Table 6. *Some distances and angles involved in the hydrogen bonds*

Donor	Acceptor	Hydrogen	X–H···O	σ	H···O	σ	X–H–O	σ
N	O(1) $(\frac{1}{2}-x;\ 1-y;\ z-\frac{1}{2})$	H(6)	3·011	6	2·30 Å	6	137°	5
O(3)	O(1) $(\frac{1}{2}+x;\ 1\frac{1}{2}-y;\ 2-z)$	H(9)	2·680	6	1·95	6	166	6

bonds (2·68 Å) connect the molecules in infinite rows along the *a* axis. Together these two hydrogen bonds form a stabilized three-dimensional intermolecular network.

The proposed intramolecular hydrogen bond for hippuric acid in solution (Schätzle & Rottenberg, 1963) between the unprotonized carboxyl oxygen atom and the nitrogen atom is found to be sterically impossible in the solid state.

This work has been supported by the Swedish Medical Research Council (Project No B70 -11X - 144 - 06A).

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The Crystal Structure of Disodium Dihydrogen Hypophosphate Hexahydrate ($Na_2H_2P_2O_6.6H_2O$) and Disodium Dihydrogen Pyrophosphate Hexahydrate ($Na_2H_2P_2O_7.6H_2O$)

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(*Received* 3 *December* 1969)

The crystal structures of the isomorphous disodium hypophosphate hexahydrate ($Na_2H_2P_2O_6.6H_2O$) and disodium dihydrogen pyrophosphate hexahydrate ($Na_2H_2P_2O_7.6H_2O$) have been determined with diffractometer data. The space group is $C2/c$ and a unit cell contains four formula units. The unit-cell dimensions of $Na_2H_2P_2O_6.6H_2O$ are $a=14{\cdot}090$ (3), $b=6{\cdot}998$ (1), $c=12{\cdot}700$ (6) Å, $\beta=115{\cdot}94$ (2)° and those of $Na_2H_2P_2O_7.6H_2O$ are $a=14{\cdot}099$ (6), $b=6{\cdot}959$ (4), $c=13{\cdot}455$ (8) Å, $\beta=117{\cdot}69$ (4)°. The hypophosphate ion has C_2 symmetry with a P–P distance of 2·190 (1) Å. The mean terminal P–O distance is 1·506 (2) Å while the terminal P–O(H) distance is 1·588 (2) Å. The pyrophosphate ion also has C_2 symmetry. The bridge P–O–P bonds make an angle of 136·1 (1)° and the P–O (bridge) distance is 1·598 (1) Å. The mean value of the terminal P–O distance is 1·494 (2) Å while the terminal P–O(H) distance is 1·569 (2) Å. The bridge oxygen atom of the pyrophosphate is not involved in any appreciable intermolecular bonding and the packing of the ions is similar in both structures.

Introduction

The unit-cell dimensions and space groups for a number of hydrated sodium hypophosphate and pyrophosphate salts have been reported by Corbridge (1957). In both the tetrasodium decahydrate and disodium dihydrogen hexahydrate series the hypophosphate salt (containing a phosphorus–phosphorus bond) and the pyrophosphate salt (containing a phosphorus–oxygen–phosphorus bridge) have the same space group and similar unit-cell dimensions. Corbridge suggested that these two hypophosphate–pyrophosphate salt pairs were isomorphous and interpreted his preliminary *b* axis projections in the disodium dihydrogen series to indicate that the P–O–P bond in the pyrophosphate was linear with the oxygen atom either on a twofold axis or at a center of symmetry. He found the P–P bond in the hypophosphate to be in a similar orientation.

We have determined the crystal structures with diffractometer data of both the disodium dihydrogen hypophosphate hexahydrate ($Na_2H_2P_2O_6.6H_2O$) and the disodium dihydrogen pyrophosphate hexahydrate ($Na_2H_2P_2O_7.6H_2O$) salts in order to study the apparent isomorphism of these two chemically different species.

Experimental

Crystal data

$Na_2H_2P_2O_6.6H_2O$, $M=314{\cdot}0$, monoclinic:
$a=14{\cdot}090\ (3)$, $b=6{\cdot}998\ (1)$, $c=12{\cdot}700\ (6)$ Å, $\beta=115{\cdot}94\ (2)°$;
$U=1125{\cdot}9$ Å^3, $D_m=1{\cdot}855$ (flotation), $D_c=1{\cdot}852$ g.cm^{-3};
$Z=4$, $F(000)=648$; Mo $K\alpha(\lambda=0{\cdot}70926$ Å for $K\alpha_1)$, $\mu=5{\cdot}28$ cm^{-1}.

$Na_2H_2P_2O_7.6H_2O$, $M=330{\cdot}0$, monoclinic;
$a=14{\cdot}099\ (6)$, $b=6{\cdot}959\ (4)$, $c=13{\cdot}455\ (8)$ Å, $\beta=117{\cdot}69\ (4)°$
$U=1169{\cdot}0$ Å^3, $D_m=1{\cdot}877$ (flotation), $D_c=1{\cdot}875$ g.cm^{-3};
$Z=4$, $F(000)=680$, Mo $K\alpha(\lambda=0{\cdot}70926$ Å for $K\alpha_1)$, $\mu=5{\cdot}20$ cm^{-1}.

Systematically absent spectra for both crystals: hkl when $h+k$ odd, $h0l$ when h odd and l odd, $0k0$ when k odd. Space group Cc or $C2/c$ determined to be $C2/c$ in the structure analysis.

Disodium dihydrogen hypophosphate was prepared by adding an aqueous sodium chlorite solution slowly to red phosphorus according to the method of Leininger & Chulski (1949). The salt was separated by a double crystallization from water and a semi-qualitative check for impurities was made with thin-layer chromatography. Phosphite, hypophosphite and orthophosphate were not detected. We were particularly concerned about pyrophosphate contamination and were able to establish by thin-layer chromatography that, if present, it must be less than 5% of the hypophosphate. A flame photometer analysis for sodium gave 14·41% (calc. 14·64%). The loss in weight on heating a sample to 120°C corresponded to 6·02 moles of water per mole of hypophosphate.

Disodium dihydrogen pyrophosphate was prepared by adding glacial acetic acid to a solution of $Na_4P_2O_7.10H_2O$ at 20°C (Bell, 1950). After the solution was cooled to 10°C, crystals of $Na_2H_2P_2O_7.6H_2O$ formed and were filtered off. The crystal from which the X-ray data were collected was prepared by saturating a 2:1 ethanol–water mixture with $Na_2H_2P_2O_7.6H_2O$ at 40°C, cooling it rapidly through 20°C and then allowing crystallization to proceed overnight at 10°C. The loss in weight on heating a sample to 110°C corresponded to 6·04 moles of water per mole of pyrophosphate.

Under certain conditions, generally when crystallization occurred quickly, twinned crystals were produced in both compounds. The relation of the twin pairs can be described either as a reflection across the $(10\bar{2})$ plane or as a 180° rotation about the normal to this plane. Twinning was more common in the pyrophosphate in accord with the somewhat better fit of the lattices of the twin pairs in this crystal. In neither case was the lattice registry of the twin pairs perfect and it was possible to detect twinned crystals by observation of reflection doubling at high scattering angles. Verification that the crystals used for the intensity measurements were indeed untwinned was made by observation of certain reflections that could not be detected above background even though they were related by the twin law to intense reflections. In this way, it was possible to conclude that if twinning were present in the crystals used for intensity measurement, the second component of the twin should make up less than 1% of the crystal.

Unlike the hypophosphate hexahydrate salt which is stable in contact with its saturated solution to 80°C, the pyrophosphate transforms to the anhydrous salt at 27°C (van Wazer, 1958). At room temperature in air the crystals turn milky within an hour and to prevent loss of water during the X-ray data collection on the pyrophosphate, a stream of air, chilled by passing it through a coil immersed in an ice bath, was blown over the crystal. After the air had been cooled to ice temperature and just before it left the nozzle directed at the crystal, it passed over a filter paper wick kept saturated with water. The temperature of the exit air measured by a thermocouple just beyond the end of the nozzle was maintained at 10±2°C by manual control of the air flow. Intensity data on the $Na_2H_2P_2O_6.6H_2O$ crystals were obtained with the crystal in air at room temperature with no attempt to control dehydration.

Lattice constants and intensity data were measured on a Picker 4-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation and pulse height analysis. The lattice constants were measured with a 0·6° target take-off angle and a symmetrically variable detector slit. A number of reflections were measured at 2θ angles high enough to resolve the α_1–α_2 doublet and the four lattice constants were determined by a least-squares fit of these data.

The crystals were under 0·25 mm in all dimensions and were mounted with their c^* axes parallel to the φ axis of the diffractometer for the intensity data collection. A 3° target take-off angle was used for the hypophosphate and a 2° angle for the pyrophosphate with a θ–2θ scan of 1°/minute. The scan range was increased with increasing 2θ to allow for dispersion and backgrounds were measured at each end of the scan range. The total time spent on background measurement was equal to that spent on the scan.

All the non-equivalent reflections up to $2\theta=60°$ were examined. With the hypophosphate, of the 1596 possible reflections, 1144 were observed by the criterion that the height above background was greater than 2·5 times the standard deviation of the net count. With the pyrophosphate, 1193 reflections out of a possible 1717 were observed. A standard reflection was measured at roughly $1\frac{1}{2}$ hour intervals and the measured intensities were corrected for the variations of this intensity through the data collection period. Although there was no change in the appearance of the crystals during data collection, there was a progressive drop in intensity of the standard reflection which amounted

Table 1. *Observed and calculated structure factors* (×10) in $Na_2H_2P_2O_6.6H_2O$

An * indicates an unobserved reflection and the observed amplitude is replaced by the value calculated from an estimate of the minimum observable intensity. Within an H, L group the +L reflections are listed first followed by the −L reflections.

