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Hydrogen Bond Studies

48.* Neutron Diffraction Study of Hydrazinium Dihydrogen Phosphate, $N_2H_5H_2PO_4$

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The crystal structure of hydrazinium dihydrogen phosphate, $N_2H_5H_2PO_4$, has been refined from three-dimensional neutron diffraction data. A correction for extinction effects was included in the least-squares refinement. The positions of the phosphorus, nitrogen, and oxygen atoms agree well with those obtained in a previous X-ray investigation by Liminga. The structure is composed of $N_2H_5^+$ and $H_2PO_4^-$ ions. $O-H\cdots O$ bonds link the $H_2PO_4^-$ ions to form a three-dimensional framework. The $N_2H_5^+$ ions are connected to this framework by $N-H\cdots O$ bonds, and are interlinked to form chains by $N-H\cdots N$ bonds. The majority of the hydrogen bonds are close to linear with $X-H\cdots Y$ angles in the range 169–177°; the only large deviation from linearity is found in a weak $N-H\cdots O$ bond, which may be regarded as bifurcated.

The crystal structures of $N_2H_5H_2PO_4$ and $N_2H_6(H_2PO_4)_2$ have been determined by X-ray methods.[1,2] The hydrogen atoms were located approximately, but since the hydrogen bonding arrangement is relatively complicated in both structures, more accurate determinations of the hydrogen positions were desired. Neutron diffraction studies of both compounds have therefore been undertaken. The result of the $N_2H_5H_2PO_4$ investigation is reported below.

CRYSTAL DATA

Hydrazinium dihydrogen phosphate, $N_2H_5H_2PO_4$. F.W. 130.04. Orthorhombic, $a=5.6737(5)$,** $b=7.8194(5)$, $c=10.6338(7)$ Å, $V=471.77$ Å^3 at 25°C.[1] $D_m=1.81$ g cm^{-3},[1] $Z=4$, $D_x=1.831$ g cm^{-3}. Space group $P2_12_12_1(D_2^4)$. Calculated neutron absorption coefficient: 2.06 cm^{-1}.

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** Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

EXPERIMENTAL

Hydrazinium dihydrogen phosphate was prepared from hydrazine hydrate and phosphoric acid as described earlier.[1] Large single crystals were obtained by recrystallization from an aqueous solution. A crystal with a volume of 132 mm^3, enclosed in thin-walled quartz tube, was used for the data collection.

The crystal was mounted with the b axis parallel to the ϕ-axis on a Hilger & Watts four-circle diffractometer at Reactor R2 of the Swedish Atomic Energy Co., Studsvik. The neutron intensity at the specimen was 5×10^4 n cm^{-2} sec^{-1} at a wavelength of 1.097 Å. The intensity data were collected automatically under the control of a PDP-8 computer. A region of reciprocal space extending out to $\sin \theta/\lambda = 0.75$ Å^{-1} was examined. A $\theta - 2\theta$ step scan technique was used with $\Delta(2\theta) = 0.08°$. Two standard reflections were measured at regular intervals to provide a check on crystal and electronic stability. No significant changes were observed in these standards.

The data were corrected for background according to the formula $I = C - t_c(B_1 + B_2)/(t_1 + t_2)$, where C is the total integrated peak count obtained in a scan time of t_c; B_1 and B_2 are the background counts obtained in times t_1 and t_2, respectively.

Standard deviations were calculated using the expression:

$$\sigma(I) = \{C + [t_c/(t_1 + t_2)]^2(B_1 + B_2)\}^{1/2}$$

Values of F^2 and $\sigma_{\text{count}}(F^2)$ were then calculated by applying the Lorentz factor and absorption corrections to the values of I and $\sigma(I)$. The crystal shape was defined by 15 rational crystal boundary planes in the calculation of the absorption correction. The resulting transmission factors were in the range 0.35 – 0.45. The linear absorption coefficient of 2.06 cm^{-1} was calculated, using a value of 34 barns for the incoherent scattering cross section for hydrogen.

