-70
-7	171	-173
-8	105	104
	h4$\bar{6}$	
1	359	380
-1	208	184
-2	48	-46
-3	163	-141
4	171	-167
-4	99	102
-5	49	-56
-7	87	-90
	h47	
	381	408
1	113	-115
-1	92	-88
2	56	-69
-2	67	60
3	60	65
-3	249	-261
4	95	-116
-4	130	116
5	141	162
7	65	-67
-7	129	-128
-8	124	119
	h4$\bar{7}$	
	137	-98
1	203	206
-1	200	193
-2	55	-111
-3	70	-68
-4	186	169
	h48	
1	72	-77
-1	103	-114
2	62	-45
-2	30	-36
3	72	-93
-3	33	-48
4	108	126
-4	105	-93
-5	127	114
-6	110	-90
7	107	-101
-7	85	-75
-8	96	85
	h4$\bar{8}$	
	141	88
1	188	179
-2	173	-163
-4	153	149
-5	103	102
-6	129	-125
	h49	
	96	70
1	166	152
-1	71	-75
2	177	-180
-2	56	-68
4	144	160
-5	135	144
6	35	52
-6	130	-136
-7	64	-39
-8	38	43
	h4$\bar{9}$	
-1	171	-148
-3	159	-167
-4	156	138
-5	136	123
-6	144	-136
	h,4,10	
	220	-229
1	297	244
-1	162	165
2	257	-252
-2	56	-41
3	53	47
-3	60	61
4	91	87
-4	72	-70
-5	165	162
-6	195	-190
	h,4,$\overline{10}$	
	46	80
1	148	-141
-1	112	-102
-3	142	-144
-4	87	82
-5	98	96
-6	129	-125
	h,4,11	
	203	-203
1	207	192
-1	217	239
2	228	-228
-2	163	-170
-3	67	-75
4	93	97
-4	87	-96
-5	149	145
6	41	-46
-6	137	-139
-7	41	38
	h,4,$\overline{11}$	
	246	282
1	103	-106
-1	129	-141
-3	89	-79
-6	106	-86
	h,4,12	
	84	-62
1	159	150
-1	191	187
2	152	-143
-2	244	-240
-3	35	-32
4	60	71
-4	99	108
-5	144	138
6	91	-109
-6	66	-57
	h,4,$\overline{12}$	
1	119	-148
-1	119	-128
-6	46	-33
	h,4,13	
-1	146	138
2	93	-84
-2	216	-210
-3	51	42
4	63	70
-4	127	138
5	44	59
-7	70	-67
	h,4,$\overline{13}$	
1	122	-130
-1	51	-79
-2	121	-145
-4	62	76
	h,4,14	
	228	213
1	101	-85
-2	152	-132
3	88	-94
4	49	61
-4	88	80
5	56	54
-7	69	-62
	h,4,$\overline{14}$	
	191	230
1	53	-85
-1	51	65
-2	167	-177
	h,4,15	
	295	307
1	94	-106
-1	112	-94
-2	92	-80
3	59	-66
-4	100	88
-6	37	41
-7	113	-88
	h,4,$\overline{15}$	
	71	55
1	52	64
-1	158	179
-2	122	-145
-4	105	90
	h,4,16	
	200	204
1	80	-104
-1	115	-101
-2	35	-29
-3	42	-29
-4	87	59
	h,4,$\overline{16}$	
1	150	167
-1	152	171
-2	139	-155
	h,4,17	
	196	207
1	51	-59
-1	107	-108
-2	41	42
-3	96	-81
-4	88	58
-6	45	-39
	h,4,$\overline{17}$	
1	134	162
-1	87	113
-2	96	-113
	h,4,18	
	106	120
-1	51	-60
2	60	-78
-3	57	-56
-4	64	51
-5	57	56
-6	96	-88
	h,4,19	
1	48	59
2	69	-90
-2	49	-45
-4	31	37
-5	56	50
	h,4,$\overline{19}$	
	60	71
	h,4,20	
	37	-45
1	66	80
-1	42	58
-2	69	-75
-4	37	35
	h,4,$\overline{20}$	
-1	77	-70
	h,4,21	
	35	-46
-1	70	82
-2	71	-83
	h50	
1	367	-240
2	41	-21
3	227	219
4	193	190
5	210	-211
-1	42	-32
-2	327	305
-3	474	-459
-4	120	110
-5	152	136
-7	102	-107
	h51	
1	113	-85
-1	289	245
2	321	116
-2	170	167
-3	493	-534
4	302	332
-4	218	223
5	232	-230
6	101	-96
-7	113	-113
	h5$\bar{1}$	
1	98	43
-1	21	25
2	156	-171
-2	332	269
-3	314	-296
5	99	-83
-5	249	237
6	60	-62
-7	87	-85
	h52	
1	66	-52
-1	102	85
2	214	220
-2	60	29
3	196	-192
-3	453	-475
4	347	384
-4	218	205
5	110	-113
6	52	-58
-6	77	76