K	FO	FC
H= 0, L= 0		
2	198	-185
4	1994	-2058
6	273	280
8	490	476
H= 1, L= 0		
1	854	843
3	285	264
5	533	-535
7	247	238
9	90*	77
H= 2, L= 0		
0	538	587
2	182	-166
4	203	191
6	317	311
8	81*	-45
H= 3, L= 0		
1	586	611
3	451	-446
5	346	-345
7	395	385
9	82	70
H= 4, L= 0		
0	2037	2168
2	314	-302
4	1269	-1275
6	299	284
8	476	466
H= 5, L= 0		
1	550	-515
3	192	-170
5	127	135
7	217	216
9	93*	10
H= 6, L= 0		
0	1043	-1035
2	214	-219
4	111	86
6	202	191
8	149	147
H= 7, L= 0		
1	755	756
3	1263	-1258
5	300	-292
7	496	482
9	145	141
H= 8, L= 0		
0	694	683
2	58*	39
4	903	-911
6	76*	-33
8	504	485
H= 9, L= 0		
1	194	199
3	521	-516
5	73*	-4
7	217	211
H= 10, L= 0		
0	63*	23
2	65*	53
4	210	-221
6	81*	34
8	200	196
H= 11, L= 0		
1	764	774
3	754	-752
5	286	-282
7	387	380
H= 12, L= 0		
0	454	459
2	72*	79
4	304	-307
6	89*	12
H= 13, L= 0		
1	115	109
3	78*	-72
5	88*	60
H= 14, L= 0		
0	309	316
2	80*	-21
4	110	-101
6	135	133
H= 15, L= 0		
1	373	382
3	253	-245
5	222	-213
H= 16, L= 0		
0	402	409
2	90*	-24
4	192	-211
H= 17, L= 0		
1	113	106
H= 0, L= 1		
2	703	-728
4	349	354
6	592	595
8	216	-227
H= 1, L= 1		
1	686	-704
3	98	85
5	555	563
7	181	188
9	90*	-88
1	751	775
3	106	95
5	481	-479
7	174	-170
9	107	117
H= 2, L= 1		
2	185	141
4	53*	38
6	661	658
8	82*	-56
2	1414	1437
4	74	74
6	722	-731
8	80*	21
H= 3, L= 1		
1	754	-762
3	395	395
5	675	663
7	121	-120
9	191	-197
1	466	459
3	626	606
5	213	-206
7	227	-219
9	172	184
H= 4, L= 1		
2	339	323
4	95	96
6	189	192
8	173	-179
2	1373	1357
4	450	-456
6	177	-157
8	369	367
H= 5, L= 1		
1	782	-779
3	453	-465
5	426	428
7	133	132
9	223	-214
1	480	-457
3	282	270
5	92	104
7	75*	-46
9	198	211
H= 6, L= 1		
2	829	-827
4	144	-140
6	342	353
8	87*	-47
2	1035	1027
4	130	-133
6	172	-161
8	153	159
H= 7, L= 1		
1	692	-687
3	573	-567
5	384	382
7	81*	2
1	64	63
3	378	361
5	152	-143
7	79*	-28
9	287	291
H= 8, L= 1		
2	462	-459
4	67*	-74
6	77*	23
8	91*	-48
2	551	554
4	312	-316
6	75*	-18
8	233	245
H= 9, L= 1		
1	540	-535
3	695	-686
5	295	301
7	191	192
1	127	129
3	368	365
5	161	-144
7	218	-195
H= 10, L= 1		
2	683	-671
4	108	121
6	201	188
2	747	760
4	71*	-35
6	416	-409
8	93*	-23
H= 11, L= 1		
1	70*	-59
3	86	-83
5	191	195
7	92*	-26
1	532	515
3	263	260
5	482	-479
7	138	-139
H= 12, L= 1		
2	126	-122
4	176	165
6	91*	73
2	71*	72
4	91	-97
6	219	-229
H= 13, L= 1		
1	253	-254
3	186	-186
5	291	312
1	321	321
3	81	94
5	324	-315
7	128	-131
H= 14, L= 1		
2	310	-326
4	165	176
2	187	187
4	86*	-42
6	330	-322
H= 15, L= 1		
1	119	-106
3	90*	6
1	270	272
3	86*	-43
5	312	-311
H= 16, L= 1		
2	249	-244
2	84	-95
4	94*	7
H= 17, L= 1		
1	298	-309
1	237	230
3	105	122
H= 0, L= 2		
0	805	-836
2	155	-158
4	352	356
6	68*	13
8	131	-154
H= 1, L= 2		
1	419	-451
3	189	-163
5	84	84
7	179	-183
9	91*	81
1	478	-500
3	524	513
5	61*	20
7	239	-240
9	92*	38
H= 2, L= 2		
0	124	-113
2	85	88
4	578	-551
6	233	-226
8	203	202
0	227	239
2	39*	-14
4	76	38
6	81	-66
8	81*	-70
H= 3, L= 2		
1	753	-753
3	176	186
5	237	243
7	337	-331
9	92*	86
1	491	-469
3	643	603
5	278	276
7	103	-79
9	176	-181
H= 4, L= 2		
0	1115	-1084
2	99	-121
4	317	331
6	120	117
8	112	-95
0	990	-989
2	66	81
4	1168	1147
6	67*	11
8	455	-470
H= 5, L= 2		
1	582	-566
3	272	263
5	278	297
7	260	-253
9	94*	-7
1	332	324
3	527	493
5	163	-167
7	82	-77
9	91*	-58
H= 6, L= 2		
0	320	-292
2	158	159
4	129	133
6	109	-109
8	88*	-31
0	936	908
2	109	115
4	67	-3
6	137	-133
8	151	-130
H= 7, L= 2		
1	392	-377
3	490	479
5	284	284
7	252	-238
1	85	93
3	269	258
5	66*	0
7	78*	-64
9	98	-103
H= 8, L= 2		
0	229	-200
2	62*	70
4	410	398
6	79*	46
8	236	-236
0	614	-620
2	122	120
4	522	522
6	196	-195
8	249	-243
H= 9, L= 2		
1	70	99
3	342	335
5	108	-97
7	185	-181
1	313	310
3	244	-248
5	184	-190
7	84*	13
H= 10, L= 2		
0	271	292
2	152	148
4	76*	68
6	185	-176
0	155	-165
2	63*	-23
4	70*	-72
6	90	-82
8	93*	35
H= 11, L= 2		
1	72*	-33
3	241	230
5	85*	-20
7	95*	-70
1	539	-535
3	138	135
5	328	325
7	125	-133
H= 12, L= 2		
0	194	-177
2	77*	-20
4	281	273
6	92*	-33
0	854	-897
2	70*	-25
4	338	350
6	87*	-45
H= 13, L= 2		
1	135	-121
3	183	177
5	91*	-51
1	72*	-58
3	182	-180
5	85*	96
7	94*	-9
H= 14, L= 2		
0	236	-236
2	87*	-40
4	161	156
0	237	-257
2	76*	18
4	84*	35
6	93*	-19
H= 15, L= 2		
1	256	-255
3	97	85
1	230	-246
3	182	193
5	218	200
H= 16, L= 2		
0	407	-406
2	94*	-34
0	86*	-44
2	88	73
4	92*	39
H= 17, L= -2		
1	166	163
3	93*	-20
H= 0, L= 3		
2	2104	-2194
4	57	-51
6	655	666
8	82*	-33
H= 1, L= 3		
1	429	415
3	50*	21
5	316	-322
7	76*	-60
9	92*	46
1	141	112
3	104	105
5	80	64
7	209	-197
9	124	-117
H= 2, L= 3		
2	552	550
4	58*	-5
6	471	-486
8	119	-105
2	1164	-1174
4	54*	-58
6	80	81
8	83*	61
H= 3, L= 3		
1	130	92
3	404	-398
5	152	-177
7	98	75
9	98	-88
1	208	181
3	592	-564
5	203	-224
7	74*	36
9	105	-86
H= 4, L= 3		
2	1020	-1030
4	142	149
6	73*	54
8	130	-124
2	501	532
4	67	-63
6	638	-627
8	83*	-6
H= 5, L= 3		
1	869	837
3	294	302
5	373	-393
7	163	-176
9	95*	-15
1	428	-422
3	682	-660
5	63*	-22
7	71	61
9	95	-93
H= 6, L= 3		
2	466	465
4	72	69
6	360	-382
8	90*	12
2	1290	-1264
4	166	-164
6	242	247
8	89	92
H= 7, L= 3		
1	339	-362
3	429	-435
7	204	211
5	254	246
1	436	450
3	119	118
5	249	-282
7	78*	-3
9	90	74
H= 8, L= 3		
2	359	-360
4	71*	29
6	196	185
8	108	98
2	594	622
4	239	230
6	216	-221
8	112	-113
H= 9, L= 3		
1	210	201
3	224	214
5	79*	-31
7	91*	1
1	79	67
3	295	249
5	71*	47
7	81*	6
H= 10, L= 3		
2	278	273
4	78*	-25
6	89*	19
2	62*	-41
4	69*	25
6	286	282
8	92*	34
H= 11, L= 3		
1	351	-361
3	147	-126
5	312	299
1	297	299
3	483	486
5	96	-101
7	85	-80
H= 12, L= 3		
2	200	206
4	87*	-37
6	94*	45
2	315	313
4	86	91
6	86*	32
H= 13, L= 3		
1	161	161
3	293	288
5	94*	-77
1	132	-137
3	75*	-38
5	81*	30
7	93*	94
H= 14, L= 3		
2	167	165
4	94*	-60
2	165	-168
4	131	-129
6	167	158
H= 15, L= 3		
1	167	-166
3	95*	-85
1	78*	57
3	83*	61
5	91*	-88
H= 16, L= -3		
2	86	81
4	91*	-30
H= 17, L= -3		
1	89*	20
3	104	-94
H= 0, L= 4		
0	1620	-1654
2	321	311
4	453	438
6	330	-331
8	85*	-62
H= 1, L= 4		
1	44*	-68
3	92	86
5	220	225
7	189	-192
9	93*	-67
1	366	-353
3	292	-280
5	293	307
7	125	-106
9	93*	-30
H= 2, L= 4		
0	337	290
2	145	144
4	108	110
6	73*	-20
8	139	-152
0	1928	-2024
2	139	-146
4	599	584
6	70*	9
8	127	-123
H= 3, L= 4		
1	239	224
3	451	454
5	141	-152
7	257	-251
9	94*	39
1	890	-883
3	117	-76
5	484	492
7	174	-169
9	91*	-70
H= 4, L= 4		
0	458	441
2	200	188
4	132	128
6	134	-135
8	150	-154
0	2016	-2027
2	213	216
4	457	451
6	367	-368
8	85*	-29
H= 5, L= 4		
1	150	-181
3	570	555
5	107	110
7	177	-165
1	281	256
3	476	-459
5	65*	60
7	77*	7
9	92*	-20
H= 6, L= 4		
0	58	52
2	110	-113
4	325	322
6	121	137
8	250	-248
0	479	-493
2	50*	65
4	389	392
6	126	-120
8	174	-175
H= 7, L= 4		
1	372	-381
3	581	579
5	77*	11
7	196	-206
1	61	-73
3	451	454
5	67*	-19
7	227	-229
9	94*	-13
H= 8, L= 4		
0	67*	-20
2	128	-126
4	122	122
6	85*	65
0	253	246
2	172	172
4	156	173
6	200	-205
8	132	-137
H= 9, L= 4		
1	352	-369
3	254	251
5	123	126
7	107	-94
1	79	74
3	319	329
5	70*	32
7	84*	-74
H= 10, L= 4		
0	229	-238
2	95	-90
4	141	117
6	91*	-7
0	296	-295
2	62*	7
4	578	586
6	79*	38
8	349	-338
H= 11, L= 4		
1	104	-105
3	81*	45
5	89*	-69
1	374	-392
3	702	713
5	79	96
7	276	-281
H= 12, L= 4		
0	83	-79
2	82*	-23
4	90*	-52
0	134	138
2	68*	-34
4	113	107
6	85*	14
H= 13, L= 4		
1	149	-135
3	90*	14
1	258	-266
3	281	299
5	101	98
7	149	-147
H= 14, L= 4		
0	289	-283
2	92*	50
0	366	-369
2	74*	-23
4	243	249
6	91*	-42
H= 15, L= 4		
1	94*	-18
1	183	-188
3	149	172
5	90*	-11
H= 16, L= -4		
0	44*	-37
2	85*	-19
4	88	-99
H= 17, L= -4		
1	206	-216
3	95	78
H= 0, L= 5		
2	583	594
4	61*	-31
6	717	-735
8	84	78
H= 1, L= 5		
1	392	389
3	210	-210
5	364	-377
7	79*	73
9	94*	135
1	929	-916
3	53*	13
5	728	726
7	115	90
9	167	-168
H= 2, L= 5		
2	598	-575
4	63*	-2
6	74*	-12
8	151	152
2	505	513
4	105	106
6	268	273
8	87*	-78
H= 3, L= 5		
1	968	970
3	535	541
5	540	-552
7	82*	-61
1	714	-712
3	317	-309
5	524	517
7	238	233
9	120	-118
H= 4, L= 5		
2	880	889
4	181	189
6	357	-363
8	91*	16
2	1834	-1881
4	176	172
6	917	916
8	99	-87
H= 5, L= 5		
1	339	331
3	393	399
5	155	-156
7	87*	-35
1	161	-178
3	242	-237
5	256	261
7	156	144
9	172	-175
H= 6, L= 5		
2	402	421
4	72*	-22
6	81*	-44
8	106	103
2	164	-165
4	230	236
6	72*	-15
8	195	-205
H= 7, L= 5		
1	545	539
3	610	603
5	339	-337
7	171	-178
1	199	-200
3	509	-498
5	181	188
7	116	127
9	261	-266
H= 8, L= 5		
2	532	533
4	78*	-69
6	194	-184
2	1431	-1454
4	292	290
6	360	368
8	257	-260
H= 9, L= 5		
1	74*	-41
3	78*	17
5	140	-139
7	95*	-7
1	373	371
3	95	-86
5	100	-102
7	84*	-20
H= 10, L= 5		
2	169	174
4	240	-248
6	118	-106
2	328	-339
4	191	197
6	79*	-32
8	202	-203
H= 11, L= 5		
1	178	169
3	138	134
5	236	-238
1	557	-564
3	584	-595
5	366	353
7	199	219
H= 12, L= 5		
2	255	239
4	107	-112
2	901	-900
4	89	78
6	425	434
H= 13, L= 5		
1	105	106
3	93*	6
1	128	-140
3	79	-84
5	167	176
7	83	98
H= 14, L= 5		
2	254	235
2	225	-222
4	91	101
6	259	272
H= 15, L= -5		
1	551	-551
3	240	-246
5	491	483
H= 16, L= -5		
2	145	-137
4	90*	51
H= 17, L= -5		
1	125	-123
3	120	112
H= 0, L= 6		
0	49*	-2
2	53*	-42
4	198	261
6	191	191
8	88*	-66
H= 1, L= 6		
1	847	836
3	391	-414
5	458	-472
7	415	415
9	91	64
1	416	415
3	215	-233
5	67*	22
7	404	375
9	162	-161
H= 2, L= 6		
0	1391	1384
2	96	-105
4	677	-686
6	110	108
8	237	240
0	1278	1294
2	109	108
4	638	-619
6	73*	50
8	271	262
H= 3, L= 6		
1	284	290
3	298	-305
5	177	-182
7	316	332
1	862	864
3	570	-581
5	343	-342
7	318	329
9	94*	78
H= 4, L= 6		
0	298	297
2	146	-138
4	243	-253
6	80*	56
8	134	138
0	47*	7
2	51*	20
4	194	-210
6	140	139
8	157	159
H= 5, L= 6		
1	589	588
3	670	-672
5	457	-456
7	375	375
1	605	594
3	843	-841
5	131	-129
7	301	302
9	101	51
H= 6, L= 6		
0	579	579
2	188	-185
4	596	-608
6	168	154
0	924	924
2	107	98
4	1061	-1063
6	73*	-76
8	505	519
H= 7, L= 6		
1	137	-143
3	207	-209
5	111	108
7	155	153
1	321	319
3	740	-741
5	165	-160
7	274	265
9	156	140
H= 8, L= 6		
0	73*	-16
2	85	-78
4	206	-202
6	96	112
0	230	-239
2	246	-254
4	288	-285
6	286	289
8	248	244
H= 9, L= 6		
1	312	320
3	447	-447
5	121	-123
1	61	-54
3	381	-393
5	71*	34
7	191	212
H= 10, L= 6		
0	343	332
2	82*	-24
4	329	-328
0	582	604
2	76	-71
4	613	-627
6	113	112
8	369	356
H= 11, L= 6		
1	85*	78
3	89*	-77
5	94*	43
1	148	164
3	269	-261
5	73	-63
7	230	240
H= 12, L= 6		
0	423	401
2	91*	57
4	293	-286
0	432	443
2	136	-133
4	196	-204
6	263	260
H= 13, L= 6		
1	413	397
3	336	348
5	88	-91
5	264	-267
7	156	153
H= 14, L= -6		
0	1083	1049
2	74*	11
4	528	-546
6	90*	52
H= 15, L= -6		
1	349	368
3	175	-179
5	205	-223
H= 16, L= -6		
0	415	402
4	140	-148
H= 17, L= -6		
1	226	217
3	114	-120
5	207	-195
H= 0, L= 7		
2	59*	-68
4	67*	9
6	343	374
8	90*	62
H= 1, L= 7		
1	477	-485
3	81	-70
5	427	443
7	85*	96
1	551	543
3	183	191
5	600	-603
7	115	-102
H= 2, L= 7		
2	439	-470
4	129	128
6	434	476
8	115	-120
2	54*	46
4	345	-348
6	129	-124
8	155	154
H= 3, L= 7		
1	586	-589
3	279	-277
5	349	359
7	156	155
1	52*	14
3	67	70
5	258	-255
7	81*	-3
9	217	224
H= 4, L= 7		
2	368	-364
4	91	-89
6	334	349
8	95*	-51
2	365	377
4	64*	-29
6	110	-108
8	88*	1
H= 5, L= 7		
1	280	-283
3	71	-70
5	183	184
7	91*	-56
1	690	695
3	713	708
5	446	-451
7	101	-100
9	353	346
H= 6, L= 7		
2	347	-345
4	114	109
6	174	164
2	629	631
4	68	-54
6	75*	-10
8	113	104
H= 7, L= 7		
1	137	-130
3	174	-156
5	87*	31
7	95*	14
1	236	265
3	569	565
5	90	-81
7	114	-127
H= 8, L= 7		
2	396	-379
4	80	45
6	111	123
2	911	922
4	68*	35
6	297	-296
8	92*	53
H= 9, L= 7		
1	138	-141
3	171	-157
5	123	113
1	506	498
3	336	340
5	328	-319
7	86*	-55
H= 10, L= 7		
2	391	-385
4	96	97
2	64*	54
4	92	-95
6	137	-120
8	127	133
H= 11, L= 7		
1	145	-142
3	238	-239
1	129	120
3	69*	-48
5	156	-159
7	69*	-33
H= 12, L= 7		
2	337	-341
2	366	387
4	156	-155
6	414	-425
H= 13, L= -7		
1	200	210
3	77	-86
5	265	-271
7	93*	-22
H= 14, L= -7		
2	74*	42
4	81*	-71
6	245	-250
H= 15, L= -7		
1	274	287
3	104	118
5	239	-228
H= 16, L= -7		
2	485	455
4	90*	-51
H= 17, L= -7		
1	143	143
3	98	97
5	147	-116
H= 0, L= 8		
0	59*	26
2	130	-130
4	70*	-104
6	80*	-12
8	92*	43
H= 1, L= 8		
1	624	-627
3	194	211
5	307	315
7	111	-112
1	133	-147
3	63*	73
5	73*	-49
7	86*	-4
H= 2, L= 8		
0	1163	-1193
2	65*	-13
4	554	563
6	82*	-100
8	143	-142
0	681	-710
2	59*	-61
4	629	629
6	77*	-32
8	258	-268
H= 3, L= 8		
1	159	148
3	341	-325
5	78*	-32
7	90*	36
1	79	-85
3	386	397
5	72*	-61
7	104	-116
H= 4, L= 8		
0	99	-107
2	112	120
4	84	-67
6	158	-177
0	1500	1473
2	59*	25
4	522	-495
6	76*	-25
8	90*	39
H= 5, L= 8		
1	163	-160
3	111	119
5	158	177
7	160	-169
1	57*	-7
3	508	533
5	135	-134
7	191	-195
H= 6, L= 8		
0	364	-359
2	166	161
4	220	226
6	150	-140
0	291	-311
2	85	60
4	523	532
6	77*	41
8	284	-297
H= 7, L= 8		
1	244	240
3	122	-100
5	91*	-46
1	58*	-57
3	305	312
5	72*	53
7	131	-142
H= 8, L= 8		
0	104	-103
2	122	116
4	169	145
0	531	516
2	61*	23
4	247	-238
6	79*	30
8	93*	32
H= 9, L= 8		
1	241	-230
3	324	311
5	184	186
1	532	-527
3	423	427
5	242	241
7	257	-253
H= 10, L= 8		
0	137	-129
2	91*	17
4	164	183
0	766	-787
2	66*	-33
4	371	367
6	82*	48
8	121	-131
H= 11, L= 8		
1	92*	-10
3	97	98
1	67*	11
3	202	-211
5	78*	25
7	92*	-41
H= 12, L= 8		
0	97*	-64
0	68*	-11
2	71*	55
4	213	-224
6	127	-131
H= 13, L= -8		
1	238	-238
3	75*	40
5	104	117
7	143	-122
H= 14, L= -8		
0	387	-381
2	75*	-8
4	152	145
6	91*	-29
H= 15, L= -8		
1	99	108
3	137	-157
5	90*	-38
H= 16, L= -8		
0	129	-115
2	45*	54
4	90*	91
H= 17, L= -8		
1	145	-157
3	190	171
5	136	141
H= 0, L= 9		
2	336	338
4	286	-87
6	112	-94
8	94*	-47
H= 1, L= 9		
1	312	-321
3	205	-249
5	78*	65
7	90*	48
1	63*	63
3	277	-290
5	95	-91
7	219	213
H= 2, L= 9		
2	158	-175
4	173	-176
6	86*	10
2	236	-251
4	162	150
6	141	-131
8	92	-72
H= 3, L= 9		
1	90	-77
3	126	-108
5	82*	-31
7	93*	-67
1	383	376
3	66*	41
5	284	-274
7	105	-85
H= 4, L= 9		
2	139	-124
4	80*	-72
6	90*	-70
2	201	-210
4	88	-73
6	148	-139
8	92*	10
H= 5, L= 9		
1	114	-102
3	269	-272
5	87*	19
1	85	54
3	134	-142
5	149	-136
7	87*	-14
H= 6, L= 9		
2	138	-130
4	86*	88
6	94*	-5
2	321	322
4	86	74
6	292	-283
8	149	-138
H= 7, L= 9		
1	211	215
3	126	143
5	94*	-50
1	212	198
3	248	241
5	170	-184
7	151	-154
H= 8, L= 9		
2	87	74
4	98	101
2	88	91
4	230	-232
6	80*	53
8	94	125
H= 9, L= 9		
1	89*	32
3	93*	-4
1	407	-416
3	112	-105
5	227	215
7	89*	45
H= 10, L= 9		
2	95*	-12
2	399	407
4	75	-50
6	86*	-14
H= 11, L= -9		
1	69*	-8
3	172	178
5	80*	23
7	93*	-10
H= 12, L= -9		
2	101	100
4	115	-128
6	169	150
H= 13, L= -9		
1	143	-150
3	77	79
5	197	179
7	95*	-47
H= 14, L= -9		
2	456	483
4	86*	28
6	197	-196
H= 15, L= -9		
1	216	220
3	141	147
5	147	-139
H= 16, L= -9		
2	86*	-86
4	91*	-19
H= 17, L= -9		
1	87*	51
3	91*	-40
H= 0, L= 10		
0	406	-428
2	71*	47
4	249	207
6	97*	1
H= 1, L= 10		
1	105	-104
3	100	102
5	169	172
7	151	-148
1	375	-368
3	252	249
5	219	208
7	288	-265
H= 2, L= 10		
0	358	-358
2	153	148
4	256	287
6	90*	-101
0	194	-171
2	67*	54
4	94	-46
6	149	-139
8	97*	31
H= 3, L= 10		
1	197	-194
3	292	284
5	194	209
1	149	-131
3	69*	-23
5	78*	11
7	111	-124
H= 4, L= 10		
0	98	-127
2	79*	66
4	215	213
6	42	-8
0	439	-420
2	97	-95
4	199	189
6	81*	-8
8	94*	-75
H= 5, L= 10		
1	80*	54
3	125	119
5	90*	-32
1	548	-536
3	423	424
5	133	142
7	244	-237
H= 6, L= 10		
0	80	-65
2	87*	73
4	158	146
6	97*	-120
0	106	-66
2	90	-99
4	116	108
6	81*	16
8	94*	-89
H= 7, L= 10		
1	87*	-59
3	98	103
1	336	-327
3	363	356
5	131	109
7	88	-102
H= 8, L= 10		
0	106	-90
2	94*	-42
4	97*	109
0	475	-464
2	66*	-43
4	549	551
6	86*	29
H= 9, L= 10		
1	122	-112
1	220	-208
3	474	475
5	78*	48
7	165	-175
H= 10, L= -10		
0	260	255
2	70*	59
4	112	100
6	94	-55
H= 11, L= -10		
1	71*	-8
3	297	274
5	82*	-13
7	148	-134
H= 12, L= -10		
0	338	-324
2	122	122
4	359	361
6	134	-134
H= 13, L= -10		
1	75*	22
3	79	84
5	88*	2
H= 14, L= -10		
0	201	-205
2	79*	63
4	100	109
6	109	-104
H= 15, L= -10		
1	248	-263
3	137	131
5	179	185
H= 16, L= -10		
0	665	-631
2	87*	24
4	325	320
H= 17, L= -10		
1	137	-148
3	41*	-23
H= 0, L= 11		
2	105	108
4	81*	-1
6	184	-222
H= 1, L= 11		
1	522	524
3	342	356
5	319	-313
1	266	-253
3	75*	-21
5	294	285
7	95*	30
H= 2, L= 11		
2	531	588
4	84*	-23
6	366	-375
2	634	-609
4	128	133
6	487	482
H= 3, L= 11		
1	79*	62
3	82*	-33
5	91*	-21
1	329	-330
3	206	-200
5	376	386
7	177	163

