$$\cos \varrho = w_{d^*}$$
$$\cos \varphi = v_{d^*}/\sin \varrho \, .$$

Thus the 2θ, ϱ and φ values for any value of hkl can be obtained and used to set the crystal to enable any desired reflexion to be studied.

5. Conclusions

The procedure described here will lead to an unambiguous result but the cell determined by this procedure need not be the one usually employed. For instance a face-centred cubic Bravais lattice has a reciprocal counterpart in which the three shortest vectors define a rhombohedral cell of side equal to $\sqrt{3}a^*$ and $\alpha^*=110°$. A body-centred cubic Bravais lattice would likewise be represented in reciprocal space by a rhombohedral cell the sides of which are $\sqrt{2}a^*$ in length and the angle $\alpha^*=60°$. There are other possible instances where the unit cell chosen by this method would have a lower symmetry than that of the usually accepted cell or lack its orthogonality. The indices determined by the present procedure could be readily transformed to those usually accepted after the measurements of the intensity of reflexion had been made.

Buerger (1942) discusses the relation between the reduced reciprocal lattice, derived by the procedure described here, and the corresponding Bravais lattice. Usually the reduced reciprocal lattice leads to the reduced Bravais lattice by the usual transformations. In a few cases, however, Buerger points out that other conditions must be applied to determine the true reduced Bravais lattice.

Another feature of this method which should be mentioned is the fact that the low-angle reflexions are very convenient for determining the approximate size and shape of the reciprocal unit cell while the high-angle reflexions are best for finding accurate values of these dimensions. It would be necessary to design the program of computation so that after finding the approximate values of a^*, b^*, c^*, α^*, β^*, γ^* these were automatically refined by taking into account the high-angle reflexions. The final values of the cell parameters would have to be based on the high-angle reflexions so that the calculated settings of the circles were correctly determined for these reflexions.

References

AZAROFF, L. V. & BUERGER, M. J. (1958). *The Powder Method in X-ray Crystallography.* New York: McGraw-Hill.

BUERGER, M. J. (1942). *X-ray Crystallography.* New York: John Wiley.

BUERGER, M. J. (1956). *Elementary Crystallography.* New York: John Wiley.

International Tables for X-ray Crystallography. (1959). Vol. II. p. 101. Birmingham: Kynoch Press.

WOOSTER, W. A. (1962). *J. Sci. Instrum.* **39**, 103.

Acta Cryst. (1964). **17**, 1352

The Crystal Structure of Diammonium Dihydrogen Hypophosphate $(NH_4)_2H_2P_2O_6$

BY A. WILSON AND H. McD. McGEACHIN

Albright and Wilson (Mfg) Ltd., Oldbury, Birmingham, England

(*Received* 30 *October* 1963)

The crystal structure of diammonium dihydrogen hypophosphate has been solved by trial and error and refined in three dimensions. The bond lengths are P–P 2·17, P–O(H) 1·57, and P–O 1·50 Å (twice). The hypophosphate ion has twofold symmetry and adopts a staggered configuration with symmetry approaching $\bar{3}m$.

Introduction

Speculation on the structure of the hypophosphate ion $[P_2O_6]^{4-}$ has a long history, chronicled by Van Wazer (1958). No complete structure determination of a hypophosphate has been reported, however.

Crystal data

$(NH_4)_2H_2P_2O_6$, M.W. 196·1, orthorhombic, $a=7{\cdot}240$, $b=11{\cdot}465$, $c=9{\cdot}350$ Å (all $\pm 0{\cdot}005$), observed density 1·679, four molecules per unit cell. Space group $Pccn$ (D_{2h}^{10}, No. 56), implied symmetry of the hypophosphate ion $\bar{1}$ or 2.

Crystals of good quality with a typical dimension of 0·15 mm were kindly supplied by D. R. Peck of this laboratory.

Structure determination

The unit cell and space group were reported by Raistrick & Hobbs (1949), who from the space group and density deduced that the hypophosphate ions existed in the symmetrical form. The resemblance of the cell to that of ammonium bicarbonate was noted by Brooks & Alcock (1950) whose structure of the bicarbonate was taken as a starting point. Adjustments of their parameters, made with Bragg–Lipson charts for a small number of reflexions, led to a structure which was satisfactorily refined on three projections by difference syntheses.