The space group absent reflections were excluded from the data, and the values of F^2 for the few reflections measured more than once were averaged. The total number of independent reflections thus obtained was 949, of which 790 had F^2 values larger than their standard deviations.

LOCATION OF THE HYDROGEN ATOMS AND REFINEMENT

A three-dimensional difference map for which the calculated structure factors were based on the heavy atom positions from the X-ray study [1] revealed the positions of the hydrogen atoms. The structure was refined, using the full-matrix least-squares program LINUS.[3] The function minimized was $\sum w(|F_o^2| - |F_c^2|)^2$. Only the 790 reflections with F^2 values larger than $\sigma(F^2)$ were included. Each reflection was assigned a weight w inversely proportional to the estimated variance of the observation

$$w^{-1} = \sigma^2(F^2)$$

and

$$\sigma^2(F^2) = \sigma^2_{\text{count}}(F^2) + (k\,F^2)^2$$

with k equal to 0.05, and σ^2_{count} based on counting statistics alone. The empirical correction term ($k\,F^2$) is included to take account of other errors in the data. The parameters refined were 42 positional parameters, 84 anisotropic thermal parameters, an overall scale factor, and one isotropic extinction parameter. In the last cycle of least-squares refinement, no parameter shifted by more than 0.1σ; the final agreement factors for the 790 observed reflections were

Table 1. Final positional and thermal parameters for $N_2H_5H_2PO_4$. The positional parameters are given as fractional coordinates $\times 10^5$. The anisotropic thermal parameters ($\times 10^5$) are defined as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. The second line given for each heavy atom parameter compares the neutron results with the X-ray results of Liminga.[1] The value given first is Δ (defined as the X-ray parameter value minus the neutron parameter value), followed by $|\Delta|/\sigma$, where σ is the combined standard deviation (see text).

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	9337(83) 108 1.3	18456(62) 103 1.6	15281(41) −10 0.2	1143(106) −280 2.5	494(54) 124 2.1	295(29) 113 3.6	−143(68) 51 0.7	−10(45) 17 0.4	14(34) 26 0.7
O(1)	−17993(81) −115 1.1	18818(70) 122 1.3	13642(38) −1 0.0	1088(97) 27 0.2	1011(65) 212 2.1	340(27) 177 3.9	−163(76) 135 1.2	−159(44) 150 2.1	109(39) −93 1.5
O(2)	18370(87) 6 0.1	36454(56) −92 1.1	17802(44) 27 0.4	1533(117) −123 0.7	610(52) 288 3.3	504(33) 168 3.3	−236(72) 274 2.6	151(56) −72 0.8	−76(36) 6 0.1
O(3)	13580(95) −151 1.2	7739(74) 34 0.3	27214(48) 103 1.6	1941(157) 94 0.4	1132(77) 341 2.9	482(36) 133 2.4	−450(86) −5 0.0	−383(60) 51 0.6	435(44) −81 1.2
O(4)	20980(87) 18 0.1	10348(61) 44 0.5	3990(43) 45 0.7	1698(134) −113 0.6	758(63) 133 1.4	408(31) 253 4.9	219(72) 27 0.2	217(51) −224 2.6	−54(36) −61 1.0
N(1)	59005(53) 151 1.4	19814(41) −24 0.3	40309(31) 115 1.9	1434(76) 173 1.0	857(39) 350 3.5	513(22) 113 2.2	−41(44) 177 1.4	−124(34) −5 0.1	−67(26) −28 0.4
N(2)	45102(48) 87 0.8	35160(34) −29 0.4	40641(27) −10 0.2	1374(69) −117 0.8	727(37) 181 2.2	399(18) 217 4.6	−38(40) −140 1.4	17(33) −2 0.0	17(21) −7 0.1
H(1)	65926(251)	18941(161)	31660(103)	3856(419)	1861(195)	667(75)	671(271)	−144(151)	−385(111)
H(2)	47405(205)	9849(137)	41136(138)	2809(325)	1215(149)	1350(126)	−541(195)	−101(206)	−148(125)
H(3)	36247(177)	37158(136)	32287(86)	2448(286)	1488(146)	526(58)	−57(182)	−200(103)	264(81)
H(4)	56468(177)	45517(117)	42391(92)	2307(282)	1149(131)	753(82)	−239(162)	27(126)	53(84)
H(5)	32488(175)	34181(123)	47804(80)	2362(241)	1281(147)	590(64)	33(174)	481(107)	−91(75)
H(6)	−23455(174)	26801(118)	6604(83)	2000(243)	1221(137)	656(71)	−259(147)	−120(106)	68(80)
H(7)	386(163)	−1607(106)	29421(78)	2353(270)	952(108)	538(59)	−7(145)	−171(96)	216(66)