Table 1 (*cont.*)

K	FO	FC
H= 4, L= 11		
2	143	143
4	88*	-10
2	231	218
4	213	202
6	88*	0
H= 5, L= 11		
1	288	285
3	215	236
5	159	-163
1	224	-199
3	95	-91
5	353	357
7	92*	-7
H= 6, L= 11		
2	332	334
4	93*	-73
2	686	-680
4	103	110
6	292	301
H= 7, L= 11		
1	92*	-18
3	95*	25
1	317	-303
3	412	-407
5	235	250
7	147	146
H= 8, L= 11		
2	278	267
2	225	-220
4	89	71
6	88*	-21
H= 9, L= -11		
1	487	-473
3	467	-459
5	305	293
7	93*	82
H= 10, L= -11		
2	751	-766
4	75	-71
6	317	310
H= 11, L= -11		
1	267	-275
3	243	-244
5	175	170
7	97*	56
H= 12, L= -11		
2	103	-106
4	108	107
6	96	90
H= 13, L= -11		
1	309	-312
3	118	-105
5	264	258
H= 14, L= -11		
2	363	-330
4	89*	19
6	333	343
H= 15, L= -11		
1	177	-192
3	88*	21
5	220	221
H= 16, L= -11		
2	140	-143
4	133	121
H= 17, L= -11		
1	269	-272
3	134	-138
H= 0, L= 12		
0	554	557
2	79*	6
4	294	-311
6	93*	72
H= 1, L= 12		
1	116	121
3	91	-74
5	90*	-71
1	470	453
3	246	-238
5	302	-269
H= 2, L= 12		
0	468	454
2	146	-127
4	231	-267
0	693	702
2	75*	5
4	462	-442
6	145	139
H= 3, L= 12		
1	107	103
3	105	-116
5	127	-145
1	213	214
3	158	-165
5	87*	-35
7	105	94
H= 4, L= 12		
0	196	218
2	128	-122
4	170	-177
0	284	280
2	73*	61
4	309	-288
6	91*	21
H= 5, L= 12		
1	90*	42
3	137	-171
1	354	357
3	483	-481
5	116	-105
7	228	230
H= 6, L= 12		
0	243	242
2	96*	-79
0	71*	65
2	93	-87
4	253	-246
6	147	160
H= 7, L= 12		
1	155	183
1	72*	-19
3	278	-265
5	82*	66
7	152	148
H= 8, L= -12		
0	151	137
2	73*	-38
4	312	-304
6	91*	-3
H= 9, L= -12		
1	433	447
3	644	-629
5	234	-232
7	355	359
H= 10, L= -12		
0	233	229
2	88	-92
4	254	-240
6	111	68
H= 11, L= -12		
1	147	166
3	176	-190
5	134	-137
H= 12, L= -12		
0	522	545
2	78*	-34
4	334	-337
6	93*	32
H= 13, L= -12		
1	383	391
3	328	-331
5	228	-201
H= 14, L= -12		
0	201	204
2	83*	-44
4	91*	-29
H= 15, L= -12		
1	101	100
3	90*	1
5	95*	-51
H= 16, L= -12		
0	492	500
2	90*	-28
4	305	-281
H= 17, L= -12		
1	214	230
3	171	-189
H= 0, L= 13		
2	127	-110
4	164	156
H= 1, L= 13		
1	219	-204
3	89*	-67
5	236	246
1	79*	-7
3	86*	2
5	102	-113
H= 2, L= 13		
2	125	-115
4	92*	51
2	513	504
4	119	-141
6	245	-265
H= 3, L= 13		
1	99	-98
3	93*	23
1	219	209
3	261	277
5	198	-204
H= 4, L= 13		
2	165	-147
2	304	301
4	114	-131
6	111	-84
H= 5, L= 13		
1	309	-298
1	76*	17
3	138	138
5	89*	-27
H= 6, L= -13		
2	564	557
4	96	-105
6	170	-175
H= 7, L= -13		
1	127	119
3	165	150
5	90	-68
H= 8, L= -13		
2	76*	19
4	82*	-46
6	94*	36
H= 9, L= -13		
1	195	214
3	132	113
5	135	-126
H= 10, L= -13		
2	410	394
4	87*	14
6	274	-256
H= 11, L= -13		
1	270	270
3	90	113
5	189	-181
H= 12, L= -13		
2	81*	16
4	89*	26
H= 13, L= -13		
1	372	385
3	143	151
5	315	-321
H= 14, L= -13		
2	187	184
4	93*	-7
H= 15, L= -13		
1	88*	102
3	92*	-24
H= 16, L= -13		
2	92*	-29
4	95*	-78
H= 17, L= -13		
1	175	169
3	96*	88
H= 0, L= 14		
0	87*	-111
2	91*	-41
4	90	71
H= 1, L= 14		
1	91*	5
3	93*	-3
1	158	-152
3	108	119
5	97*	25
H= 2, L= 14		
0	91*	-11
2	95*	-45
0	125	101
2	87*	-38
4	93*	-23
H= 3, L= 14		
1	221	-213
1	44*	5
3	106	100
5	95*	-89
H= 4, L= 14		
0	196	-199
0	288	-243
2	45*	-7
4	280	277
H= 5, L= -14		
1	135	-114
3	151	159
5	148	132
H= 6, L= -14		
0	43*	13
2	102	91
4	90*	67
6	104	-70
H= 7, L= -14		
1	125	122
3	45*	15
5	92*	-38
H= 8, L= -14		
0	242	-214
2	97	86
4	170	162
6	96*	-52
H= 9, L= -14		
1	44*	36
3	86*	-37
5	105	59
H= 10, L= -14		
0	44*	-21
2	122	112
4	90*	-78
H= 11, L= -14		
1	45*	23
3	88	-105
5	95*	12
H= 12, L= -14		
0	392	-353
2	87*	-28
4	153	138
H= 13, L= -14		
1	167	-183
3	92*	35
5	95*	120
H= 14, L= -14		
0	104	-90
2	90*	-13
4	95*	-13
H= 15, L= -14		
1	91*	-91
3	94*	20
H= 16, L= -14		
0	108	-109
2	94*	-52
H= 17, L= -14		
1	95*	-45
H= 0, L= 15		
2	95*	-23
H= 1, L= 15		
1	96*	-7
1	149	147
3	97	100
H= 2, L= -15		
2	183	186
4	96*	-3
H= 3, L= -15		
1	89*	-4
3	92*	-32
H= 4, L= -15		
2	91*	-24
4	95*	-9
H= 5, L= -15		
1	91	102
3	92*	42
5	170	-159
H= 6, L= -15		
2	89*	-6
4	127	-122
H= 7, L= -15		
1	149	-141
3	91*	-89
5	95*	5
H= 8, L= -15		
2	88*	43
4	93*	-48
H= 9, L= -15		
1	165	177
3	206	203
5	163	-159
H= 10, L= -15		
2	88*	108
4	94*	0
H= 11, L= -15		
1	77	12
3	102	102
H= 12, L= -15		
2	204	214
4	96*	48
H= 13, L= -15		
1	191	200
3	150	160
H= 14, L= -15		
2	93*	-51
H= 15, L= -15		
1	93*	13
3	97*	-54
H= 16, L= -15		
2	96*	83
H= 0, L= 16		
0	99	-87
H= 1, L= -16		
1	96*	-10
H= 2, L= -16		
0	362	-387
2	96*	13
H= 3, L= -16		
1	243	-228
3	108	117
H= 4, L= -16		
0	184	-185
2	95*	-38
H= 5, L= -16		
1	142	-127
3	96*	82
H= 6, L= -16		
0	327	-330
2	92*	-20
4	249	266
H= 7, L= -16		
1	109	-108
3	115	131
H= 8, L= -16		
0	104	93
2	91*	16
4	97*	12
H= 9, L= -16		
1	110	-77
3	205	210
H= 10, L= -16		
0	201	-207
2	92*	35
4	224	244
H= 11, L= -16		
1	92*	-92
3	138	173
H= 12, L= -16		
0	94*	-63
2	94*	54
H= 13, L= -16		
1	199	-196
3	234	238
H= 14, L= -16		
0	269	-270
2	96*	25
H= 15, L= -16		
1	96*	-79

to 5% for $Na_2H_2P_2O_6.6H_2O$ and 15% for $Na_2H_2P_2O_7.6H_2O$. This was not caused by movement of the crystal, but probably represents some decomposition. Since a number of reflections measured at different times showed little change when corrected for the variation of the standard intensity, if decomposition were occurring it had little effect on the relative intensities of the reflections. The intensities were corrected for Lorentz and polarization factors and put on an approximate scale with a Wilson (1942) plot.