Structures in the space group *Pccn* cannot be unambiguously determined by three axial projections, since an atom at x, y, z cannot be distinguished from one at, for example, $\frac{1}{2}-x, y, z$. Having fixed the position of the hypophosphate ion by refinement from the bicarbonate structure, we were thus faced with two possible sites for the ammonium ion. Com-

Table 1. *Observed and calculated structure factors*

h	k	ℓ	$10F_o$	$10F_c$
0	0	2	526	-577
0	0	4	307	-278
0	0	6	807	630
0	0	8	513	-467
0	0	10	47	-45
0	0	12	103	108
0	1	2	1291	-1086
0	1	4	140	157
0	1	6	62	-71
0	1	8	669	-502
0	1	10	236	196
0	1	12	11	-4
0	2	0	1561	-1355
0	2	2	643	546
0	2	4	96	-96
0	2	6	746	-681
0	2	8	273	278
0	2	10	116	112
0	2	12	71	-60
0	3	2	155	238
0	3	4	78	-66
0	3	6	12	6
0	3	8	452	360
0	3	10	133	-132
0	4	0	1262	884
0	4	2	33	31
0	4	4	283	-238
0	4	6	243	209
0	4	8	152	-168
0	4	10	63	-65
0	5	2	709	-611
0	5	4	354	348
0	5	6	23	-25
0	5	8	181	-179
0	5	10	219	184
0	6	0	382	-310
0	6	2	419	408
0	6	4	269	235
0	6	6	497	-458
0	6	8	121	107
0	6	10	1131	104
0	7	2	525	496
0	7	4	919	-792
0	7	6	63	78
0	7	8	210	183
0	7	10	216	-170
0	8	0	355	322
0	8	2	232	-231
0	8	4	343	-315
0	8	6	264	236
0	8	8	67	-74
0	8	10	64	-58
0	9	2	419	-375
0	9	4	441	353
0	10	0	60	98
0	10	2	86	94
0	10	4	144	133
0	10	6	118	-120
0	11	2	46	28
0	11	4	259	-239
0	11	8	52	52
0	12	0	56	61
0	12	2	77	-77
0	12	4	106	-94
0	12	6	91	83
0	13	2	186	-179
0	13	4	113	110
0	14	0	180	-168
0	14	2	97	97
1	0	2	118	-255
1	0	4	691	558
1	0	6	45	-63
1	0	8	280	-306
1	0	10	92	99
1	1	0	917	-912
1	1	1	34	62
1	1	2	331	360
1	1	3	580	-546
1	1	4	123	145
1	1	5	219	225
1	1	6	309	-375
1	1	8	125	154
1	1	9	20	-31
1	1	10	53	60
1	1	11	39	43
1	1	12	67	-77
1	2	1	118	-124
1	2	2	839	732
1	2	3	67	79
1	2	5	355	333
1	2	8	112	116
1	2	10	130	-142
1	2	11	78	76
1	3	0	554	552
1	3	1	29	35
1	3	2	46	-79
1	3	3	840	756
1	3	4	154	-159
1	3	5	245	-244
1	3	6	147	180
1	3	7	46	52
1	3	8	89	-106
1	3	10	36	-43
1	3	11	87	-87
1	4	1	601	-425
1	4	4	365	337
1	4	5	218	-234
1	4	6	22	-15
1	4	7	132	-166
1	4	8	207	-197
1	4	10	69	70
1	4	11	139	-98
1	5	0	143	-146
1	5	1	280	-272
1	5	2	196	227
1	5	3	340	-350