$$R = \frac{\sum ||F_o^2| - |F_c^2||}{\sum |F_o^2|} = 0.109$$

$$R_w = \left\{ \frac{\sum w(|F_o^2| - |F_c^2|)^2}{\sum w |F_o^4|} \right\}^{1/2} = 0.125$$

The corresponding conventional R factor based on F was 0.077. The standard deviation of an observation of unit weight, $S = [\sum w(|F_o^2| - |F_c^2|)^2/(m-n)]^{1/2}$ was 1.03. In this expression, w is the weight of an observation, m the total number of observations, and n the number of parameters varied. The final positional and thermal parameters are presented in Table 1, and the root-mean-square displacements along principal axes of the thermal ellipsoids are given in Table 2. The refined value of the isotropic extinction parameter is $g = 11780(908)$. This value corresponds to a mosaic spread parameter of approximately 5 sec, or a domain size of 1.3 μm, depending on whether a Zachariasen [4] Type I or Type II description is chosen. The observed and calculated structure factors are listed in Table 3, together with the calculated extinction corrections defined as

Table 2. Root-mean-square amplitudes of vibration (in units of 10^{-3} Å).

Atom	Axis 1	Axis 2	Axis 3
P	115 (8)	130 (6)	144 (7)
O(1)	117 (6)	143 (6)	186 (6)
O(2)	126 (7)	151 (7)	185 (6)
O(3)	110 (7)	153 (7)	242 (7)
O(4)	125 (7)	160 (6)	183 (6)
N(1)	144 (4)	163 (4)	179 (4)
N(2)	145 (4)	152 (4)	153 (4)
H(1)	169 (13)	223 (14)	284 (15)
H(2)	167 (13)	233 (13)	280 (13)
H(3)	152 (11)	200 (12)	230 (11)
H(4)	175 (12)	204 (12)	209 (11)
H(5)	144 (11)	200 (12)	227 (11)
H(6)	169 (11)	187 (11)	211 (11)
H(7)	143 (10)	188 (11)	207 (11)

$$E = \left[1 + \frac{2\overline{T}|F_c^2|\, g\lambda^3}{V^2 \sin 2\theta} \right]^{-1/2}$$

where $|F_c^2|$ is on an absolute scale, λ is in Å, and the cell volume V is in Å^3. The mean path length through the crystal for the reflection concerned is given by $\overline{T}$, calculated using the expression $\overline{T} \simeq -{}^{e}\log A^*/\mu$, where A^* is the transmission factor, and μ is the linear absorption coefficient in cm^{-1}. The observed $|F_o|$ values in Table 3 are corrected for extinction:

$$|F_o|_{\text{corr}} = |F_o|/E^{1/2}$$

The neutron scattering lengths used were (in units of 10^{-12} cm) $\overline{b}_P = 0.51$, $\overline{b}_O = 0.577$, $\overline{b}_N = 0.94$, $\overline{b}_H = -0.372$.

Table 3. Observed and calculated neutron structure amplitudes for $N_2H_5H_2PO_4$. The five columns are, in order, the indices k and l, $100|F_o|$, $100|F_c|$ (in units of 10^{-12} cm) and $100 \times E$. The entry for the extinction correction, E, is not included for $E > 0.99$. The values of F_o have been divided by $E^{1/2}$. A negative value for F_o indicates an unobserved reflection which was not included in the least-squares refinement.