Structure determination and refinement

The intensity statistics suggested that both structures were centrosymmetric and the structure determinations were carried out on the assumption that the space group was $C2/c$. The atomic scattering factors for H, O^{2-}, P and Na^+ were taken from Table 3·3·1A of *International Tables for X-ray Crystallography* (1962).

Trial positions for all atoms in the hypophosphate structure (excluding hydrogen) were found by an interpretation of the unsharpened Patterson function. The R index $[R=\sum(|F_{\text{obs}}|-|F_{\text{calc}}|)/|F_{\text{obs}}|]$ based on the initial trial parameters was 0·33 and an electron density map using phases calculated from these trial positions revealed all the atoms with no extraneous large peaks. Five cycles of block-diagonal least-squares with individual atom isotropic temperature factors, a Hughes (1941) weighting scheme and inclusion of unobserved values only when $|F_{\text{calc}}|$ was greater than the threshold value of the structure factor for that reflection reduced R to 0·067. Three further cycles using anisotropic thermal parameters reduced R to 0·050. The hydrogen atoms were located by a difference Fourier synthesis based on reflections with $\sin\theta/\lambda$ less than 0·45. Seven peaks appeared with a height between 0·4 and 0·5 e.Å^{-3}. These seven peaks were assigned to the seven hydrogen atoms in the asymmetric unit and were included with isotropic temperature factors in three least-squares cycles in which R dropped to 0·042. The isotropic thermal parameters for the hydrogen atoms stayed between 2·0 and 2·5 Å^2 except for one, H(15), for which the thermal parameter dropped to the unreasonably low value of 0·60 Å^2. Seven reflections classified as unobserved calculated much too high and a data collection error (probably in setting the diffractometer angles) was suspected. These reflections were remeasured and included in two more least-squares cycles in which all the hydrogen atom thermal parameters were held fixed at 2·5 Å^2. A weighting scheme with

$$w=\frac{1}{\left[1+\left(\frac{|F_{\text{obs}}|-40}{50}\right)^4\right]}$$

gave a reasonably constant value when the mean values of $w(|F_{\text{obs}}|-|F_{\text{calc}}|)^2$ were plotted against $|F_{\text{obs}}|$.

Although the structure at this point was considered as refined, there was some doubt about the validity of the standard deviations derived from a block-diagonal least-squares calculation. When a full-matrix least-squares program became available to us, two cycles were calculated. The 049 reflection which was in very bad agreement was omitted. There were only small parameter shifts and no significant change in R. The final R value, excluding unobserved reflections and 049 was 0·037. The observed and calculated structure factors are listed in Table 1 and the final atomic parameters are given in Table 2.

The approximate structure for the pyrophosphate was derived by first transforming the centered cell to a primitive cell and then applying the symbolic addition procedure (Karle & Karle, 1966). This gave two undetermined symbols and signs were assigned to these so that the signs of the larger E values were in agreement with the signs of the corresponding reflec-

Table 2. *Positional and thermal parameters in* $Na_2H_2P_2O_6.6H_2O$

The U_{ij} values are coefficients in $T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*)\right]$.

Standard deviations are given in parentheses.

	x	y	z	$U_{11}\times 10^4$	$U_{22}\times 10^4$	$U_{33}\times 10^4$	$2U_{12}\times 10^4$	$2U_{23}\times 10^4$	$2U_{31}\times 10^4$
P(1)	0·00148 (4)	0·13517 (9)	0·16451 (5)	133 (2)	151 (3)	174 (4)	14 (4)	24 (4)	132 (4)
O(2)	−0·10942 (13)	0·10786 (28)	0·07065 (16)	164 (8)	288 (10)	215 (9)	22 (14)	10 (16)	120 (12)
O(3)	0·05980 (14)	0·30826 (27)	0·15327 (18)	206 (9)	212 (9)	307 (10)	−40 (14)	90 (16)	236 (16)
O(4)	0·07116 (14)	−0·04784 (28)	0·17315 (18)	169 (8)	204 (9)	308 (10)	62 (14)	38 (16)	196 (16)
O(5)	0·26224 (18)	0·12426 (36)	0·12098 (20)	330 (11)	346 (12)	344 (11)	−54 (20)	−84 (20)	372 (18)
O(6)	0·21851 (16)	0·64529 (32)	0·11450 (18)	242 (9)	269 (10)	281 (10)	60 (18)	88 (18)	240 (16)
O(7)	−0·04475 (17)	0·64855 (33)	0·08454 (20)	331 (11)	213 (10)	358 (11)	54 (16)	−50 (18)	302 (18)
Na(8)	0·23850 (8)	0·38336 (17)	0·23565 (9)	228 (5)	207 (5)	293 (6)	−44 (8)	36 (8)	212 (8)
H(9)	0·2164 (36)	0·0828 (67)	0·0616 (42)	An isotropic temperature factor of $B=2.5$ Å^2 was used for all hydrogen atoms					
H(10)	0·2639 (36)	0·6306 (71)	0·1028 (40)						
H(11)	−0·0185 (36)	0·5562 (71)	0·1030 (41)						
H(12)	0·3056 (37)	0·1324 (73)	0·1036 (41)						
H(13)	−0·0548 (34)	0·6591 (68)	0·0134 (44)						
H(14)	0·1759 (36)	0·7105 (69)	0·0577 (43)						
H(15)	0·0349 (35)	−0·1389 (68)	0·1491 (40)						

tions in the isomorphous hypophosphate whose structure was known at this stage.

An E map based on this set of signs showed peaks for all the non-hydrogen atoms plus three peaks comparable in size with an oxygen peak, that were not in structurally reasonable positions.

The atomic coordinates from the E map with isotropic temperature factors for P, O and Na of 1·24, 2·5 and 1·24 respectively were used to calculate a set of structure factors which gave an R index of 0·40 for all observed reflections. An electron density map calculated with the observed amplitudes and phases from this structure factor calculation showed all the non-hydrogen atoms with no extraneous peaks. This gave a set of atomic position parameters with $R=0.24$. Three cycles of block-diagonal least-squares reduced R to 0·049. At this point, a difference Fourier synthesis based on reflections with sin θ/λ less than 0·46 showed a number of peaks that were assigned to hydrogen atoms.

One least-squares cycle with the hydrogen atoms assigned isotropic thermal parameters gave a large increase in the thermal parameters of H(12), H(13) and H(15). Also, the positions of H(13) and H(15) were unreasonable. Three least-squares cycles were performed omitting H(13) and H(15) and all parameters refined by the criterion that the parameter shifts in the last cycle were less than the calculated standard deviations. An analysis of the structure factor agreement as a function of $|F_{\text{obs}}|$ showed that a more constant value of the mean $w(|F_{\text{obs}}|-|F_{\text{calc}}|)^2$ could be obtained with the same weighting scheme finally used for the hypophosphate and this was used in all subsequent calculations. A difference Fourier synthesis using the refined signs showed the two hydrogen atoms that had been omitted from the refinement. These were then included in several cycles of block-diagonal least-squares in which the 400 and $20\bar{8}$ reflections were omitted because of poor agreement between $|F_{\text{calc}}|$ and $|F_{\text{obs}}|$ and the hydrogen atoms were assigned fixed isotropic thermal parameters of 2·5 Å^2. This was followed by two cycles of full-matrix least squares. In the last cycle, the shifts were less than the standard deviations except for the y parameter of H(11) which had a shift of 1·05 times its calculated standard deviation. The final R value was 0·040. The observed and calculated structure factors are listed in Table 3 and the final atomic parameters in Table 4.

To aid in comparing the structures of $Na_2H_2P_2O_6.6H_2O$ and $Na_2H_2P_2O_7.6H_2O$, the numbering of the atoms is the same in both except that the additional oxygen atom in $Na_2H_2P_2O_7.6H_2O$ is labelled O (bridge). The standard deviations reported for the atomic parameters are those derived from the full-matrix least-squares treatments which are only about 10% higher than those derived from the block-diagonal calculation. The errors in bond distances and angles reported here include the errors in unit-cell dimensions and were calculated using the variance–covariance matrix from the least-squares calculation. Actually, the introduction of the variance–covariance matrix had no significant effect on the estimated errors.

Symmetry-related atoms in the Figures and text are denoted by superscripts which correspond to the following transformations:

Table 3. *Observed and calculated structure factors* (×10) *in* $Na_2H_2P_2O_7.6H_2O$

An * indicates an unobserved reflection and the observed amplitude is replaced by the value calculated from an estimate of the minimum observable intensity. Within an H, L group the +L reflections are listed first followed by the −L reflections.