1	5	4	53	78
1	5	5	81	103
1	5	6	281	-275
1	5	7	31	-36
1	5	8	58	70
1	5	9	21	19
1	5	10	62	62
1	5	11	64	65
1	6	1	331	305
1	6	2	459	454
1	6	3	11	12
1	6	4	206	-213
1	6	5	202	188
1	6	7	92	106
1	6	8	74	79
1	6	10	127	-122
1	6	11	77	90
1	7	0	464	459
1	7	2	113	-135
1	7	3	380	381
1	7	4	186	-201
1	7	5	98	-121
1	7	6	110	145
1	7	8	77	-93
1	7	9	37	46
1	7	10	19	-23
1	8	1	226	237
1	8	2	146	-165
1	8	3	29	-35
1	8	4	250	295
1	8	5	229	-244
1	8	7	84	93
1	8	8	106	-112
1	8	9	23	-26
1	8	10	77	71
1	9	0	43	-27
1	9	1	116	131
1	9	2	106	142
1	9	3	285	-336
1	9	4	28	42
1	9	5	124	141
1	9	6	218	-173
1	9	7	45	64
1	9	8	22	29
1	9	9	115	-104
1	10	1	290	-268
1	10	2	102	124
1	10	3	24	38
1	10	4	72	-85
1	10	5	135	160
1	10	7	163	-149
1	10	8	29	33
1	11	0	117	145
1	11	1	84	-87
1	11	3	66	88
1	11	4	70	-83
1	11	6	15	15
1	11	7	68	-67
1	11	8	17	-32
1	12	1	156	145
1	12	2	51	-65
1	12	4	75	77
1	12	5	45	-53
1	12	7	57	97
1	13	0	26	-35
1	13	1	70	68
1	13	2	59	74
1	13	3	20	-23
1	14	1	181	-150
1	14	2	58	61
2	0	0	1055	1123
2	0	2	433	-424
2	0	4	251	244
2	0	6	448	445
2	0	8	209	-211
2	0	10	20	-31
2	1	1	331	-276
2	1	2	209	-249
2	1	3	20	-20
2	1	4	163	-195
2	1	5	101	135
2	1	6	43	-40
2	1	7	36	-39
2	1	8	301	-255
2	1	9	20	24
2	1	10	27	28
2	1	11	19	25
2	2	0	1186	-1215
2	2	1	159	-150
2	2	2	118	-94
2	2	3	422	459
2	2	4	30	5
2	2	5	155	-158
2	2	6	64	-54
2	2	8	156	172
2	2	9	50	59
2	2	10	18	-14
2	2	11	42	-46
2	3	1	74	96
2	3	2	48	82
2	3	3	65	-80
2	3	4	312	289
2	3	5	187	-197
2	3	7	39	52
2	3	8	103	111
2	3	10	18	-23
2	3	11	58	-56
2	4	0	155	-125
2	4	1	51	-58
2	4	2	36	-36
2	4	3	277	-230
2	4	4	81	109
2	4	5	61	81
2	4	6	119	152
2	4	7	21	20
2	4	8	23	-18
2	4	9	34	-46
2	4	10	44	-48
2	4	11	36	38
2	5	1	75	90
2	5	2	16	-12
2	5	3	20	-39
2	5	4	173	167
2	5	5	96	98
2	5	6	27	-28
2	5	7	21	-26
2	5	8	71	-82
2	5	10	39	29
2	5	11	51	56
2	6	0	261	-207
2	6	1	20	-15
2	6	2	18	31
2	6	3	154	179
2	6	4	175	174
2	6	5	33	-38
2	6	6	36	-39
2	6	7	23	-28
2	6	8	24	29
2	6	9	53	56
2	6	10	14	15
2	7	1	154	147
2	7	2	348	340
2	7	3	23	-28
2	7	4	323	-280
2	7	5	170	-175
2	7	6	30	38
2	7	7	101	98
2	7	8	37	-28
2	7	10	109	-88
2	8	0	134	-137
2	8	1	136	133
2	8	2	100	-123
2	8	3	332	-316