*** H = 0 ***				
0	0	--	838	
0	2	59	64	94
0	4	609	621	37
0	6	248	281	73
0	8	454	466	59
0	10	80	67	98
0	12	86	83	98
0	14	133	126	95
1	1	110	92	87
1	2	186	187	72
1	3	378	375	52
1	4	246	235	74
1	5	802	821	33
1	6	98	122	93
1	7	728	721	41
1	8	-0	66	98
1	9	608	601	52
1	10	79	92	97
1	11	308	319	77
1	12	-72	6	
1	13	120	108	97
1	14	-0	117	96
1	15	146	169	92
2	0	522	540	36
2	1	250	263	63
2	2	-0	15	
2	3	-44	31	99
2	4	682	687	37
2	5	210	202	83
2	6	129	134	92
2	7	178	187	88
2	8	93	120	95
2	9	593	585	53
2	10	186	210	88
2	11	-0	28	
2	12	95	85	98
2	13	219	265	84
2	14	-46	101	97
2	15	115	117	96
3	1	527	528	44
3	2	339	333	63
3	3	258	257	74
3	4	286	282	73
3	5	239	242	80
3	6	379	378	66
3	7	109	142	93
3	8	87	107	96
3	9	352	352	73
3	10	-0	24	
3	11	210	227	87
3	12	353	347	76
3	13	198	218	88
3	14	107	82	98
3	15	-50	74	98
4	0	609	642	42
4	1	-0	7	
4	2	-0	2	
4	3	489	475	56
4	4	98	11	
4	5	476	458	60
4	6	170	189	88
4	7	109	126	95
4	8	311	311	77
4	9	264	248	84
4	10	119	96	97
4	11	-70	42	99
4	12	78	68	99
4	13	104	56	99
4	14	70	1	
5	1	-0	71	98
5	2	132	143	92
5	3	281	289	77
5	4	915	913	36
5	5	658	667	48
5	6	-46	47	99
5	7	241	240	85
5	8	232	245	85
5	9	217	211	88
5	10	-49	6	
5	11	271	241	86
5	12	289	325	79
5	13	-0	24	
5	14	-0	36	
6	0	292	295	77
6	1	586	602	51
6	2	191	169	91
6	3	514	515	58
6	4	745	745	45
6	5	88	125	95
6	6	197	205	88
6	7	430	454	66
6	8	-0	52	99
6	9	210	227	87
6	10	-0	64	99
6	11	105	154	94
6	12	255	272	83
6	13	110	152	94
7	1	-77	82	98
7	2	140	126	95
7	3	185	182	91
7	4	320	332	76
7	5	94	110	96
7	6	154	165	93
7	7	250	269	83
7	8	636	627	55
7	9	87	87	98
7	10	107	119	96
7	11	194	193	91
7	12	-37	66	99
8	0	306	319	78
8	1	243	231	87
8	2	162	143	94
8	3	256	272	83
8	4	198	213	89
8	5	133	84	98
8	6	-80	69	99
8	7	-0	97	97
8	8	208	234	87
8	9	-75	129	96
8	10	139	126	96
8	11	-46	26	
9	1	114	117	96
9	2	-80	97	97
9	3	-0	18	
9	4	205	195	91
9	5	154	152	94
9	6	285	310	80
9	7	147	141	95
9	8	81	34	
9	9	85	75	98
9	10	77	80	98
10	0	158	164	93
10	1	207	191	91
10	2	152	165	93
10	3	-0	10	
10	4	-0	5	
10	5	163	160	93
10	6	80	64	99
10	7	-11	34	
10	8	-34	61	99
11	1	85	96	97
11	2	188	185	91
11	3	-76	21	
11	4	222	237	87
11	5	-0	16	
*** H = 1 ***				
0	1	213	232	60
0	2	320	318	53
0	3	323	328	57
0	4	259	267	69
0	5	211	215	79
0	6	351	343	66
0	7	611	602	47
0	8	364	375	67
0	9	501	487	59
0	10	247	232	85
0	11	269	299	79
0	12	231	251	84
0	13	217	208	89
0	14	73	49	99
0	15	-0	44	99