-8	55	-54
	h5$\bar{2}$	
1	59	-44
2	306	-283
-2	60	51
3	439	525
-3	119	-99
4	194	-200
-4	261	-228
-5	174	173
6	120	-113
-7	98	-92
-8	37	36
	h53	
1	109	-106
-1	79	54
2	232	262
-2	130	-122
3	220	-241
-3	243	-224
4	196	213
5	55	-67
6	37	-35
-6	129	115
-8	96	-95
	h5$\bar{3}$	
1	438	-356
-1	332	345
2	294	-281
-2	186	-146
-3	156	141
4	194	-223
-4	274	-258
5	46	58
-5	134	125
6	149	-117
-7	51	-59
	h54	
1	218	-210
-1	102	98
2	159	150
-2	220	-242
-4	193	-190
-5	101	94
6	69	-68
-6	124	115
-8	105	-106
	h5$\bar{4}$	
1	265	-318
-1	450	433
2	50	-56
-2	295	-259
3	257	266
-3	213	184
4	106	-102
-4	106	-98
-5	203	198
-6	95	82
	h55	
1	192	-201
-1	203	216
2	35	-61
-2	238	-222
3	187	197
-3	202	205
4	98	-109
-4	313	-322
-5	213	210
6	49	-63
-6	55	54
-8	72	-73
	h5$\bar{5}$	
1	378	-441
-1	386	416
-2	331	-285
3	102	93
-3	174	-155
-4	153	-131
-5	106	85
-6	139	126
-7	44	31
	h56	
1	123	-133
-1	188	207
2	139	-146
-2	151	-139
3	218	208
-3	221	228
4	65	-75
-4	344	-391
-5	230	216
	h5$\bar{6}$	
-1	167	192
-2	71	-26
-3	258	-237
-4	102	-66
-5	58	-52
-6	119	99
-7	66	47
	h57	
1	70	98
-1	119	136
2	307	-363
-2	42	51
3	278	283
4	40	-43
-4	198	-209
-5	106	106
-6	105	87
-7	56	-46
-8	28	29
	h5$\bar{7}$	
1	159	-160
-1	42	-38
-2	159	153
-3	223	-213
-6	70	71
-7	44	28
	h58	
1	107	88
-1	67	-94
2	259	-274
-2	144	141
3	215	278
-3	174	-194
-5	55	59
-6	74	63
	h5$\bar{8}$	
1	41	40
-1	124	-119
2	56	12
-2	181	189
-3	277	-295
-4	101	88
-6	65	58
	h59	
1	160	-161
-1	109	-92
-2	299	359
3	87	111
-3	211	-210
-4	105	112
5	55	-98
-6	46	45
	h5$\bar{9}$	
1	113	120
-1	80	-77
2	146	-144
-3	193	-194
-6	60	54
-7	49	-33
	h,5,10	
1	171	-178
-1	150	144
2	73	81
-2	235	270
-3	259	-280
4	56	125
-4	88	74
5	79	-123
-5	60	-60
-6	89	74
	h,5,$\overline{10}$	
1	86	76
2	164	-184
-3	50	-51
-4	96	-108
-5	95	86
	h,5,11	
1	151	-179
-1	170	174
2	93	123
-3	229	-260
4	50	114
-4	59	50
5	88	-127
-6	79	67
	h,5,$\overline{11}$	
-1	49	46
-4	121	-128
-5	105	101
	h,5,12	
1	146	-170
-1	160	180
2	79	124
-2	74	-88
-3	110	-104
-4	38	45
5	48	-83
-6	48	46
	h,5,$\overline{12}$	
1	59	-60
-1	94	105
-3	63	51
-4	115	-106
-5	99	91
-6	40	30
	h,5,13	
1	105	-155
-1	168	174
-2	116	-120
-4	62	-63
-5	64	62
-6	41	36
	h,5,$\overline{13}$	
1	92	-117
-1	78	90
-4	51	-55
-5	69	65
	h,5,14	
1	46	-73
-1	146	162
-2	121	-120
-4	122	-114
-5	112	96
-6	29	28
-7	60	-37
	h,5,$\overline{14}$	
1	66	-84
-1	87	118
-2	80	-84
	h,5,15	
-1	58	75
3	38	100
-4	103	-110
-5	110	108
	h,5,$\overline{15}$	
1	84	-113
-1	132	171
-3	51	-75
	h,5,16	
-1	66	59
3	46	95
-3	33	-47
-4	92	-88
-5	123	109
	h,5,$\overline{16}$	
1	116	-148
-1	58	88
-3	105	-108
	h,5,17	
3	44	77
-3	60	-74
-5	80	73
	h,5,$\overline{17}$	
-3	139	-133
	h,5,18	
-2	59	76
-3	83	-95
-4	38	36
	h,5,$\overline{18}$	
-3	109	-109
	h,5,19	
-2	69	74
-3	71	-89
-4	30	27
	h,5,$\overline{19}$	
-3	69	-60
	h,5,20	
-2	22	43
-3	59	-73