K	FO	FC
H= 0, L= 0		
2	432	-413
4	1630	-1742
6	65*	50
8	472	499
H= 1, L= 0		
1	912	936
3	140	112
5	371	-357
7	171	174
9	90*	-43
H= 2, L= 0		
0	835	897
2	441	-422
4	377	357
6	189	169
8	81*	27
H= 3, L= 0		
1	647	656
3	616	-613
5	234	-225
7	354	373
9	92*	57
H= 4, L= 0		
0	2092	2421
2	639	-599
4	1209	-1241
6	360	354
8	527	533
H= 5, L= 0		
1	671	-620
3	288	-276
5	301	302
7	222	224
9	93*	52
H= 6, L= 0		
0	779	-792
2	347	-338
4	58*	17
6	261	271
8	198	176
H= 7, L= 0		
1	731	755
3	1259	-1236
5	232	-250
7	413	407
9	242	244
H= 8, L= 0		
0	854	883
2	82	-63
4	918	-929
6	142	118
8	413	403
H= 9, L= 0		
1	90	123
3	390	-390
5	91	70
7	125	93
H= 10, L= 0		
0	161	166
2	62*	41
4	204	-219
6	84*	35
8	131	136
H= 11, L= 0		
1	820	830
3	796	-795
5	309	-284
7	349	368
H= 12, L= 0		
0	503	510
2	74*	-39
4	247	-253
6	90*	100
H= 13, L= 0		
1	76*	58
3	81*	-70
5	88*	97
H= 14, L= 0		
0	391	379
2	108	-79
4	88*	-82
H= 15, L= 0		
1	438	449
3	391	-385
5	197	-207
H= 16, L= 0		
0	354	370
2	90*	-85
4	94*	-111
H= 17, L= 0		
1	127	112
H= 0, L= 1		
2	876	-885
4	505	499
6	468	470
8	191	-208
H= 1, L= 1		
1	819	-784
3	484	453
5	328	336
7	273	290
9	122	-132
1	800	815
3	232	-232
5	265	-264
7	129	-141
9	91*	94
H= 2, L= 1		
2	161	104
4	328	319
6	621	634
8	139	-150
2	1482	1570
4	52*	-21
6	594	-600
8	83*	-48
H= 3, L= 1		
1	1062	-1056
3	747	735
5	517	523
7	75*	-45
9	264	-262
1	458	434
3	560	527
5	60*	-49
7	203	-197
9	91*	112
H= 4, L= 1		
2	46*	0
4	249	236
6	201	210
8	225	-233
2	1240	1232
4	537	-522
6	68*	16
8	259	256
H= 5, L= 1		
1	853	-856
3	243	-246
5	245	248
7	172	171
9	210	-224
1	264	-250
3	167	148
5	60*	-28
7	91	87
9	206	207
H= 6, L= 1		
2	760	-745
4	115	-130
6	210	226
8	88*	-46
2	1103	1106
4	205	-190
6	189	-175
8	86*	77
H= 7, L= 1		
1	907	-909
3	577	-574
5	342	328
7	82*	-26
1	50*	47
3	204	195
5	115	-109
7	79*	60
9	245	233
H= 8, L= 1		
2	504	-494
4	65*	-89
6	81*	-78
8	91*	5
2	413	418
4	390	-383
6	78*	80
8	234	226
H= 9, L= 1		
1	489	-477
3	569	-591
5	257	255
7	133	127
1	309	295
3	246	258
5	171	-141
7	98	-118
H= 10, L= 1		
2	566	-547
4	153	155
6	127	91
2	745	748
4	67*	39
6	393	-373
8	94*	-74
H= 11, L= 1		
1	258	-235
3	131	-124
5	384	376
7	93*	-56
1	467	474
3	92	95
5	264	-262
7	117	-120
H= 12, L= 1		
2	74*	-60
4	250	236
6	91*	30
2	67*	61
4	134	-146
6	154	-160
H= 13, L= 1		
1	225	-215
3	82*	-108
5	325	331
1	403	406
3	76*	34
5	244	-246
H= 14, L= 1		
2	351	-344
4	218	208
2	149	166
4	87*	-62
6	298	-306
H= 15, L= 1		
1	245	-241
3	90*	-29
1	220	222
3	151	-173
5	238	-240
H= 16, L= 1		
2	185	-189
2	89*	-89
4	92*	-104
H= 17, L= -1		
1	241	234
3	95*	116
H= 0, L= 2		
0	778	-795
2	68	-56
4	198	213
6	65*	37
8	124	-154
H= 1, L= 2		
1	318	-333
3	153	-136
5	116	-106
7	74*	-22
9	89*	35
1	362	-356
3	552	548
5	320	-305
7	75*	-38
9	91*	16
H= 2, L= 2		
0	205	199
2	294	287
4	925	-922
6	84	-88
8	216	221
0	458	436
2	116	-114
4	155	-172
6	65*	-8
8	83*	52
H= 3, L= 2		
1	860	-862
3	425	415
5	151	150
7	260	-276
9	125	110
1	365	-345
3	328	315
5	99	88
7	221	245
9	261	-262
H= 4, L= 2		
0	1391	-1396
2	101	80
4	134	143
6	308	302
8	88*	-88
0	828	-848
2	71	81
4	894	907
6	64*	23
8	309	-311
H= 5, L= 2		
1	345	-346
3	56*	26
5	235	237
7	94	-83
9	95*	23
1	353	363
3	419	388
5	296	-300
7	120	111
9	92*	-108
H= 6, L= 2		
0	146	-124
2	350	348
4	319	-301
6	74*	38
8	108	100
0	609	605
2	247	246
4	57*	-59
6	68*	-94
8	86*	-69
H= 7, L= 2		
1	475	-455
3	569	573
5	311	301
7	253	-257
1	409	400
3	56*	-11
5	64*	-82
7	79*	69
9	168	-169
H= 8, L= 2		
0	206	-192
2	226	209
4	202	203
6	80*	83
8	176	-183
0	554	-580
2	416	416
4	290	275
6	228	-217
8	223	-204
H= 9, L= 2		
1	339	356
3	133	129
5	223	-208
7	126	-111
1	406	400
3	238	-247
5	233	-250
7	85*	20
H= 10, L= 2		
0	343	369
2	247	228
4	76*	-67
6	220	-226
0	191	-206
2	137	133
4	257	-262
6	81*	30
8	93*	48
H= 11, L= 2		
1	169	-148
3	358	359
5	86*	-7
7	139	-122
1	259	-262
3	122	-133
5	203	203
7	90*	30
H= 12, L= 2		
0	110	-89
2	76*	-45
4	160	185
6	93*	-18
0	834	-842
2	66*	60
4	131	137
6	87*	45
H= 13, L= 2		
1	80*	-17
3	85*	38
5	126	-146
1	73*	-94
3	203	-187
5	85*	58
7	99*	94
H= 14, L= 2		
0	281	-278
2	87*	-78
4	170	159
0	124	-138
2	76*	-17
4	110	-126
6	130	125
H= 15, L= 2		
1	342	-340
3	131	137
1	102	-113
3	85*	60
5	92*	79
H= 16, L= 2		
0	300	-267
2	97*	-69
0	85*	-1
2	87*	76
4	91*	4
H= 17, L= -2		
1	172	166
3	93*	-1
H= 18, L= -2		
0	287	285
2	95*	26
H= 0, L= 3		
2	2085	-2243
4	301	-305
6	894	897
8	225	-231
H= 1, L= 3		
1	153	153
3	79	79
5	158	-171
7	212	-214
9	90*	-14
1	572	517
3	489	473
5	59*	-16
7	255	-265
9	91*	-35
H= 2, L= 3		
2	260	264
4	178	-184
6	68*	-87
8	269	-277
2	732	-713
4	75	81
6	207	-205
8	236	228
H= 3, L= 3		
1	69	-103
3	584	-555
5	115	105
7	77*	46
9	154	-152
1	271	254
3	342	-335
5	405	-401
7	76*	-12
9	92*	61
H= 4, L= 3		
2	1044	-1028
4	199	188
6	320	316
8	267	-283
2	1068	1101
4	221	-217
6	912	-919
8	145	156
H= 5, L= 3		
1	744	725
3	125	128
5	65*	-25
7	243	-259
1	632	-583
3	321	-302
5	343	-353
7	78*	-78
9	92*	110
H= 6, L= 3		
2	57*	18
4	63*	52
6	77*	-65
8	91*	-3
2	1045	-1029
4	424	-430
6	66*	86
8	211	211
H= 7, L= 3		
1	250	-256
3	666	-684
5	425	21
7	243	247
1	235	246
3	400	403
5	620	-636
7	79*	-33
9	216	236
H= 8, L= 3		
2	505	-530
4	158	164
6	252	250
8	94*	19
2	913	951
4	61*	49
6	380	-366
8	88*	-34
H= 9, L= 3		
1	224	237
3	68*	15
5	113	122
7	92*	17
1	142	-137
3	499	500
5	143	-144
7	77*	6
H= 10, L= 3		
2	72*	26
4	78*	26
6	130	128
2	91	77
4	67*	40
6	209	209
8	93*	61
H= 11, L= 3		
1	299	-296
3	206	-203
5	385	389
1	552	546
3	799	805
5	394	-397
7	89*	-79
H= 12, L= 3		
2	117	93
4	86*	121
6	95*	95
2	486	499
4	127	133
6	145	-142
H= 13, L= 3		
1	81*	75
3	193	196
5	94*	24
1	66*	-39
3	73*	35
5	95	-101
7	98*	111
H= 14, L= 3		
2	89*	34
4	94*	-72
2	74*	-45
4	100	-95
6	92*	-29
H= 15, L= 3		
1	279	-274
3	138	-145
1	377	372
3	193	184
5	354	-337
H= 16, L= -3		
2	109	95
4	91*	-12
H= 17, L= -3		
1	88*	76
3	92*	-99
H= 18, L= -3		
2	146	168
H= 0, L= 4		
0	1798	-1780
2	431	420
4	648	667
6	428	-419
8	196	-200
H= 1, L= 4		
1	187	157
3	154	165
5	346	342
7	522	-523
9	91*	28
1	385	-370
3	135	-129
5	327	333
7	266	-278
9	120	112
H= 2, L= 4		
0	44*	-71
2	449	440
4	380	396
6	248	-233
8	320	-325
0	1696	-1786
2	462	-440
4	834	866
6	67*	-11
8	279	-270
H= 3, L= 4		
1	264	251
3	441	414
5	120	121
7	529	-530
9	96*	55
1	1281	-1261
3	227	242
5	497	494
7	242	-244
9	92*	35
H= 4, L= 4		
0	209	-204
2	378	350
4	454	472
6	360	-346
8	215	-217
0	1854	-1950
2	387	-345
4	841	884
6	349	-353
8	151	-148
H= 5, L= 4		
1	271	-281
3	533	501
5	350	345
7	365	-363
1	154	-163
3	73	-61
5	63*	8
7	78*	-106
9	92*	33
H= 6, L= 4		
0	317	-337
2	163	-169
4	576	575
6	79*	0
8	224	-240
0	309	-351
2	387	-360
4	843	848
6	266	-262
8	339	-337
H= 7, L= 4		
1	514	-526
3	569	551
5	171	151
7	295	-283
1	330	-321
3	703	705
5	65*	-5
7	361	-371
9	94*	-30
H= 8, L= 4		
0	61*	-187
2	186	-197
4	332	333
6	165	-128
0	204	230
2	55*	29
4	475	485
6	433	-442
8	211	-197
H= 9, L= 4		
1	453	-463
3	332	348
5	145	139
7	196	-188
1	111	85
3	349	359
5	69*	52
7	228	-242
H= 10, L= 4		
0	190	-195
2	179	-190
4	284	272
6	92*	-102
0	425	-438
2	58*	-6
4	768	770
6	119	-109
8	367	-354
H= 11, L= 4		
1	248	-245
3	273	286
5	110	-69
1	468	-475
3	695	698
5	279	286
7	410	-419
H= 12, L= 4		
0	82*	-86
2	77*	-48
4	103	99
0	152	-159
2	64*	82
4	230	239
6	100	-117
H= 13, L= 4		
1	250	-249
3	198	196
1	256	-271
3	264	264
5	262	280
7	308	-299
H= 14, L= 4		
0	324	-330
2	92*	11
0	597	-635
2	95	68
4	384	393
6	91*	-75
H= 15, L= 4		
1	171	-145
1	276	-282
3	301	298
5	152	127
H= 16, L= -4		
0	106	-105
2	84*	67
4	90*	-46
H= 17, L= -4		
1	226	-237
3	173	147
H= 18, L= -4		
0	464	-473
2	91*	1
H= 19, L= -4		
1	206	-217
H= 0, L= 5		
2	961	984
4	260	-241
6	824	-824
8	282	273
H= 1, L= 5		
1	44*	33
3	181	-185
5	309	-317
7	78*	75
9	208	223
1	352	-374
3	170	-173
5	836	838
7	127	113
9	311	-296
H= 2, L= 5		
2	450	-454
4	61*	94
6	135	-131
8	309	318
2	443	449
4	363	382
6	218	214
8	168	-166
H= 3, L= 5		
1	1346	1358
3	811	815
5	611	-617
7	133	-117
1	285	247
3	496	-485
5	513	517
7	190	196
9	116	-131
H= 4, L= 5		
2	1024	1017
4	368	370
6	516	-516
8	173	178
2	1959	-2101
4	330	355
6	867	879
8	85*	-85
H= 5, L= 5		
1	372	371
3	303	304
5	74*	-83
7	86*	60
1	244	223
3	607	-573
5	464	462
7	120	113
9	180	-171
H= 6, L= 5		
2	256	246
4	174	163
6	140	-136
8	186	174
2	300	-275
4	185	194
6	91	89
8	168	-164
H= 7, L= 5		
1	837	827
3	697	698
5	588	-604
7	125	-138
1	53*	-2
3	609	-591
5	304	309
7	81*	57
9	211	-215
H= 8, L= 5		
2	350	356
4	105	-105
6	270	-257
2	1317	-1355
4	220	236
6	517	537
8	351	-343
H= 9, L= 5		
1	136	-141
3	98	-70
5	287	-284
1	186	175
3	61*	-44
5	115	104
7	137	-147
H= 10, L= 5		
2	208	194
4	259	-276
6	181	-203
2	112	-107
4	67*	-13
6	98	119
8	308	-296
H= 11, L= 5		
1	335	328
3	331	336
5	501	-533
1	568	-594
3	403	-422
5	296	290
7	89*	81
H= 12, L= 5		
2	223	248
4	167	-162
2	769	-775
4	74*	-41
6	504	501
H= 13, L= 5		
1	92*	9
3	103	84
1	260	-260
3	99	-95
5	132	138
7	94*	49
H= 14, L= 5		
2	387	416
2	194	-189
4	80*	-57
6	290	293
H= 15, L= -5		
1	465	-494
3	264	-262
5	431	422
H= 16, L= -5		
2	228	-223
4	128	124
H= 17, L= -5		
1	86*	-42
3	90*	37
H= 18, L= -5		
2	91*	-58
H= 19, L= -5		
1	204	-191
H= 0, L= 6		
0	497	-478
2	392	378
4	61*	57
6	152	139
8	86*	-58
H= 1, L= 6		
1	855	869
3	457	-466
5	460	-479
7	298	302
9	107	76
1	222	213
3	236	-247
5	333	335
7	223	229
9	235	-222
H= 2, L= 6		
0	529	526
2	101	100
4	405	-420
6	76*	7
8	98	116
0	46*	142
2	566	567
4	499	-493
6	128	138
8	155	163
H= 3, L= 6		
1	221	215
3	286	-290
5	170	-164
7	304	311
1	788	757
3	370	-382
5	195	-197
7	158	158
9	94*	77
H= 4, L= 6		
0	152	135
2	128	-118
4	160	-162
6	81*	-37
8	92*	73
0	621	-561
2	406	395
4	114	-115
6	219	215
8	86*	-22
H= 5, L= 6		
1	300	288
3	411	-408
5	447	-468
7	423	417
1	252	247
3	313	-316
5	65*	49
7	116	113
9	93*	-75
H= 6, L= 6		
0	135	132
2	293	-298
4	229	-217
6	214	203
0	829	866
2	291	278
4	937	-945
6	74*	-69
8	312	317
H= 7, L= 6		
1	197	-212
3	127	-128
5	83*	56
7	323	312
1	192	172
3	211	-203
5	384	-364
7	154	151
9	95*	108
H= 8, L= 6		
0	67*	16
2	106	-111
4	142	-123
6	131	123
0	171	-174
2	344	-349
4	126	-107
6	285	286
8	90*	61
H= 9, L= 6		
1	205	203
3	244	-231
5	158	-155
1	350	-355
3	61*	-29
5	67*	-64
7	247	253
H= 10, L= 6		
0	294	287
2	81*	19
4	243	-246
0	555	580
2	221	-233
4	501	-506
6	79*	105
8	294	300
H= 11, L= 6		
1	175	182
3	88*	-65
5	96*	-15
1	233	-247
3	67*	109
5	76*	-81
7	224	223
H= 12, L= 6		
0	348	348
2	180	174
4	298	-289
0	61*	45
2	225	-234
4	74*	51
6	290	285
H= 13, L= 6		
1	299	314
1	150	136
3	74*	36
5	178	-171
7	126	117
H= 14, L= -6		
0	621	654
2	117	132
4	388	-388
6	91*	-49
H= 15, L= -6		
1	201	181
3	78*	24
5	89*	-73
H= 16, L= -6		
0	105	114
2	79*	107
4	88*	-74
H= 17, L= -6		
1	249	242
3	101	-111
5	115	-115
H= 18, L= -6		
0	89*	81
2	109	109
4	192	-190
H= 19, L= -6		
1	93*	-42
H= 0, L= 7		
2	234	219
4	64*	-27
6	76*	-3
8	251	264
H= 1, L= 7		
1	303	314
3	226	-231
5	130	126
7	82*	73
1	161	-155
3	287	302
5	478	-493
7	82*	-76
9	95*	87
H= 2, L= 7		
2	59*	24
4	67*	61
6	79*	-33
8	90*	26
2	526	-539
4	293	-312
6	169	167
8	89*	-21
H= 3, L= 7		
1	57*	-75
3	283	-283
5	143	142
7	85*	38
1	695	-674
3	134	-140
5	118	-94
7	81*	65
9	95*	34
H= 4, L= 7		
2	100	101
4	175	-194
6	84*	8
8	94*	3
2	553	-549
4	56*	62
6	74*	79
8	87*	-40
H= 5, L= 7		
1	156	163
3	146	154
5	138	-114
7	182	-179
1	279	282
3	229	227
5	218	-210
7	81*	86
9	94*	101
H= 6, L= 7		
2	110	103
4	79*	-18
6	87*	-18
2	244	-254
4	310	319
6	148	153
8	89*	79
H= 7, L= 7		
1	112	-93
3	78*	-37
5	86*	-94
7	95*	-53
1	54*	-28
3	136	148
5	356	375
7	83*	60
H= 8, L= 7		
2	78*	-47
4	202	-198
6	93*	84
2	217	225
4	470	488
6	121	-119
8	91*	36
H= 9, L= 7		
1	81*	2
3	84*	30
5	92*	-100
1	391	405
3	144	192
5	73*	66
7	86*	60
H= 10, L= 7		
2	157	-154
4	90*	-46
2	300	-301
4	230	236
6	80*	45
8	93*	83
H= 11, L= 7		
1	90*	-45
3	91*	-123
1	348	-359
3	234	-255
5	218	236
7	90*	72
H= 12, L= 7		
2	96*	-52
2	67*	3
4	74*	-80
6	172	-170
H= 13, L= -7		
1	232	-228
3	187	-160
5	81*	-72
7	93*	44
H= 14, L= -7		
2	344	-329
4	129	-109
6	91*	68
H= 15, L= -7		
1	363	-377
3	80*	-75
5	89*	74
H= 16, L= -7		
2	242	216
4	88*	-81
H= 17, L= -7		
1	175	-173
3	89*	79
5	95*	30
H= 18, L= -7		
2	138	-140
4	94*	26
H= 19, L= -7		
1	152	-150
H= 0, L= 8		
0	959	934
2	586	-596
4	517	-522
6	230	239
8	318	325
H= 1, L= 8		
1	458	-466
3	64*	-32
5	124	128
7	215	219
1	152	151
3	542	-520
5	203	-212
7	343	351
H= 2, L= 8		
0	57*	82
2	334	-345
4	105	102
6	81*	2
8	92*	89
0	133	-272
2	326	-334
4	165	154
6	175	167
8	91*	90
H= 3, L= 8		
1	687	686
3	609	-614
5	466	-465
7	358	354
1	53*	-4
3	165	-155
5	157	144
7	83*	43
H= 4, L= 8		
0	785	803
2	130	-141
4	302	-309
6	86*	-4
0	1875	1893
2	55*	33
4	1016	-1056
6	114	99
8	345	360
H= 5, L= 8		
1	66*	87
3	76*	-22
5	83*	34
7	93*	40
1	681	689
3	317	-312
5	144	-149
7	81*	-57
H= 6, L= 8		
0	256	265
2	77*	67
4	82*	-52
6	90*	-52
0	240	216
2	260	258
4	87	-87
6	77*	80
8	89*	29
H= 7, L= 8		
1	551	560
3	491	-466
5	170	-152
1	543	534
3	320	-333
5	111	98
7	77*	-21
H= 8, L= 8		
0	115	93
2	81*	19
4	87*	-31
0	1315	1347
2	58*	49
4	812	-821
6	146	154
8	326	332
H= 9, L= 8		
1	87*	-32
3	87*	-32
5	188	188
1	59*	34
3	144	-143
5	92	113
7	87*	55
H= 10, L= 8		
0	115	127
2	92*	44
4	145	-149
0	131	-117
2	196	-214
4	70*	73
6	193	213
8	94*	76
H= 11, L= 8		
1	316	290
3	333	-339
1	253	265
3	458	-480
5	77*	-94
7	278	274
H= 12, L= 8		
0	97*	56
0	795	813
2	254	-269
4	490	-491
6	87*	64
H= 13, L= -8		
1	65*	7
3	160	-172
5	153	-139
7	189	190
H= 14, L= -8		
0	291	292
2	271	-261
4	80*	-79
6	91*	45
H= 15, L= -8		
1	363	382
3	433	-438
5	294	-288
H= 16, L= -8		
0	453	456
2	150	-144
4	206	-222
H= 17, L= -8		
1	85*	53
3	102	-116
5	95*	-19
H= 18, L= -8		
0	167	176
2	89*	-76
4	95*	-56
H= 19, L= -8		
1	256	271
H= 0, L= 9		
2	600	-597
4	70*	78
6	170	159
8	138	-141
H= 1, L= 9		
1	831	-854
3	537	-533
5	272	268
7	165	170
1	351	352
3	59*	32
5	335	-325
7	124	114
H= 2, L= 9		
2	423	-444
4	181	-177
6	165	166
2	288	296
4	245	-273
6	164	-140
8	93*	61
H= 3, L= 9		
1	742	-741
3	228	-226
5	227	245
7	91*	-13
1	382	394
3	344	334
5	518	-538
7	202	-200
H= 4, L= 9		
2	415	-419
4	80*	-34
6	261	251
2	571	589
4	558	-574
6	209	-232
8	136	109
H= 5, L= 9		
1	535	-534
3	137	-146
5	306	290
1	56*	3
3	59*	-60
5	352	-347
7	85*	-50
H= 6, L= 9		
2	101	-115
4	174	160
6	228	208
2	831	829
4	252	-257
6	422	-422
8	108	-74
H= 7, L= 9		
1	290	-289
3	86*	83
5	318	343
1	589	610
3	476	468
5	422	-435
7	337	-319
H= 8, L= 9		
2	207	-199
4	187	195
2	681	686
4	353	-357
6	306	-307
8	198	181
H= 9, L= 9		
1	218	-207
3	123	-113
1	182	171
3	139	-144
5	76*	-67
7	89*	-4
H= 10, L= 9		
2	304	-300
2	684	705
4	72*	-46
6	425	-436
8	163	162
H= 11, L= 9		
1	180	-180
1	634	642
3	114	125
5	229	-223
7	92*	-51
H= 12, L= -9		
2	266	267
4	182	-162
6	164	-157
H= 13, L= -9		
1	285	297
3	75*	-30
5	85*	-11
7	94*	30
H= 14, L= -9		
2	635	671
4	81*	68
6	367	-373
H= 15, L= -9		
1	517	528
3	277	259
5	256	-247
H= 16, L= -9		
2	222	233
4	89*	-95
H= 17, L= -9		
1	227	227
3	163	176
5	219	-188
H= 18, L= -9		
2	413	426
4	95*	-114
H= 19, L= -9		
1	167	173
H= 0, L= 10		
0	423	-441
2	63*	-17
4	405	410
6	85*	42
H= 1, L= 10		
1	164	-173
3	354	359
5	80*	62
7	108	-128
1	717	-714
3	794	800
5	162	148
7	260	-265
H= 2, L= 10		
0	209	-221
2	192	198
4	217	229
6	103	-101
0	57*	-20
2	59*	-46
4	107	102
6	123	-101
8	119	-91
H= 3, L= 10		
1	347	-348
3	570	570
5	186	192
7	333	-344
1	264	-255
3	285	297
5	154	-143
7	87*	-91
H= 4, L= 10		
0	264	-264
2	244	233
4	170	152
6	92*	-92
0	465	-474
2	59*	-46
4	279	274
6	134	-105
8	161	-162
H= 5, L= 10		
1	105	94
3	114	96
5	89*	-47
1	600	-591
3	571	574
5	76*	4
7	279	-281
H= 6, L= 10		
0	398	-402
2	215	214
4	142	146
0	342	-332
2	61*	60
4	66*	7
6	81*	-60
8	93*	-78
H= 7, L= 10		
1	332	-317
3	217	254
5	174	167
1	298	-300
3	135	149
5	135	121
7	89*	-99
H= 8, L= 10		
0	434	-445
2	92*	34
4	134	155
0	1099	-1134
2	221	225
4	476	472
6	83*	-20
8	205	-216
H= 9, L= 10		
1	195	-182
3	94*	57
1	352	-346
3	353	362
5	238	249
7	271	-248
H= 10, L= 10		
0	538	-520
0	428	-447
2	294	309
4	142	131
6	86*	-36
H= 11, L= -10		
1	67*	39
3	136	126
5	79*	117
7	156	-164
H= 12, L= -10		
0	614	-640