1	0	134	121	85
1	1	216	217	66
1	2	561	572	35
1	3	99	104	91
1	4	492	492	47
1	5	257	254	75
1	6	452	465	55
1	7	342	338	70
1	8	154	170	90
1	9	200	217	86
1	10	213	215	87
1	11	194	199	89
1	12	161	158	93
1	13	-52	59	99
1	14	199	218	88
1	15	140	137	95
2	0	418	411	49
2	1	81	60	97
2	2	140	146	85
2	3	639	626	38
2	4	256	263	73
2	5	621	612	44
2	6	258	253	78
2	7	447	435	61
2	8	252	223	85
2	9	205	230	85
2	10	-62	95	97
2	11	-0	32	
2	12	-0	32	
2	13	208	218	88
2	14	163	188	91
2	15	91	105	97
3	0	174	171	84
3	1	254	263	70
3	2	325	333	63
3	3	106	57	98
3	4	366	372	63
3	5	116	151	90
3	6	287	302	74
3	7	453	433	63
3	8	243	236	84
3	9	165	153	93
3	10	173	143	94
3	11	259	248	85
3	12	110	129	95
3	13	-0	82	98
3	14	-70	94	97
3	15	-0	10	
4	0	90	20	
4	1	301	310	69
4	2	141	135	91
4	3	249	240	79
4	4	376	355	68
4	5	215	198	86
4	6	362	339	72
4	7	325	339	73
4	8	421	405	68
4	9	251	237	85
4	10	208	208	89
4	11	96	127	95
4	12	122	162	93
4	13	187	205	89
4	14	91	113	96
5	0	428	414	63
5	1	424	438	59
5	2	522	525	53
5	3	358	348	70
5	4	186	182	89
5	5	358	346	72
5	6	279	273	80
5	7	179	147	93
5	8	354	334	76
5	9	262	242	85
5	10	83	106	97
5	11	-0	26	
5	12	139	186	91
5	13	159	180	92
5	14	168	179	91
6	0	180	170	91
6	1	191	206	86
6	2	410	421	64
6	3	308	293	78
6	4	354	341	73
6	5	313	327	76
6	6	553	555	57
6	7	308	303	79
6	8	-73	87	98
6	9	329	309	80
6	10	304	310	80
6	11	272	292	82
6	12	-44	87	98
6	13	-68	101	97
7	0	85	70	98
7	1	330	337	74
7	2	390	398	68
7	3	258	238	85
7	4	-75	102	97
7	5	515	506	61
7	6	279	270	83
7	7	-0	57	99
7	8	100	91	98
7	9	102	102	97
7	10	-19	18	
7	11	268	290	82
7	12	88	56	99
8	0	-63	107	97
8	1	179	186	90
8	2	158	159	93
8	3	94	106	97
8	4	291	273	83
8	5	106	116	96
8	6	238	240	86
8	7	117	92	98
8	8	151	157	94
8	9	162	145	94
8	10	154	164	93
8	11	-55	91	98
9	0	-0	6	
9	1	-86	103	97
9	2	102	127	95
9	3	198	204	89
9	4	98	31	
9	5	85	115	96
9	6	98	65	99
9	7	169	148	94
9	8	164	147	94
9	9	139	145	94
10	0	117	156	94
10	1	-84	65	99
10	2	115	119	96
10	3	170	148	94
10	4	280	266	84
10	5	86	47	99
10	6	131	115	96
10	7	-11	25	
11	0	203	222	88
11	1	137	186	91
11	2	-0	17	
11	3	150	146	94
11	4	-42	15	
*** H = 2 ***				
0	0	85	53	98
0	1	72	2	
0	2	228	241	72
0	3	-0	35	99
0	4	239	244	75
0	5	78	87	96
0	6	275	296	73
0	7	-66	7	
0	8	-73	59	99
0	9	524	491	60
0	10	251	258	83
0	11	114	150	93
0	12	327	317	78
0	13	-0	10	
0	14	-20	28	
0	15	-0	31	
1	0	525	531	43
1	1	433	436	49
1	2	181	179	82