thyl phosphate has the shortest C–O bond and the largest P–O–C angle. The large P–O–C angle must be due to packing the big planar naphthyl group into the cell. The short C–O bond is characteristic of C–O bonds on aromatic carbon atoms and probably indicates some double bond character.

Calcium coordination

Each calcium ion is coordinated to seven oxygen atoms. Four of the latter are contributed by four nearby phosphate groups and the other three from water molecules. The oxygen atoms around the calcium are arranged in a distorted pentagonal bipyramid, O(5), O(10′), O(12), O(14), and O(13) being approximately in a plane containing the calcium ion and O(6′) and O(8) forming the two apices of the bipyramid. Table 6 shows the bond distances for the calcium to oxygen bonds and Table 7 the oxygen–calcium–oxygen angles. The O–Ca–O angles range from 67·5° to 77·9°. The angles from the two apices to the oxygens in the plane range from 80·7° to 99·0°, and the two apex oxygen atoms and calcium form an O–Ca–O angle of 166·2°. It should be noted that the two shortest Ca–O distances are to apex oxygen atoms. The average Ca–O distance is about the same as that in calcium thymidylate (Trueblood, Horn & Luzzati, 1961), although the range in calcium thymidylate is from 2·29 to 2·65 Å. The much smaller range in calcium naphthyl phosphate is probably due to the fact that all the oxygen atoms are from different phosphate groups or water molecules. Thus the coordinated oxygen atoms do not need to conform to any other coordination or valence structure and will