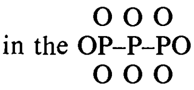
Table 3 (*cont.*)

K	FO	FC
H= 12, L= -10		
2	377	373
4	390	387
6	207	-211
H= 13, L= -10		
1	73*	36
3	199	203
5	86*	5
H= 14, L= -10		
0	77*	-115
2	169	153
4	119	109
6	149	-141
H= 15, L= -10		
1	78*	-95
3	164	156
5	90*	-13
H= 16, L= -10		
0	507	-486
2	77*	10
4	372	361
H= 17, L= -10		
1	254	-244
3	147	165
H= 18, L= -10		
0	198	-195
2	106	-102
H= 19, L= -10		
1	211	-229
H= 0, L= 11		
2	67*	98
4	77*	-32
6	114	114
H= 1, L= 11		
1	283	277
3	358	372
5	169	-158
7	152	-143
1	63*	0
3	73*	25
5	81*	77
7	93*	-50
H= 2, L= 11		
2	241	239
4	176	-163
6	91*	48
2	370	-369
4	150	133
6	122	110
H= 3, L= 11		
1	139	-126
3	133	-171
5	88*	81
1	405	-414
3	267	-262
5	270	272
7	291	274
H= 4, L= 11		
2	140	131
4	87*	-8
6	95*	7
2	426	423
4	155	150
6	118	-102
H= 5, L= 11		
1	256	259
3	157	151
5	93*	-72
1	137	-158
3	402	402
5	166	185
7	89*	-99
H= 6, L= 11		
2	150	184
4	93*	-55
2	65*	-78
4	75*	72
6	198	194
H= 7, L= 11		
1	91*	67
3	94*	-75
1	422	-437
3	68*	31
5	79*	95
7	107	122
H= 8, L= 11		
2	207	237
2	349	359
4	75*	-41
6	123	-131
H= 9, L= -11		
1	404	-419
3	70*	47
5	80*	-14
7	92*	-84
H= 10, L= -11		
2	456	-484
4	231	-240
6	194	164
H= 11, L= -11		
1	234	-240
3	182	-163
5	136	-115
7	94*	45
H= 12, L= -11		
2	75*	43
4	79*	25
6	160	-163
H= 13, L= -11		
1	75*	-75
3	78*	-35
5	87*	13
H= 14, L= -11		
2	273	-267
4	97	69
6	93*	74
H= 15, L= -11		
1	201	200
3	100	111
5	91*	-15
H= 16, L= -11		
2	86*	49
4	248	253
H= 17, L= -11		
1	88*	37
3	91*	-12
H= 18, L= -11		
2	152	-172
H= 19, L= -11		
1	110	67
H= 0, L= 12		
0	300	-294
2	75*	40
4	217	236
6	91*	-69
H= 1, L= 12		
1	255	-256
3	120	114
5	267	259
1	83	72
3	77*	69
5	85*	33
7	169	-157
H= 2, L= 12		
0	121	-124
2	81*	-77
4	86*	-16
6	110	100
0	313	339
2	68*	13
4	79*	52
6	88*	-85
H= 3, L= 12		
1	216	-193
3	86*	45
5	116	136
1	68*	4
3	272	275
5	82*	40
7	220	-205
H= 4, L= 12		
0	238	-230
2	87*	-11
4	90*	54
0	63*	13
2	66*	24
4	364	376
6	251	-249
H= 5, L= 12		
1	89*	-97
3	91*	14
1	164	189
3	74*	-2
5	122	-119
7	91*	2
H= 6, L= 12		
0	121	99
2	93*	-33
0	62*	7
2	204	-203
4	315	315
6	86*	-50
H= 7, L= 12		
1	95*	-29
1	444	-419
3	287	287
5	170	179
7	93*	-75
H= 8, L= -12		
0	474	-466
2	148	-165
4	423	417
6	87*	-107
H= 9, L= -12		
1	68*	13
3	197	-202
5	82*	-16
7	94*	75
H= 10, L= -12		
0	389	-383
2	124	-103
4	264	255
6	100	-55
H= 11, L= -12		
1	290	-289
3	193	173
5	176	177
7	215	-218
H= 12, L= -12		
0	193	-204
2	109	98
4	81*	80
6	156	-162
H= 13, L= -12		
1	154	185
3	188	-168
5	89*	19
H= 14, L= -12		
0	339	-349
2	121	105
4	241	237
6	95*	-70
H= 15, L= -12		
1	221	-218
3	248	255
5	261	241
H= 16, L= -12		
0	85*	-35
2	87*	73
4	92*	73
H= 17, L= -12		
1	89*	-3
3	92*	51
H= 18, L= -12		
0	246	-237
2	93*	2
H= 19, L= -12		
1	121	-163
H= 0, L= 13		
2	419	434
4	86*	54
6	198	-180
H= 1, L= 13		
1	110	116
3	149	141
5	144	-155
1	478	-471
3	596	-598
5	388	385
H= 2, L= 13		
2	142	136
4	90*	4
2	211	-208
4	82*	-31
6	91*	27
H= 3, L= 13		
1	395	387
3	158	191
1	75*	11
3	229	-229
5	213	209
H= 4, L= 13		
2	90*	30
4	95*	-99
2	490	-478
4	130	142
6	206	194
H= 5, L= 13		
K	FU	FC
1	93*	23
3	95*	-127
1	214	-211
3	356	-343
5	436	429
7	94*	46
H= 6, L= -13		
2	75*	-45
4	159	150
6	121	128
H= 7, L= -13		
1	67*	-62
3	108	-100
5	267	280
7	94*	31
H= 8, L= -13		
2	633	-628
4	122	118
6	496	485
H= 9, L= -13		
1	296	-300
3	223	-205
5	309	294
H= 10, L= -13		
2	154	-185
4	80*	15
6	321	329
H= 11, L= -13		
1	267	-265
3	98	-89
5	225	209
H= 12, L= -13		
2	510	-512
4	85*	59
6	452	448
H= 13, L= -13		
1	137	-153
3	81*	-49
5	153	151
H= 14, L= -13		
2	157	-157
4	89*	38
H= 15, L= -13		
1	195	-196
3	182	-169
5	170	187
H= 16, L= -13		
2	451	-426
4	93*	44
H= 17, L= -13		
1	90*	-90
K	FO	FC
3	250	-228
H= 18, L= -13		
2	280	-285
H= 19, L= -13		
1	167	-158
H= 0, L= 14		
0	152	150
2	85*	35
4	349	-363
H= 1, L= 14		
1	208	213
3	305	-319
1	156	165
3	387	-362
5	92*	-19
H= 2, L= 14		
0	89*	57
2	89*	-42
4	154	-186
0	110	95
2	82*	70
4	347	-346
6	94*	75
H= 3, L= 14		
1	92*	69
3	143	-156
1	438	441
3	444	-461
5	297	-286
H= 4, L= 14		
0	317	316
2	94*	-1
0	176	186
2	80*	49
4	302	-303
6	93*	92
H= 5, L= -14		
1	168	145
3	273	-267
5	88*	17
H= 6, L= -14		
0	214	222
2	79*	13
4	195	-199
6	92*	100
H= 7, L= -14		
1	402	395
3	288	-288
5	297	-272
H= 8, L= -14		
0	347	355
2	79*	-59
4	149	-160
/C		
6	143	156
H= 9, L= -14		
1	171	164
3	80*	-109
5	104	-95
H= 10, L= -14		
0	579	586
2	80*	10
4	355	-354
6	94*	7
H= 11, L= -14		
1	394	381
3	269	-246
5	342	-344
H= 12, L= -14		
0	325	336
2	82*	-79
4	278	-282
H= 13, L= -14		
1	81*	46
3	139	-141
5	93*	-63
H= 14, L= -14		
0	282	304
2	87*	-5
4	440	-427
H= 15, L= -14		
1	87*	96
3	238	-247
H= 16, L= -14		
0	88*	6
2	91*	-54
4	223	-224
H= 17, L= -14		
1	92*	44
3	167	-152
H= 18, L= -14		
0	272	260
2	96*	66
H= 0, L= 15		
2	101	-106
4	94*	38
H= 1, L= 15		
1	90*	62
3	93*	-99
1	108	118
3	233	223
H= 2, L= 15		
2	274	-274
2	315	313
4	90*	-33
H= 3, L= 15		
1	96*	-53
1	83*	90
3	159	174
5	109	-98
H= 4, L= -15		
2	104	104
4	88*	78
H= 5, L= -15		
1	359	358
3	214	208
5	317	-305
H= 6, L= -15		
2	82*	89
4	88*	-8
H= 7, L= -15		
1	101	83
3	77*	-69
5	148	-167
H= 8, L= -15		
2	127	-110
4	88*	-21
H= 9, L= -15		
1	319	311
3	120	111
5	365	-363
H= 10, L= -15		
2	83*	37
4	89*	3
H= 11, L= -15		
1	81*	0
3	102	87
5	92*	-85
H= 12, L= -15		
2	213	212
4	90*	34
H= 13, L= -15		
1	230	215
3	358	359
5	213	-220
H= 14, L= -15		
2	184	190
4	93*	30
H= 15, L= -15		
1	127	-122
3	93*	112
H= 16, L= -15		
2	237	233
H= 17, L= -15		
1	93*	44
H= 0, L= 16		
0	138	134
2	93*	4
H= 1, L= 16		
1	94*	-24
1	262	251
3	146	-131
H= 2, L= -16		
0	90*	-33
2	90*	63
4	95*	57
H= 3, L= -16		
1	89*	-65
3	90*	-17
H= 4, L= -16		
0	87*	-10
2	87*	-29
4	92*	-64
H= 5, L= -16		
1	85*	23
3	139	-157
5	94*	37
H= 6, L= -16		
0	264	-273
2	87*	-52
4	91*	91
H= 7, L= -16		
1	131	-155
3	89*	-42
5	163	186
H= 8, L= -16		
0	225	221
2	87*	-74
4	155	-156
H= 9, L= -16		
1	85*	63
3	89*	-18
5	95*	-68
H= 10, L= -16		
0	119	133
2	108	-66
4	92*	54
H= 11, L= -16		
1	86*	39
3	90*	41
H= 12, L= -16		
0	450	453
2	89*	-81
4	93*	-105
H= 13, L= -16		
1	88*	-4
3	118	119
H= 14, L= -16		
0	127	108
2	112	-112
H= 15, L= -16		
1	92*	11
3	95*	-4
H= 16, L= -16		
0	153	183
2	95*	-58
H= 17, L= -16		
1	96*	-17
H= 1, L= -17		
1	130	141
H= 2, L= -17		
2	94*	93
H= 3, L= -17		
1	226	221
3	260	244
H= 4, L= -17		
2	321	339
H= 5, L= -17		
1	167	153
3	92*	82
H= 6, L= -17		
2	91*	47
4	95*	-28
H= 7, L= -17		
1	299	290
3	108	106
H= 8, L= -17		
2	249	224
4	95*	-94
H= 9, L= -17		
1	158	149
3	135	-120
H= 10, L= -17		
2	131	120
4	95*	-11
H= 11, L= -17		
1	379	381
3	131	106
H= 12, L= -17		
2	270	268
H= 13, L= -17		
1	91*	86
3	95*	-89
H= 14, L= -17		
2	221	229
H= 15, L= -17		
1	205	215
H= 4, L= -18		
0	243	-235
H= 5, L= -18		
1	270	-262
H= 6, L= -18		
0	290	-273
2	113	111
H= 7, L= -18		
1	134	-120
H= 8, L= -18		
0	294	-304
2	144	144
H= 9, L= -18		
1	230	-217
3	263	254
H= 10, L= -18		
0	268	-280
2	94*	97
H= 11, L= -18		
1	165	-161
H= 12, L= -18		
0	373	-385
2	96*	50
H= 13, L= -18		
1	256	-268
H= 14, L= -18		
0	271	-269