1	3	284	292	68
1	4	248	240	76
1	5	373	384	62
1	6	108	88	96
1	7	396	366	68
1	8	211	237	83
1	9	116	136	94
1	10	-25	83	98
1	11	187	156	93
1	12	156	184	91
1	13	149	147	94
1	14	158	158	93
1	15	201	200	90
2	0	662	641	39
2	1	255	240	75
2	2	387	394	57
2	3	524	500	49
2	4	204	201	83
2	5	482	454	57
2	6	351	366	67
2	7	179	142	92
2	8	720	675	47
2	9	189	198	88
2	10	169	146	94
2	11	128	120	96
2	12	-48	77	98
2	13	88	114	96
2	14	103	93	98
2	15	-37	61	99
3	0	221	217	81
3	1	148	160	88
3	2	342	338	66
3	3	403	406	60
3	4	348	348	67
3	5	231	205	85
3	6	255	265	79
3	7	446	436	63
3	8	93	53	99
3	9	246	243	84
3	10	254	253	84
3	11	-0	63	99
3	12	201	183	91
3	13	172	134	95
3	14	185	204	89
4	0	133	71	98
4	1	98	134	92
4	2	232	214	83
4	3	132	112	95
4	4	399	377	66
4	5	214	203	86
4	6	346	350	72
4	7	101	115	96
4	8	246	236	85
4	9	-0	32	
4	10	197	219	88
4	11	180	142	94
4	12	228	244	86
4	13	117	99	97
4	14	161	123	96
5	0	-55	71	98
5	1	487	480	58
5	2	250	241	82
5	3	249	231	83
5	4	-68	75	98
5	5	331	320	75
5	6	466	456	63
5	7	204	187	90
5	8	304	278	82
5	9	218	183	91
5	10	151	143	94
5	11	238	245	86
5	12	-0	39	
5	13	252	242	86
6	0	248	248	83
6	1	160	152	92
6	2	294	286	79
6	3	436	430	65
6	4	294	279	80
6	5	236	225	86
6	6	186	200	89
6	7	127	152	93
6	8	98	107	97
6	9	165	133	95
6	10	146	137	95
6	11	94	104	97
6	12	83	110	97
6	13	216	206	89
7	0	-36	136	95
7	1	304	290	80
7	2	460	450	65
7	3	108	139	94
7	4	114	91	97
7	5	156	153	93
7	6	-64	63	99
7	7	135	112	96
7	8	167	210	89
7	9	193	189	91
7	10	122	131	95
7	11	125	80	98
7	12	224	212	89
8	0	165	117	96
8	1	206	181	91
8	2	136	69	99
8	3	-0	65	99
8	4	-20	106	97
8	5	196	177	92
8	6	160	156	93
8	7	245	265	84
8	8	138	117	96
8	9	191	221	88
8	10	109	115	96
9	0	234	241	87
9	1	137	112	97
9	2	189	143	94
9	3	111	145	94
9	4	216	202	90
9	5	-73	86	98
9	6	289	322	79
9	7	-0	76	98
9	8	-51	91	98
9	9	-68	43	99
10	0	143	169	93
10	1	166	193	91
10	2	166	187	91
10	3	161	159	93
10	4	-0	57	99
10	5	238	254	85
10	6	-52	101	97
10	7	133	152	94
11	0	174	150	94
11	1	108	150	94
11	2	163	135	95
11	3	-0	44	99
*** H = 3 ***				
0	1	836	857	32
0	2	-0	20	
0	3	77	67	98
0	4	329	341	68
0	5	111	131	93
0	6	500	475	58
0	7	311	331	73
0	8	130	142	93
0	9	121	106	96
0	10	-0	4	
0	11	-74	114	96
0	12	-0	8	
0	13	-0	112	96
0	14	-0	73	98
1	0	243	257	76
1	1	299	285	72
1	2	429	446	56
1	3	305	309	71
1	4	172	166	89
1	5	435	426	61
1	6	428	448	61
1	7	207	207	86
1	8	241	236	84
1	9	187	200	88