Table 4. *The bond distances for covalent bonds*

Bond	Distance	σ	Bond	Distance	σ
(*a*) Phosphorus–oxygen:					
P(2)–O(4)	1·529 Å	0·008	P(3)–O(8)	1·475 Å	0·008
P(2)–O(5)	1·505	0·008	P(3)–O(9)	1·573	0·008
P(2)–O(6)	1·494	0·008	P(3)–O(10)	1·472	0·008
P(2)–O(7)	1·592	0·008	P(3)–O(11)	1·591	0·008
(*b*) Carbon–oxygen:					
O(7)–C(24)	1·413 Å	0·013	O(11)–C(34)	1·391 Å	0·012
(*c*) Carbon–carbon:					
C(15)–C(16)	1·348 Å	0·03	C(25)–C(26)	1·390 Å	0·03
C(15)–C(24)	1·345	0·02	C(25)–C(34)	1·322	0·02
C(16)–C(17)	1·347	0·03	C(26)–C(27)	1·324	0·03
C(17)–C(18)	1·403	0·03	C(27)–C(28)	1·419	0·03
C(18)–C(19)	1·405	0·03	C(28)–C(33)	1·403	0·02
C(18)–C(23)	1·363	0·03	C(28)–C(29)	1·477	0·03
C(19)–C(20)	1·319	0·03	C(29)–C(30)	1·272	0·03
C(20)–C(21)	1·395	0·03	C(30)–C(31)	1·362	0·03
C(21)–C(22)	1·384	0·03	C(31)–C(32)	1·356	0·02
C(22)–C(23)	1·406	0·02	C(32)–C(33)	1·358	0·02
C(23)–C(24)	1·430	0·02	C(33)–C(34)	1·452	0·02

Table 5. *Bond angles for covalent bonds*

Angle	Degrees	σ	Angle	Degrees	σ
(*a*) Phosphate groups					
O(4)–P(2)–O(5)	108·3°	0·4°	O(8)–P(3)–O(9)	111·5°	0·4°
O(4)–P(2)–O(6)	111·9	0·4	O(8)–P(3)–O(10)	116·6	0·4
O(4)–P(2)–O(7)	104·4	0·4	O(8)–P(3)–O(11)	109·7	0·4
O(5)–P(2)–O(6)	116·8	0·4	O(9)–P(3)–O(10)	109·7	0·4
O(5)–P(2)–O(7)	103·6	0·4	O(9)–P(3)–O(11)	105·2	0·4
O(6)–P(2)–O(7)	110·8	0·4	O(10)–P(3)–O(11)	102·9	0·4
(*b*) Ester linkage and naphthyl groups					
P(2)–O(7)–C(24)	125·4°	0·7°	P(3)–O(11)–C(34)	124·7°	0·6°
C(24)–C(15)–C(16)	118·8	1·7	C(34)–C(25)–C(26)	118·0	1·7
C(15)–C(16)–C(17)	122·2	2·0	C(25)–C(26)–C(27)	123·2	1·8
C(16)–C(17)–C(18)	120·3	1·8	C(26)–C(27)–C(28)	119·2	1·7
C(17)–C(18)–C(19)	120·8	1·7	C(27)–C(28)–C(33)	120·9	1·7
C(17)–C(18)–C(23)	119·0	1·7	C(27)–C(28)–C(29)	123·8	1·8
C(19)–C(18)–C(23)	120·2	1·7	C(33)–C(28)–C(29)	115·3	1·7
C(18)–C(19)–C(20)	120·6	2·0	C(28)–C(29)–C(30)	123·8	1·7
C(19)–C(20)–C(21)	122·0	2·2	C(29)–C(30)–C(31)	118·5	1·6
C(20)–C(21)–C(22)	117·2	2·0	C(30)–C(31)–C(32)	122·0	1·6
C(22)–C(21)–C(23)	121·6	1·8	C(31)–C(32)–C(33)	121·7	1·5
C(22)–C(23)–C(24)	123·8	1·8	C(32)–C(33)–C(28)	118·6	1·5
C(22)–C(23)–C(18)	118·2	1·8	C(32)–C(33)–C(34)	126·8	1·5
C(18)–C(23)–C(24)	118·0	1·8	C(28)–C(33)–C(34)	114·7	1·5
C(23)–C(24)–C(15)	121·5	1·8	C(33)–C(34)–C(35)	123·9	1·5