(i) $\bar{x}, \quad 1-y, \quad \bar{z}$
(ii) $\frac{1}{2}+x, \quad \frac{1}{2}+y, \quad z$
(iii) $\frac{1}{2}-x, \quad \frac{1}{2}+y, \frac{1}{2}-z$
(iv) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(v) $\bar{x}, \quad y, \frac{1}{2}-z$
(vi) $x, -1+y, \quad z$

Discussion of the structures

The general features of the $Na_2H_2P_2O_6 . 6H_2O$ structure can be seen in Fig. 1(*a*). The phosphorus–phosphorus bond in the hypophosphate ion is perpendicular to the twofold axis and the ion has C_2 symmetry in agreement with Corbridge's (1957) suggestion. The PO_3 groups are in a staggered conformation. Hypophosphate ions are linked together in sheets in the *bc* plane by a hydrogen bond network that involves the water molecule containing O(7). The sodium ions and the water molecules coordinated to them hold the sheets together through a combination of hydrogen bonding and direct sodium–oxygen coordination. The sodium ions are each surrounded in a slightly distorted octahedral coordination by four water molecules in a plane and by two hypophosphate oxygen atoms in a direction nearly perpendicular to the plane of water molecules. The oxygen octahedra share edges to form chains parallel to the *b* axis. Some of the angles and distances in the sodium coordination octahedra are given in Table 5. Thermal motion of the non-hydrogen atoms is low. The isotropic thermal parameters in Å^2 are: P, 1·21; Na^+, 1·93; the mean for O within the hypophosphate ion, 1·79, the mean for the O atoms in water, 2·32.

The bond distances and angles within the hypophosphate ion are shown in Table 6 along with the corresponding distances in diammonium dihydrogen hypophosphate (Wilson & McGeachin, 1964), the only other hypophosphate whose structure has been determined. The P–P distance is 0·02 Å longer and the P(1)–O(4) distance 0·016 Å longer in the sodium structure. These differences are significantly greater than the reported standard deviations. The mean P–P distance of 2·180 Å in the two structures is shorter than the corresponding distances of 2·225 and 2·248 Å found by Mootz & Altenburg (1969) in the  $\overset{\mathrm{O\ O\ O}}{\underset{\mathrm{O\ O\ O}}{\mathrm{OP{-}P{-}PO}}}$ ion. In agreement with structures of phosphate salts and esters, phosphorus–oxygen distances to the non-acid oxygen atoms are smaller than to the acid oxygen atom and the O–P–O angle between these short oxygen–phosphorus bonds is greater than the tetrahedral angle. The P–P–O angles involving the non-acid oxygen atoms are also larger than the corresponding angle involving the acid oxygen atom. Thermal vibration corrections increase the P–O bond lengths by 0·007 Å if the oxygen atoms are assumed to ride on the phosphorus atom.

Bond distances and angles in the three non- equivalent water molecules of the structure are shown in

Table 7. These are in the range observed in other structures, but the observed oxygen–hydrogen bond distances determined by X-ray scattering are smaller than the oxygen–hydrogen internuclear distances of 0·957 Å found by gas phase infrared spectroscopy (Benedict, Gailar & Plyler, 1956).

The water molecules coordinated to sodium each make two hydrogen bonds to other oxygen atoms in directions pointing away from the sodium ions. The third water molecule participates in four hydrogen bonds, two as a donor and two as an acceptor. These bonds are in a roughly tetrahedral direction about the oxygen atom O(7). On the hypophosphate ion O(2) is an acceptor for three hydrogen bonds from water molecules, whereas O(3) which is also coordinated to sodium, is an acceptor for two hydrogen bonds. The acidic oxygen atom of the hypophosphate ion, O(4), is coordinated to sodium and takes part in only one hydrogen bond. The hydrogen bond between O(4) and O(7) is the shortest hydrogen-bonded O–O contact in the structure (2·615 Å). A list of all hydrogen-bonded distances is given in Table 8. Three of these are around 2·9 Å and somewhat longer than the average accepted hydrogen bond distance. Nonetheless, the hydrogen atoms involved in these bonds lie close to the line joining the two oxygen atoms, and hence, probably lead to some lowering of the energy of the structure.

The bond distances and angles within the pyrophosphate ion are listed in Table 9. The PO_3 groups take on a staggered conformation about the phosphorus–phosphorus axis and the bridge oxygen atom lies on a twofold axis similar to the hypophosphate ion in the $Na_2H_2P_2O_6.6H_2O$ structure. The central P–O–P bridge is not linear, but makes an angle of 136·1°. The pyro- and tri-phosphates that have been studied to date have either a linear bridge, as in the high temperature phases of certain M^{2+} pyrophosphates (Robertson & Calvo, 1968), or a bent bridge with the angle varying between 122° in $Na_5P_3O_{10}$ (Cruickshank, 1964) and 144° in the low temperature form of $Mg_2P_2O_7$ (Calvo, 1967). McDonald & Cruickshank (1967) have pointed out the correlation which exists between the bridge angle and the P–O distances involved in the bridge. The larger the bridge angle, and presumably, the greater the π-bonding between phosphorus and oxygen, the shorter are the P–O bridge bonds. The angle and bond lengths in the bridge of the dihydrogen pyrophosphate are all three of intermediate value and in agreement with this deduction.

The P–O bonds to the two non-equivalent oxygen atoms that do not carry a hydrogen atom are equal in length within the error of the measurements. Their mean value is 1·494 Å (1·500 Å when corrected for thermal vibration assuming a riding motion for the oxygen atom on the phosphorus atom) and this is considerably shorter than the P(1)–O(4) bond length of 1·569 Å (1·577 Å when corrected for thermal vibration assuming a riding motion of the oxygen atom on the phosphorus atom) to the acidic oxygen atom. The

Table 4. *Positional and thermal parameters in* $Na_2H_2P_2O_7.6H_2O$

The U_{ij} values are coefficients in $T=\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{23}klb^*c^*+2U_{31}lhc^*a^*)\right]$.

	x	y	z	$U_{11}\times10^4$	$U_{22}\times10^4$	$U_{33}\times10^4$	$2U_{12}\times10^4$	$2U_{23}\times10^4$	$2U_{31}\times10^4$
P(1)	0·00216 (4)	0·13738 (8)	0·14090 (5)	112 (3)	130 (3)	129 (3)	4 (2)	8 (2)	100 (2)
O(2)	−0·10976 (14)	0·09231 (28)	0·05536 (15)	119 (7)	249 (9)	177 (8)	−8 (6)	16 (6)	16 (6)
O(3)	0·06160 (14)	0·28641 (28)	0·11190 (15)	188 (8)	206 (8)	209 (9)	−48 (6)	48 (6)	220 (6)
O(4)	0·07157 (14)	−0·04976 (27)	0·18346 (16)	158 (8)	157 (8)	260 (9)	78 (6)	24 (6)	98 (6)
O(Bridge)	0·0	0·22327 (37)	0·25000	350 (14)	156 (11)	175 (11)	0	0	314 (10)
O(5)	0·27511 (17)	0·11760 (33)	0·13621 (19)	249 (10)	320 (11)	308 (10)	−72 (8)	−122 (8)	312 (8)
O(6)	0·22922 (16)	0·65086 (30)	0·12043 (17)	226 (9)	244 (9)	238 (9)	104 (8)	132 (8)	206 (8)
O(7)	−0·03882 (17)	0·64174 (30)	0·09694 (17)	300 (10)	174 (9)	265 (9)	48 (8)	−14 (18)	296 (8)
Na(8)	0·23735 (8)	0·38162 (15)	0·22957 (9)	190 (5)	193 (5)	254 (5)	−44 (4)	24 (4)	160 (4)
H(9)	0·2255 (46)	0·0810 (77)	0·0728 (48)						
H(10)	0·2777 (46)	0·6233 (73)	0·1052 (46)						
H(11)	−0·0078 (43)	0·5692 (88)	0·1079 (47)						
H(12)	0·3317 (46)	0·1208 (72)	0·1301 (48)						
H(13)	−0·0560 (44)	0·6669 (75)	0·0216 (51)						
H(14)	0·1851 (44)	0·7222 (84)	0·0715 (49)						
H(15)	0·0308 (44)	−0·1490 (79)	0·1643 (45)						

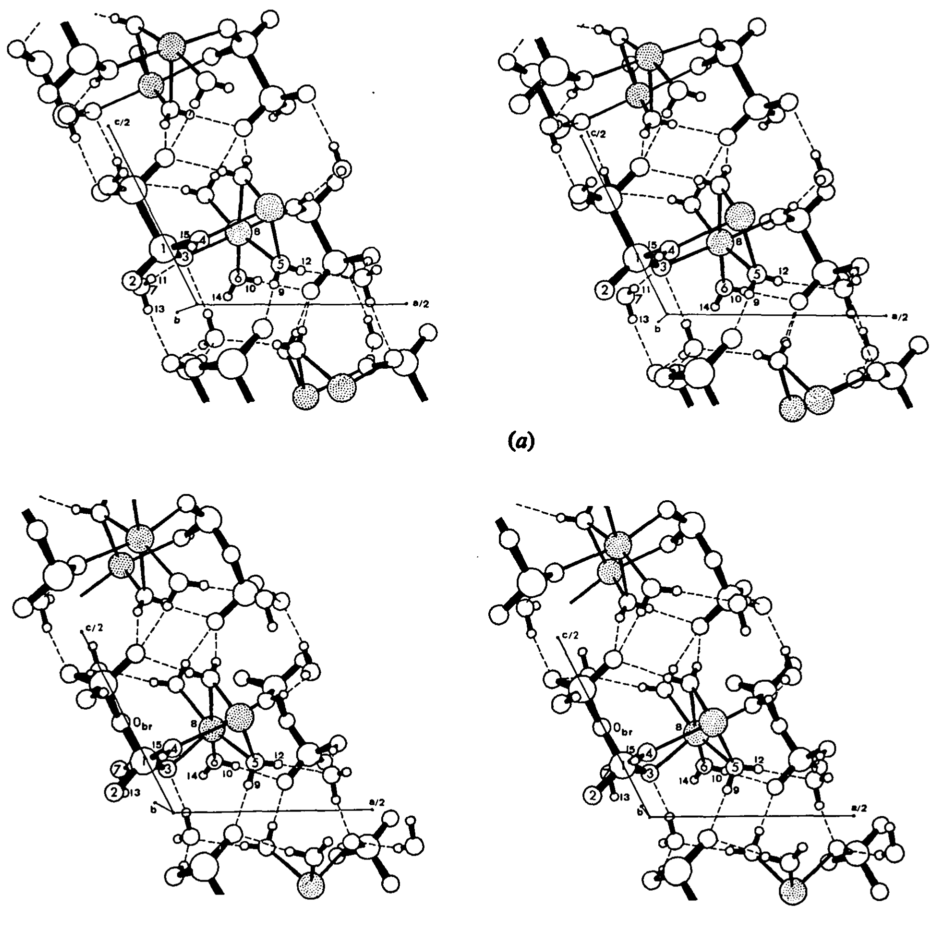
An isotropic temperature factor of $B=2·5$ Å^2 was used for all hydrogen atoms

Table 5. *Angles and distances about the sodium atom in* $Na_2H_2P_2O_6.6H_2O$

Standard deviations are 0·09° in the angles and 0·003 Å in the distances.

Na(8)-O(3)	2·325 Å
Na(8)-O(4^{iii})	2·459
Na(8)-O(5)	2·438
Na(8)-O(5^{iii})	2·485
Na(8)-O(6)	2·329
Na(8)-O(6^{iv})	2·399
O(5) —O(6)	3·692 Å
O(5^{iii})-O(6)	3·253
O(5^{iii})-O(6^{iv})	3·402
O(5) —O(6^{iv})	3·253
O(3) —O(5)	3·314
O(3) —O(5^{iii})	3·620
O(3) —O(6)	3·430
O(3) —O(6^{iv})	3·420
O(4^{iii})-O(5)	3·499
O(4^{iii})-O(5^{iii})	3·271
O(4^{iii})-O(6)	3·300
O(4^{iii})-O(6^{iv})	3·291

O(5) —Na(8)-O(6)	101·58°
O(5) —Na(8)-O(6^{iv})	84·52
O(5^{iii})-Na(8)-O(6)	84·96
O(5^{iii})-Na(8)-O(6^{iv})	88·30
O(3) —Na(8)-O(5)	88·15
O(3) —Na(8)-O(6)	94·95
O(3) —Na(8)-O(5^{iii})	97·60
O(3) —Na(8)-O(6^{iv})	92·75
O(4^{iii})-Na(8)-O(5)	91·18
O(4^{iii})-Na(8)-O(6)	87·07
O(4^{iii})-Na(8)-O(5^{iii})	82·84
O(4^{iii})-Na(8)-O(6^{iv})	85·26
O(3) —Na(8)-O(4^{iii})	177·95



(a)

(b)

Fig. 1. Stereoscopic views of the hypophosphate and pyrophosphate structures. (*a*) $Na_2H_2P_2O_6.6H_2O$. (*b*) $Na_2H_2P_2O_7.6H_2O$. The large circles are phosphorus atoms (open) and sodium atoms (dotted). The intermediate circles are oxygen atoms and the small circles are hydrogen atoms. Hydrogen bonds are indicated by dashed lines.