2	8	4	93	-101
2	8	5	137	151
2	8	6	97	110
2	8	7	59	70
2	8	9	162	-115
2	9	1	386	-315
2	9	4	269	278
2	9	5	218	196
2	9	7	182	-160
2	9	9	17	20
2	10	0	115	141
2	10	1	174	-155
2	10	3	236	227
2	10	4	59	6
2	10	5	90	-92
2	10	6	18	23
2	10	7	61	-62
2	10	8	32	-38
2	11	1	196	178
2	11	2	53	62
2	11	4	31	-37
2	11	5	114	-114
2	11	6	21	-21
2	11	7	141	119
2	12	0	50	-60
2	12	1	65	68
2	12	2	18	-27
2	12	3	93	-94
2	12	4	31	-37
2	12	5	56	52
2	12	6	13	15
2	13	1	161	-126
2	13	2	11	7
2	13	3	14	-5
2	13	4	94	99
2	13	5	62	80
2	14	0	40	-56
2	14	1	109	-88
2	14	2	43	52
3	0	2	914	-977
3	0	4	294	293
3	0	6	46	-61
3	0	8	258	-284
3	0	10	161	201
3	1	0	1259	-1240
3	1	1	56	42
3	1	2	347	376
3	1	3	159	-182
3	1	4	165	189
3	1	5	22	27
3	1	6	491	-493
3	1	7	39	-46
3	1	8	251	244
3	1	9	18	25
3	1	10	57	66
3	1	11	24	28
3	2	1	150	150
3	2	2	223	237
3	2	3	10	6
3	2	4	369	-373
3	2	5	56	60
3	2	6	29	37
3	2	7	64	96
3	2	8	362	325
3	2	10	115	-115
3	2	11	26	28
3	3	0	386	368
3	3	1	201	188
3	3	2	175	-158
3	3	3	250	267
3	3	4	69	-67
3	3	5	106	-136
3	3	6	320	323
3	3	7	50	56
3	3	8	105	-122
3	3	9	45	-50
3	3	10	70	-76
3	3	11	25	-29
3	4	1	451	-366
3	4	2	449	-395
3	4	3	15	-26
3	4	4	63	106
3	4	5	92	-77
3	4	7	149	-147
3	4	8	135	-137
3	4	10	153	143
3	5	1	140	-149
3	5	2	139	155
3	5	3	151	-155
3	5	4	217	219
3	5	5	18	6
3	5	6	211	-229
3	5	7	64	-80
3	5	8	121	115
3	5	9	83	86
3	5	10	53	52
3	6	1	344	275
3	6	2	364	341
3	6	3	15	-21
3	6	4	588	-513
3	6	5	26	25
3	6	6	29	35
3	6	7	165	171
3	6	8	195	187
3	6	10	131	-132
3	7	0	323	313
3	7	1	144	146
3	7	2	309	-323
3	7	3	38	56
3	7	4	149	-176
3	7	5	29	-19
3	7	6	376	338
3	7	7	31	41
3	7	9	55	-58
3	8	1	100	-111
3	8	2	412	-384
3	8	3	38	-48
3	8	4	375	341
3	8	5	20	-9
3	8	7	46	-63
3	9	0	209	-220
3	9	1	23	-42
3	9	2	55	96
3	9	3	36	11
3	9	4	158	106
3	9	5	30	-27
3	9	6	94	-103
3	9	7	18	-26
3	10	2	63	88
3	10	4	179	-168
3	10	5	30	-36
3	10	7	21	31
3	11	0	22	-23
3	11	2	63	-75
3	11	3	89	-99
3	11	4	30	-37
3	11	5	40	51
3	11	6	103	103
3	12	1	20	-34
3	12	2	97	-95
3	12	3	15	-17
3	12	4	91	93
3	12	5	50	58
3	13	0	197	-176
3	13	2	46	52
3	13	3	100	110
3	13	4	64	70
4	0	0	74	105
4	0	2	304	319
4	0	4	242	241
4	0	6	371	-353