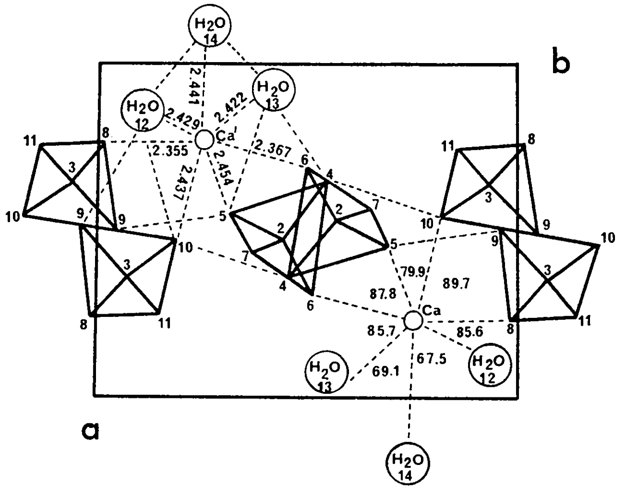

Fig. 4. The projection of the structure of calcium 1-naphthyl phosphate trihydrate down the *c* axis.

arrange themselves around the calcium in a manner consistent only with close packing. The large O–P–O bond angle for oxygen atoms involved in short P–O bonds must be due to the fact that each oxygen atom is coordinated to a different calcium atom, tending to extend the bond angle.

Hydrogen bonding

Although hydrogen positions have not been found, hydrogen bonding appears to play a very significant part in linking the phosphate groups in the crystal. Table 6(*c*) shows the O---O distances for oxygen atoms presumed to be involved in hydrogen bonding. In Fig. 4, the *ab* projection shows the network of hydrogen bonds, and Fig. 5, showing the five planar oxygen atoms coordinated to the calcium, indicates in more detail the part played by the water molecules. In each phosphate group, two of the oxygen atoms are hydrogen bonded to a single water molecule, *i.e.* O(4)

Table 6. *Interatomic distances for pairs of atoms not directly covalently linked*

Bond	Distance	σ	Bond	Distance	σ
(*a*) O---O distance in same phosphate group					
O(4)–O(5)	2·460 Å	0·008	O(8)–O(9)	2·520 Å	0·008
O(4)–O(6)	2·505	0·008	O(8)–O(10)	2·507	0·008
O(4)–O(7)	2·467	0·008	O(8)–O(11)	2·509	0·008
O(5)–O(6)	2·555	0·008	O(9)–O(10)	2·496	0·008
O(5)–O(7)	2·433	0·008	O(9)–O(11)	2·514	0·008
O(6)–O(7)	2·541	0·008	O(10)–O(11)	2·397	0·008
(*b*) Ca---O distance in Ca-coordination					
Ca–O(5)	2·454 Å	0·006	Ca–O(12)	2·429 Å	0·008
Ca–O(6′)	2·367	0·006	Ca–O(13)	2·422	0·008
Ca–O(8)	2·355	0·006	Ca–O(14)	2·441	0·008
Ca–O(10′)	2·437	0·008			
(*c*) H-bonding distance for O---O					
O(5)–O(9)	2·533 Å	0·006	O(12)–O(14)	2·707 Å	0·008
O(4)–O(10′)	2·568	0·006	O(13)–O(14)	2·758	0·008
O(4)–O(13)	2·809	0·007	O(12)–O(9′)	2·807	0·007
O(5)–O(13)	2·900	0·007	O(12)–O(10′)	2·946	0·007
(*d*) Van der Waals distance					
C(21)–C(28)	3·719 Å	0·015	C(19)–C(30)	3·620 Å	0·015
C(21)–C(27)	3·760	0·015	C(19)–C(19′)	3·797	0·015
C(17)–C(31′)	3·762	0·015			
(*e*) Miscellaneous					
O(7)–C(15)	2·453 Å	0·02	P(2)–C(24)	2·672 Å	0·014
O(7)–C(23)	2·369	0·02	P(2)–C(15)	3·163	0·02
O(11)–C(25)	2·402	0·02	P(3)–C(25)	3·084	0·015
O(11)–C(33)	2·352	0·02	P(3)–C(34)	2·644	0·012