Table 6. *Distances and angles in the dihydrogen hypophosphate ion*

Standard deviations in the last figure are given in parentheses.

	$Na_2H_2P_2O_6.6H_2O$	$(NH_4)_2H_2P_2O_6$ (Wilson & McGeachin, 1964)
P(1)–P(1$^{\mathrm{v}}$)	2·190 (2) Å	2·170 (5) Å
P(1)–O(2)	1·507 (2)	1·503 (5)
P(1)–O(3)	1·505 (2)	1·501 (5)
P(1)–O(4)	1·588 (2)	1·572 (5)
O(4)–H(15)	0·79 (5)	
P(1$^{\mathrm{v}}$)–P(1)–O(2)	108·8 (1)°	106·6 (3)°
P(1$^{\mathrm{v}}$)–P(1)–O(3)	110·0 (1)	106·8 (3)
P(1$^{\mathrm{v}}$)–P(1)–O(4)	102·2 (1)	106·7 (3)
O(2)—P(1)–O(3)	116·6 (1)	116·7 (4)
O(2)—P(1)–O(4)	110·4 (1)	106·2 (4)
O(3)—P(1)–O(4)	108·0 (1)	113·3 (4)
H(15)–O(4)–P(1)	110 (4)	

Table 7. *Water molecule geometry in* $Na_2H_2P_2O_6.6H_2O$

Standard deviations in distances are 0·06 Å and in angles 5°.

O(5)—H(9)	0·80 Å
O(5)—H(12)	0·74
H(9)—O(5)—H(12)	100°
O(6)—H(10)	0·72 Å
O(6)—H(14)	0·84
H(10)–O(6)—H(14)	105°
O(7)—H(11)	0·73 Å
O(7)—H(13)	0·85
H(11)–O(7)—H(13)	104°

O–P–O angles involving the non-acidic oxygen atom are larger than those that involve the acidic oxygen atom, an observation that is in general accord with those in other phosphate and pyrophosphate structures. The thermal vibration parameters of the phosphorus atom are smaller and more isotropic than those of the oxygen atoms to which it is bonded and there is a marked thermal anisotropy of the bridge oxygen atom corresponding to a greater vibration normal to the P–O–P plane than in it. This was also found by McDonald & Cruickshank (1967) in their refinement of $Na_4P_2O_7.10H_2O$ and they attributed this to a folding motion of the phosphate groups about a line in the P–O plane through the bridge oxygen atom. The thermal vibrations of the oxygen atoms in the $H_2P_2O_7^{2-}$ ion in the hexahydrate crystal appear more complex and an analysis of the thermal ellipsoids of vibration in terms of a simple folding motion or a folding motion plus a rotation of the PO_3 groups does not appear possible.

Table 9. *Distances and angles in the dihydrogen pyrophosphate ion*

Standard deviations in the last figure are given in parentheses.

P(1)–P(1$^{\mathrm{V}}$)	2·965 (2) Å
P(1)–O(bridge)	1·598 (1)
P(1)–O(2)	1·492 (2)
P(1)–O(3)	1·495 (2)
P(1)–O(4)	1·569 (2)
O(4)–H(15)	0·86 (6)
P(1)——O(bridge)–P(1$^{\mathrm{V}}$)	136·1 (1)°
O(bridge)–P(1)——O(2)	108·8 (1)
O(bridge)–P(1)——O(3)	103·4 (1)
O(bridge)–P(1)——O(4)	104·5 (1)
O(2)——P(1)——O(3)	117·7 (1)
O(2)——P(1)——O(4)	111·3 (1)
O(3)——P(1)——O(4)	109·9 (1)
H(15)——O(4)——P(1)	110 (4)

The bond distances and angles in the water molecules are shown in Table 10 and the hydrogen bond distances and angles in Table 11. The latter show significant variation from the corresponding values in $Na_2H_2P_2O_6.6H_2O$, but they still remain reasonable values. The shortest hydrogen bond is still between O(4) and O(7), but it is now 2·589 (3) Å as compared with 2·615 (4) Å in the hypophosphate structure. The three long hydrogen bonds join the same oxygen atoms as do the three long hydrogen bonds in $Na_2H_2P_2O_6.6H_2O$.

Table 10. *Water molecule geometry in* $Na_2H_2P_2O_7.6H_2O$

Standard deviations in the last figure are given in parentheses.

O(5)—H(9)	0·85 (6) Å
O(5)—H(12)	0·84 (7)
H(9)—O(5)—H(12)	107 (6)°
O(6)—H(10)	0·82 (7) Å
O(6)—H(14)	0·83 (6)
H(10)–O(6)—H(14)	110 (6)°
O(7)—H(11)	0·64 (6) Å
O(7)—H(13)	0·94 (6)
H(11)–O(7)—H(13)	102 (7)°

The coordination of the sodium atom is similar to that already described for the hypophosphate. Some angles and distances in the octahedron are given in Table 12. The mean Na–O distance is 2·415 Å which can be compared with 2·406 Å in $Na_2H_2P_2O_6.6H_2O$ and 2·485 and 2·447 Å in $Na_4P_2O_7.10H_2O$ (McDonald & Cruickshank, 1967). The mean O–O distance is 3·412 Å, a little larger than the mean of 3·395 Å in $Na_2H_2P_2O_6.6H_2O$. The root-mean-square deviation of

Table 8. *Hydrogen-bond distances and angles in* $Na_2H_2P_2O_6.6H_2O$

Standard deviations are as follows: O–H, 0·06; H···O, 0·06; O···O, 0·003 Å; O–H···O angle, 5°.

	O–H	H···O	O···O	O–H···O angle
O(4)–H(15)···O(7$^{\mathrm{vi}}$)	0·79 Å	1·83 Å	2·615 Å	176°
O(5)–H(9)····O(2$^{\mathrm{i}}$)	0·80	2·16	2·935	163
O(5)–H(12)···O(7$^{\mathrm{ii}}$)	0·74	2·23	2·956	170
O(6)–H(10)···O(2$^{\mathrm{ii}}$)	0·72	2·00	2·727	176
O(6)–H(14)···O(2$^{\mathrm{i}}$)	0·84	1·95	2·777	166
O(7)–H(11)···O(3)	0·73	2·00	2·734	177
O(7)–H(13)···O(3$^{\mathrm{i}}$)	0·85	2·10	2·949	173

the O–O distances from the mean is 0·212 in the pyrophosphate and 0·140 in the hypophosphate and this suggests a somewhat more distorted coordination octahedron in the pyrophosphate structure.

The general features of the packing of the ions in $Na_2H_2P_2O_7.6H_2O$ and $Na_2H_2P_2O_6.6H_2O$ are the same. [Compare Fig. 1(*a*) and (*b*)]. The bridge oxygen atom on the pyrophosphate group plays no apparent role in holding the structure together. The closest atoms to it, and external to the pyrophosphate ion, are a hydrogen atom, H(10), at 2·90 Å and O(7) at 3·42 Å. The closest sodium ion is at 4·30 Å. The situation is similar in $Na_4P_2O_7.10H_2O$ (McDonald & Cruickshank, 1967) where the closest intermolecular approach to the bridge oxygen atom is a water molecule at 3·35 Å and the nearest sodium ion is at 3·71 Å. In β-$Ca_2P_2O_7$ (Webb, 1966) the bridge oxygen atom does appear to be bonded to calcium since there are calcium–bridge oxygen distances that are 2·78 and 2·93 Å. In Fig. 2, a projection of parts of the two structures down the *c* axis shows the relative positions of the various oxygen, hydrogen and phosphorus atoms. The registry of the outer oxygen atoms joined to phosphorus is not particularly good, but the water molecules can move around, adjusting themselves to the altered environment. This also involves a rearrangement of the coordination around sodium (see Table 12), but again, this can be accomplished with rather small distortions of the already distorted octahedral coordination. In summary, the close similarity of the two structures can be attributed to (*a*) the non-involvement of the bridge oxygen atom in intermolecular bonding and (*b*) the intermolecular bonds that are formed all involve either hydrogen bonding to water molecules or coordination with sodium neither of which impose severe restrictions on bonding geometry.

Computer programs used

The calculations were carried out on an IBM 360/44 computer with a 32K memory. The least-squares calculations of lattice constants and the calculation of setting and scan angles for intensity data collection were done with our modification of J. A. Ibers' *PICK* 2 program (itself a modified version of W. C. Hamilton's *MODE* 1). The full-matrix least-squares program was a modified version of *SFLS*-5 by C. Prewitt. The analysis of thermal motion was carried out with a modified version of *ORFFE* by Busing, Martin & Levy. The stereoscopic views in Fig. 1(*a*) and (*b*) were drawn with the program *ORTEP* of C. K. Johnson. All other calculations were done with the NRC crystallographic programs for the IBM/360 System of F. R. Ahmed, S. R. Hall, M. E. Pippy & C. P. Saunderson.

Table 11. *Hydrogen-bond distances and angles in* $Na_2H_2P_2O_7.6H_2O$

Standard deviations are as follows: O–H, 0·06; H···O, 0·06; O···O, 0·003 Å; O–H···O angle, 5°.

	O–H	H···O	O···O	O–H···O angle
O(4)–H(15)···O(7^{vi})	0·86 Å	1·76 Å	2·589 Å	164°
O(5)–H(9)···O(2^{i})	0·85	2·12	2·937	162
O(5)–H(12)···O(7^{ii})	0·84	2·08	2·912	174
O(6)–H(10)···O(2^{ii})	0·82	2·00	2·817	172
O(6)–H(14)···O(2^{i})	0·83	2·01	2·815	165
O(7)–H(11)···O(3)	0·64	2·19	2·810	165
O(7)–H(13)···O(3^{i})	0·94	1·79	2·722	169

Table 12. *Angles and distances involved in sodium coordination in* $Na_2H_2P_2O_7.6H_2O$

Standard deviations are 0·09° in the angles and 0·003 Å in distances.

Na(8)–O(3)	2·332 Å
Na(8)–O(4^{iii})	2·434
Na(8)–O(5)	2·420
Na(8)–O(5^{iii})	2·507
Na(8)–O(6)	2·350
Na(8)–O(6^{iv})	2·447
O(5) —O(6)	3·756
O(5^{iii})–O(6)	3·311
O(5^{iii})–O(6^{iv})	3·299
O(5) —O(6^{iv})	3·311
O(3) —O(5)	3·104
O(3) —O(5^{iii})	3·853
O(3) —O(6)	3·432
O(3) —O(6^{iv})	3·562
O(4^{iii})–O(5)	3·323
O(4^{iii})–O(5^{iii})	3·419
O(4^{iii})–O(6)	3·148
O(4^{iii})–O(6^{iv})	3·428

O(5) —Na(8)–O(6)	103·86°
O(5) —Na(8)–O(6^{iv})	85·72
O(5^{iii})–Na(8)–O(6)	85·90
O(5^{iii})–Na(8)–O(6^{iv})	83·50
O(3) —Na(8)–O(5)	81·52
O(3) —Na(8)–O(6)	94·26
O(3) —Na(8)–O(5^{iii})	105·49
O(3) —Na(8)–O(6^{iv})	96·32
O(4^{iii})–Na(8)–O(5)	86·40
O(4^{iii})–Na(8)–O(6)	82·28
O(4^{iii})–Na(8)–O(5^{iii})	87·57
O(4^{iii})–Na(8)–O(6^{iv})	89·21
O(3) —Na(8)–O(4^{iii})	166·28

The authors wish to thank Mr James Voytas for his help with the data collection and the computations on $Na_2H_2P_2O_7.6H_2O$.

This paper is based on work performed in part under United States Public Health Service Training Grant No. 1 Tl DE 175-01 and in part under contract with the U. S. Atomic Energy Commission at the University of Rochester Atomic Energy Project and has been assigned Report Number UR-49-1195.

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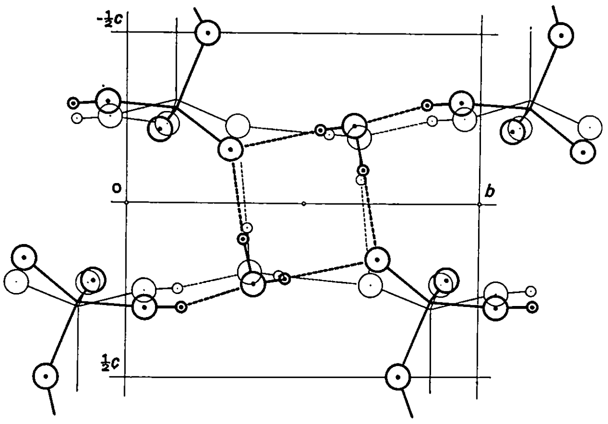

Fig. 2. Projection of parts of the $Na_2H_2P_2O_7.6H_2O$ (heavy lines) and $Na_2H_2P_2O_6.6H_2O$ (light lines) structures down the *b* axis. The large circles represent oxygen atoms and the small circles hydrogen atoms. Dashed lines represent hydrogen bonds.

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A Redetermination of the Crystal Structure of Tetramethyldiphosphine Disulphide

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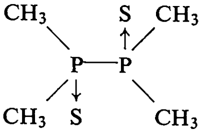
(*Received* 14 *March* 1970)

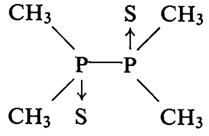
The crystal structure of tetramethyldiphosphine disulphide



has been determined from three-dimensional X-ray diffraction data. The unit cell is monoclinic with space group $C2/m$ (number 12), dimensions $a = 18{\cdot}882$, $b = 10{\cdot}703$, $c = 6{\cdot}984$ Å; $\beta = 94°42'$, and contains six molecules, which occupy two different sets of special positions. The structure was refined by full-matrix least-squares methods on 916 independent observed reflexions to $R = 8{\cdot}9\%$. The molecules adopt a non-eclipsed ethane-like conformation. There are appreciable differences in bond lengths between the two sets of molecules (P–P, 2·245 and 2·161 Å; P–S, 1·951, 1·970 and 1·965 Å; P–C, 1·80, 1·82 and 1·82 Å). Apart from some molecular crowding round the sulphur atoms of one set, there is no obvious reason for these differences.

Introduction

The structure of tetramethyldiphosphine disulphide was originally assigned by Christen, van der Linde & Hooge (1959), as containing a P–P linkage (I)



(I)