4	0	8	32	21
4	0	10	92	96
4	1	1	74	-56
4	1	2	375	393
4	1	3	68	95
4	1	4	645	-594
4	1	5	112	120
4	1	7	54	-51
4	1	8	100	101
4	1	9	12	-2
4	1	10	167	-152
4	2	0	308	296
4	2	1	33	-42
4	2	2	113	-150
4	2	3	343	351
4	2	4	322	-322
4	2	5	132	-146
4	2	6	193	179
4	2	8	61	-71
4	2	9	21	34
4	2	10	43	-50
4	3	1	66	47
4	3	2	367	-368
4	3	3	14	29
4	3	4	403	386
4	3	5	116	-134
4	3	7	24	-43
4	3	8	82	-92
4	3	9	20	-21
4	3	10	146	139
4	4	0	119	-146
4	4	1	43	-60
4	4	2	292	263
4	4	3	159	-184
4	4	4	105	123
4	4	5	22	26
4	4	6	303	-298
4	4	7	17	-24
4	4	8	71	71
4	4	10	179	63
4	5	1	219	215
4	5	2	206	212
4	5	3	27	32
4	5	4	302	-295
4	5	5	52	62
4	5	7	67	73
4	5	8	197	160
4	5	9	15	-22
4	5	10	100	-96
4	6	0	57[illegible]	496
4	6	1	82	94
4	6	2	135	-152
4	6	3	97	94
4	6	4	133	-144
4	6	5	29	-33
4	6	6	222	183
4	6	8	119	-123
4	7	1	62	48
4	7	2	280	-278
4	7	4	69	81
4	7	5	97	-91
4	7	8	145	-126
4	8	0	327	-327
4	8	1	91	97
4	8	2	155	152
4	8	3	154	-201
4	8	4	31	35
4	8	5	64	64
4	8	6	256	-202
4	8	8	69	98
4	9	1	221	-182
4	9	2	66	90
4	9	3	30	31
4	9	4	64	-89
4	9	5	123	114
4	9	7	121	-104
4	9	8	56	143
4	10	0	296	277
4	10	1	67	-60
4	10	2	62	-64
4	10	3	114	105
4	10	4	27	-32
4	10	5	91	-70
4	10	6	122	102
4	10	7	29	-42
4	11	1	105	96
4	11	2	163	-142
4	11	3	108	8
4	11	5	36	-37
4	12	0	167	-152
4	12	1	61	50
4	12	2	42	44
4	12	3	41	4
4	12	4	13	17
4	13	1	70	-53
4	13	2	48	45
5	0	6	34	-43
5	0	8	89	-112
5	0	10	26	-35
5	1	0	304	-310
5	1	1	123	-119
5	1	2	17	26
5	1	3	50	50
5	1	4	55	-78
5	1	5	24	24
5	1	6	49	-69
5	1	8	49	66
5	1	9	28	28
5	1	10	12	-13
5	2	1	231	221
5	2	2	18	45
5	2	4	195	221
5	2	5	31	-41
5	2	7	77	98
5	2	10	9	13
5	3	1	38	57
5	3	2	74	105
5	3	4	34	54
5	3	5	31	33
5	3	6	45	-59
5	3	7	56	69
5	3	9	78	-78
5	4	1	169	-173
5	4	2	146	167
5	4	3	24	22
5	4	4	35	-55
5	4	7	118	-122
5	5	0	90	138
5	5	1	119	-120
5	5	2	14	-6
5	5	3	19	-32
5	5	4	23	-25
5	5	5	34	40
5	5	7	41	-44
5	5	8	22	-28
5	5	9	72	67
5	6	1	211	190
5	6	2	78	83
5	6	3	24	32
5	6	4	37	-51
5	6	5	18	-24
5	6	6	15	8
5	6	7	104	106
5	6	8	45	-44
5	7	1	109	99
5	7	3	58	-75
5	7	4	43	-68
5	7	5	64	62
5	8	1	228	-190
5	8	3	17	18
5	8	4	125	137
5	8	5	118	98
5	9	0	125	161
5	9	1	160	-134
5	9	3	154	161