Table 7. *Bond angles* O–Ca–O *in* Ca–O *coordination for pentagonal bipyramid*

Angle	Degrees	σ	Angle	Degrees	σ
(*a*) Girdle oxygen atoms					
O(5)–Ca–O(10′)	77·9°	0·3	O(14)–Ca–O(13)	69·1°	0·4
O(10′)–Ca–O(12)	74·5	0·3	O(13)–Ca–O(5)	73·0	0·3
O(12)–Ca–O(14)	67·5	0·4			
(*b*) Apex-girdle oxygen atoms					
O(6′)–Ca–O(5)	87·8°	0·3	O(8)–Ca–O(5)	80·7°	0·3
O(6′)–Ca–O(10′)	79·9	0·3	O(8)–Ca–O(10′)	89·7	0·3
O(6′)–Ca–O(12)	99·9	0·3	O(8)–Ca–O(12)	85·6	0·3
O(6′)–Ca–O(14)	98·3	0·4	O(8)–Ca–O(13)	99·0	0·3
O(6′)–Ca–O(13)	85·7	0·3	O(8)–Ca–O(14)	95·9	0·4
(*c*) Apex–apex oxygen atoms					
O(6′)–Ca–O(8)	166·2°	0·3			

and O(5) are hydrogen bonded to water oxygen atom 13 through its two hydrogen atoms, and O(9′) to O(10′) to water oxygen atom 12 through its hydrogen atoms. Both water oxygen atoms 12 and 13 are hydrogen bonded to water oxygen atom 14 through its hydrogen atoms. Also phosphate oxygen atom 9 is hydrogen bonded to O(5) on an adjacent phosphate group. Thus the phosphate groups are held together through P–O–H---O hydrogen bonds, which are the shortest, and through hydrogen bonds from the water molecules, which are somewhat longer. Thus hydrogen bonding and coordination of oxygen atoms 5, 6, 8, and 10 to calcium produce a relatively strong network of secondary binding throughout the crystal. O(6) and O(8) (apex oxygen atoms in the calcium coordination pentagonal bipyramid) do not appear to be hydrogen bonded.

The oxygen–oxygen distances and angles for oxygen atoms involved in hydrogen bonding are shown in Fig. 5. The angles subtended by O(5)–O(13)–O(4) and O(9)–O(12)–O(10) indicate that the hydrogen atoms on O(12) and O(13) cannot be on a line between O(13) and O(4), O(13) and O(5), O(12) and O(9), and O(12) and O(10). These are probably the weakest of the various hydrogen bonds in the crystal.

The naphthyl groups

The naphthyl groups are assumed to be normal; however, considerable variation in bond distances and angles occurs. The C–C distances range from 1·345 to 1·430 Å and average 1·377 Å for the first naphthyl group and range from 1·272 to 1·452 with an average of 1·376 for the second. The range of C–C–C angles is from 117·2 to 123·8 in the first group and from 114·70 to 126·80 in the second. The minimum C–C bond length involves the two carbons which are closest

Table 8. *Comparison of calcium* 1-*naphthyl phosphate with four other organic phosphates*

	Calcium naphthyl phosphate		Adenosine phosphate	2-Aminoethanol phosphate	Ca Thymidylate	Dibenzylphosphoric acid
	PO_4(1)	PO_4(2)	5′–PO_4	PO_4		
P–O						
Range	1·494 Å –1·592	1·472 Å –1·591	1·514 Å –1·610	1·493 Å –1·591	1·474 Å –1·587	1·469 Å –1·566
Average	1·531	1·528	1·546	1·536	1·515	1·531
P–OR	1·592	1·591	1·610	1·591	1·587	1·566 1·545
P–OH	1·529	1·573	1·566	1·557	—	1·545
C–O(PO_4)	1·413	1·391	1·475	1·429	1·472	1·464 1·465
O–P–O						
Range	103·6° to 116·8°	102·9° to 116·6°	105·7° to 118·2°	103·9° to 117·4°	102·1° to 118·4°	103·8° to 117·2°
Angle between 2 short P–O	116·8° (max.)	116·6° (max.)	118·2° (man.)	117·4° (max.)	118·4° (max.)	117·2° (max.)
Angle between longest and shortest P–O	103·6° (min.)	102·9° (min.)	105·7° (min.)	103·9° (min.)	102·1° (min.)	103·8° (min.)
P–O–C	125·4°	124·7°	114·7°	118·7°	118·8°	118·8° 122·3°