5	9	5	67	-75
5	10	1	155	151
5	10	3	27	30
5	10	5	106	-93
5	11	0	46	-69
5	11	1	77	67
5	11	3	130	-128
5	11	4	19	-24
5	12	1	62	-58
6	0	0	280	-321
6	0	2	115	145
6	0	4	179	197
6	0	6	160	-177
6	0	8	68	73
6	1	1	24	-19
6	1	2	283	283
6	1	3	24	-29
6	1	4	338	-321
6	1	5	14	18
6	1	6	18	24
6	1	7	33	38
6	1	8	74	81
6	1	9	18	19
6	2	0	58	75
6	2	2	141	-152
6	2	3	74	108
6	2	4	87	-101
6	2	5	26	-34
6	2	6	191	200
6	2	7	24	33
6	2	8	32	-31
6	2	9	16	-20
6	3	1	108	-127
6	3	2	104	-127
6	3	3	45	-54
6	3	4	211	203
6	3	5	24	-35
6	3	7	43	-63
6	3	8	61	-72
6	4	0	165	-176
6	4	1	136	-112
6	4	2	53	65
6	4	3	30	-44
6	4	4	81	110
6	4	6	74	-88
6	4	7	23	-36
6	4	8	61	51
6	5	2	185	180
6	5	3	27	-29
6	5	4	156	-132
6	5	5	19	-20
6	5	7	162	134
6	5	8	66	66
6	6	0	190	209
6	6	2	151	-155
6	6	3	17	-17
6	6	4	55	-66
6	6	5	48	48
6	6	6	189	173
6	6	7	40	48
6	7	1	103	-128
6	7	2	133	-144
6	7	3	28	-25
6	7	4	195	165
6	8	0	228	-249
6	8	2	87	93
6	8	3	21	33
6	8	4	50	63
6	9	2	109	114
6	9	4	20	-25
6	9	5	34	-39
6	10	0	82	96
6	10	2	36	-38
6	10	3	70	-67
6	11	1	49	-44
7	0	2	162	175
7	0	4	341	-318
7	1	0	97	107
7	1	2	126	-136
7	1	3	26	37
7	1	4	145	-148
7	1	5	46	-45
7	1	6	160	150
7	1	7	17	-20
7	1	8	21	-31
7	2	1	87	88
7	2	2	255	-246
7	2	3	21	-22
7	2	4	232	234
7	2	5	21	-30
7	2	7	41	45
7	3	0	182	-197
7	3	1	62	54
7	3	2	128	128
7	3	3	23	-21
7	3	4	112	123
7	3	5	20	-24
7	3	6	168	-143
7	4	1	29	-34
7	4	2	159	160
7	4	4	229	-216
7	5	0	210	208
7	5	1	36	28
7	5	2	106	-120
7	5	3	56	-63
7	5	4	62	-69
7	5	6	137	157
7	6	2	175	-166
7	6	3	14	-11
7	6	4	81	79
7	6	5	19	20
7	7	0	239	-244
7	7	2	62	60
7	7	4	49	52
7	8	1	113	-79
7	8	2	101	90
7	8	3	15	-19
7	8	4	56	-52
7	9	0	166	160
7	9	1	50	-38
7	9	2	49	-60
7	9	3	43	42
8	0	0	54	76
8	1	1	56	56
8	1	2	26	-39
8	1	3	29	29
8	2	0	55	-75
8	2	1	37	45
8	2	2	46	56
8	2	6	99	-67
8	3	1	53	-69
8	3	2	75	79
8	3	3	21	18
8	3	4	64	-79
8	3	5	13	6
8	4	0	152	143
8	4	1	32	-40
8	4	2	29	-37
8	4	3	17	-24
8	4	4	39	-37
8	5	1	156	98
8	5	2	79	-73
8	5	3	21	22
8	5	4	33	33
8	6	0	19	-23
8	6	1	100	67
8	6	2	10	10
8	6	3	17	-7
8	7	1	94	-77
9	0	2	93	92
9	1	0	31	23
9	1	1	25	-19
9	1	2	43	-47
9	2	1	14	11
9	2	2	42	-43
9	3	0	13	-10
9	3	1	26	-29
9	3	2	26	34

parison of observed F_{hkl} with those calculated for each possibility resolved the ambiguity, happily indicating the site which gave the more reasonable lengths for the hydrogen bonds.

The structure was subsequently refined in three dimensions by least squares on the Pegasus computer at Leeds University, using the SFLS program (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) on the 733 independent reflexions whose intensities were estimated visually from Weissenberg photographs. After five cycles the R index was 11·7% and the largest shift in atomic coordinates about half a standard deviation. The refinement was stopped there although there was a shift in the thermal vibration parameters U_{ij} of more than twice a standard deviation; the vibrations are thus less adequately refined than the coordinates. The hydrogen atoms were ignored.

Observed and calculated structure factors are shown in Table 1.

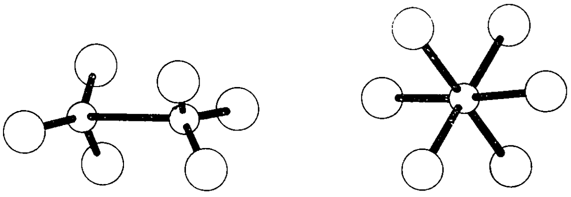

Fig. 1. (a) A drawing of the $[P_2O_6]^{4-}$ ion. (b) View of the ion looking down the P–P bond. In both the twofold axis is vertical.

Discussion of the structure

The atomic coordinates with their standard deviations are shown in Table 2, the thermal parameters U_{ij} (which are related to the more conventional B_{ij} by $B_{ij}=8\pi^2U_{ij}$) in Table 3 and their standard deviations in Table 4.

Fig. 1(a) is a drawing of the hypophosphate ion; the interesting dimensions are given in Table 5. Fig. 1(b) shows the ion projected down the P–P bond; it adopts, as suggested by Palmer (1961) on the basis of infrared work, a staggered configuration with symmetry approaching $\bar{3}m$ (D_{3d}). The P–O bond lengths are much as expected: the hydrogen atom is presumably attached to O(1) and the lengths P–O(H) and P–O are compared with others in Table 6. The P–P bond (2·17 Å) seems to be the shortest yet reported: the usual value is 2·22 Å and the shortest previously published is 2·18 Å in polycrystalline black phosphorus (Hultgren, Gingrich & Warren, 1935). The irregularity in the O–P–O angles does not seem to be simply explicable.

The hypophosphate ions are linked together, rather like the rungs of a ladder, into columns parallel to the c axis by the short hydrogen bonds O(1) · · · O(3) of length 2·53 Å. Three of the four expected N–H · · · O bonds can be identified unambiguously by their lengths (2·75, 2·84, 2·92 Å) but the fourth cannot, the three next shortest contacts being 3·14, 3·18 and 3·20 Å in length. By examining the angles that all these contacts make at the nitrogen atom, and by comparing them with Fuller's (1959) data

Table 2. *Atomic coordinates and standard deviations* (Å)

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
P	0·7336	2·7280	1·5720	0·0016	0·0017	0·0014
N	1·9289	5·9521	3·8598	0·0051	0·0058	0·0058
O(1)	0·1783	3·5076	2·8194	0·0049	0·0045	0·0044
O(2)	0·4863	1·2488	1·6390	0·0055	0·0052	0·0048
O(3)	0·2078	3·4467	0·3616	0·0048	0·0046	0·0044

Table 3. *Thermal parameters* U_{ij}

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0·0396	0·0294	0·0334	0·0012	0·0009	−0·0011
N	0·0521	0·0344	0·0516	−0·0014	−0·0007	−0·0117
O(1)	0·0525	0·0435	0·0353	0·0103	0·0044	0·0098
O(2)	0·0521	0·0272	0·0688	−0·0093	0·0013	−0·0129
O(3)	0·0527	0·0498	0·0384	0·0304	0·0021	−0·0110

Table 4. *Standard deviations in thermal parameters*, $\sigma(U_{ij})$

	$\sigma(U_{11})$	$\sigma(U_{22})$	$\sigma(U_{33})$	$\sigma(U_{12})$	$\sigma(U_{13})$	$\sigma(U_{23})$
P	0·0009	0·0008	0·0009	0·0012	0·0011	0·0011
N	0·0032	0·0024	0·0035	0·0045	0·0049	0·0049
O(1)	0·0025	0·0026	0·0020	0·0045	0·0036	0·0038
O(2)	0·0028	0·0021	0·0034	0·0042	0·0041	0·0041
O(3)	0·0023	0·0026	0·0022	0·0045	0·0039	0·0038