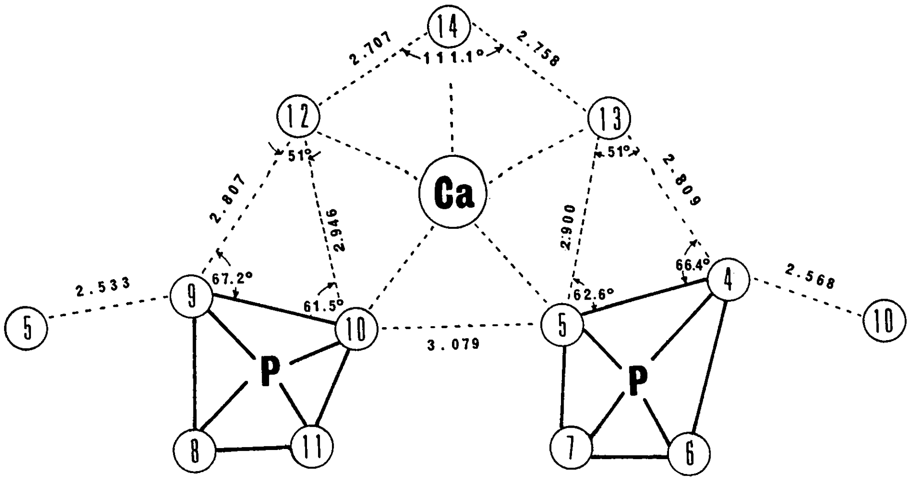

Fig. 5. Hydrogen bonding network around the calcium ion in calcium 1-naphthyl phosphate trihydrate.

to nearby naphthyl groups. Van der Waals distances between carbons in neighboring naphthyl groups are between 3·620 and 3·719 Å.

Conclusions

The significant features of the structure can be summarized in the following manner. The calcium ion is coordinated to seven oxygen atoms, all almost equidistant from the calcium, arranged in a distorted pentagonal bipyramid. Phosphate and other bond distances and angles appear normal except that the $\mathrm{C{-}O(PO_3)}$ bond distances are significantly shorter and the C–O–P bond angles are significantly larger in calcium 1-naphthyl phosphate than in other organic phosphates for which the structures are known. The organic phosphates with which this is compared involve non-aromatic carbon atoms.

Since hardly any data are available on hydrolysis rates of the organic phosphates discussed here, no conclusions regarding hydrolysis rates can be made at this time. However, the short C–O bond distances and the longer P–OR bond distances suggest hydrolysis attack at P–O rather than C–O in aromatic organic phosphates.

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Refinement of the Crystal Structure of Triphenyl Phosphate

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The structure of triphenyl phosphate has been refined by full-matrix least-squares computations to a final R of 0·109 for 762 reflections with measurable intensities. The space group is $P2_1/a$ with unit-cell dimensions of $a = 17{\cdot}124$, $b = 5{\cdot}833$, $c = 16{\cdot}970$ Å and $\beta = 105°21'$. The P–O bond distances are 1·599, 1·554, 1·549 and 1·432 Å. O–P–O bond angles range from 119·1° to 96·6°. The remaining bond distances and angles are in agreement with previously determined structures.

Introduction

We are interested in the structures of organic phosphates as part of a program to correlate the structural data with hydrolysis rate studies. Such a correlation requires accurate structural details for a variety of organic phosphates including monosubstituted, disubstituted and trisubstituted phosphates.

Accurate structures are known for calcium thymidylate as determined by Trueblood, Horn & Luzzati (1961), 2-aminoethanol phosphate as determined by Kraut (1961), adenosine-5′ -phosphate, determined by Kraut & Jensen (1963) and calcium 1-naphthyl phosphate, determined by Li & Caughlan (1965), all of which are monosubstituted organic phosphates. The

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