Table 5. *Bond lengths and angles*

	l	$\sigma(l)$		φ	$\sigma(\varphi)$
PO(1)	1·572 Å	0·005 Å	PPO(1)	106·7°	0·3
PO(2)	1·501	0·005	PPO(2)	106·8	0·3
PO(3)	1·503	0·005	PPO(3)	106·6	0·3
P–P	2·170	0·003	O(1)PO(2)	113·3	0·4
			O(2)PO(3)	116·7	0·4
			O(3)PO(1)	106·2	0·4

Table 6. *Bond lengths in phosphates*

Compound	P–OH	P–O	Reference
$(NH_4)_2H_2P_2O_6$	1·57	1·50	This work
KH_2PO_4	1·58	1·51	Bacon & Pease (1955)
H_3PO_4	1·57	1·52	Furberg (1955)

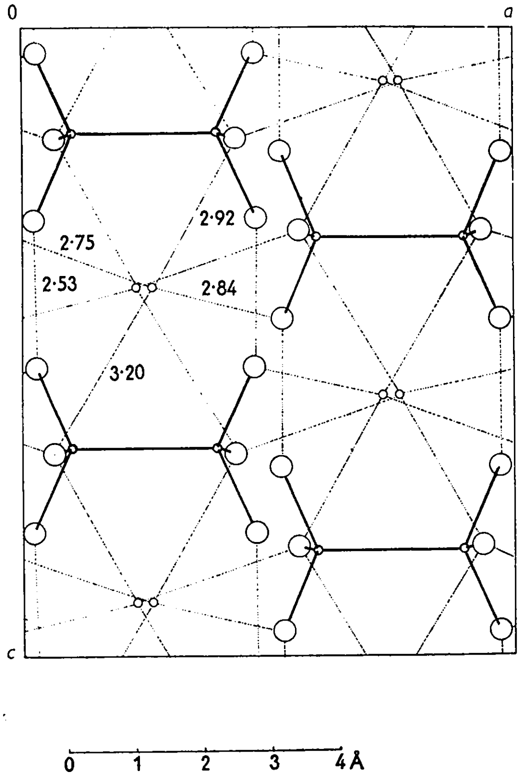

Fig. 2. The crystal structure projected down the *b* axis. The hydrogen bonds are shown by broken lines.

on hydrogen bonds, it is possible to draw a firm inference that the contact of length 3·20 Å is in fact the fourth hydrogen bond: the six angles at the nitrogen atom are then 109, 111, 102, 93, 122 and 121°. The contacts of length 3·14 and 3·18 Å make angles with the three clearly identified hydrogen bonds of 146, 72, 102° and 73, 66, 168° respectively: the extremes of these are not considered acceptable. The value 3·20 Å is very large for an N–H · · · O bond but larger values have been reported (*e.g.* Yakel & Hughes, 1954; Chesnut & Marsh, 1958).

The N–H · · · O bonds form a three-dimensional framework; two of them reinforce the ladder-like arrangement of the hypophosphate ions while the other two link one of these columns to two adjacent ones. The projection of the structure down the *b* axis is shown in Fig. 2.

We are very grateful to Dr M. R. Truter of the University of Leeds who supervised the three-dimensional refinement and supplied much valuable advice.

References

Bacon, G. E. & Pease, R. S. (1955). *Proc. Roy. Soc.* A, **230**, 359.

Brooks, R. & Alcock, T. C. (1950). *Nature, Lond.* **166**, 435.

Chesnut, D. B. & Marsh, R. E. (1958). *Acta Cryst.* **11**, 413.

Cruickshank, D. W. J., Pilling, D. E., and (in part) Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Oxford: Pergamon Press.

Fuller, W. (1959). *J. Phys. Chem.* **63**, 1705.

Furberg, S. (1955). *Acta Chem. Scand.* **9**, 1557.

Hultgren, R., Gingrich, N. S. & Warren, B. E. (1935). *J. Chem. Phys.* **3**, 351.

Palmer, W. G. (1961). *J. Chem. Soc.* p. 1552.

Raistrick, B. & Hobbs, E. (1949). *Nature, Lond.* **164**, 113.

Van Wazer, J. R. (1958). *Phosphorus and its Compounds, I.* pp. 403–406. New York: Interscience.

Yakel, H. L. Jr. & Hughes, E. W. (1954). *Acta Cryst.* **7**, 291.