1	10	164	165	92
1	11	84	110	96
1	12	110	130	95
1	13	105	95	97
1	14	180	183	91
2	0	178	205	84
2	1	431	439	58
2	2	344	323	70
2	3	342	358	67
2	4	152	172	89
2	5	643	618	48
2	6	156	149	92
2	7	-41	49	99
2	8	203	212	87
2	9	-65	94	97
2	10	370	341	76
2	11	351	324	78
2	12	291	279	83
2	13	163	156	93
2	14	216	199	90
3	0	123	150	91
3	1	478	479	56
3	2	338	330	71
3	3	191	182	88
3	4	180	176	89
3	5	278	293	77
3	6	600	572	53
3	7	360	355	72
3	8	171	156	93
3	9	354	350	75
3	10	426	386	72
3	11	101	107	97
3	12	-75	126	96
3	13	89	71	99
3	14	255	240	86
4	0	86	96	96
4	1	550	560	52
4	2	236	244	82
4	3	362	353	70
4	4	270	300	77
4	5	242	239	84
4	6	234	224	86
4	7	209	204	88
4	8	109	127	95
4	9	112	92	97
4	10	142	136	95
4	11	-0	23	
4	12	151	175	92
4	13	251	232	87
5	0	-51	10	
5	1	89	71	98
5	2	114	107	96
5	3	323	302	77
5	4	252	237	84
5	5	116	94	97
5	6	232	264	83
5	7	231	228	87
5	8	161	138	95
5	9	146	115	96
5	10	408	373	74
5	11	147	123	96
5	12	180	157	93
5	13	121	154	94
6	0	450	440	66
6	1	384	389	70
6	2	201	185	90
6	3	211	242	85
6	4	209	227	86
6	5	206	222	87
6	6	125	123	96
6	7	-0	23	
6	8	124	129	95
6	9	156	154	94
6	10	105	81	98
6	11	-19	64	99
6	12	257	273	83
7	0	-59	75	98
7	1	171	166	92
7	2	-0	55	99
7	3	258	213	88
7	4	132	147	94
7	5	-77	91	98
7	6	135	161	93
7	7	205	231	87
7	8	-0	91	98
7	9	237	234	87
7	10	79	97	97
7	11	164	159	93
8	0	348	334	78
8	1	140	129	95
8	2	375	352	76
8	3	-39	30	
8	4	120	144	94
8	5	-0	27	
8	6	166	120	96
8	7	176	182	92
8	8	-0	89	98
8	9	217	217	89
8	10	140	108	97
9	0	-74	47	99
9	1	-0	41	
9	2	133	126	96
9	3	335	331	78
9	4	277	275	84
9	5	209	185	91
9	6	219	223	88
9	7	268	255	85
9	8	-69	71	99
10	0	237	242	87
10	1	105	50	99
10	2	433	411	71
10	3	109	77	98
10	4	152	124	96
10	5	-78	17	
*** H = 4 ***				
0	0	428	425	62
0	1	93	111	95
0	2	192	190	87
0	3	121	113	95
0	4	123	130	94
0	5	222	246	82
0	6	223	255	82
0	7	229	235	85
0	8	169	129	95
0	9	115	159	93
0	10	-40	4	
0	11	156	156	93
0	12	-68	27	
0	13	302	284	82
0	14	175	160	93
1	0	80	41	99
1	1	372	371	67
1	2	348	343	70
1	3	409	408	64
1	4	324	337	72
1	5	225	232	84
1	6	253	254	82
1	7	179	178	90
1	8	340	327	76
1	9	325	332	76
1	10	125	116	96
1	11	112	73	98
1	12	-0	71	99
1	13	172	168	93
2	0	93	69	98
2	1	332	353	70
2	2	355	351	70
2	3	81	119	95
2	4	722	728	44
2	5	111	114	96
2	6	153	145	93
2	7	410	401	69
2	8	326	333	76
2	9	83	101	97
2	10	100	97	97
2	11	191	195	90
2	12	307	294	81
2	13	109	112	96
3	0	629	630	49
3	1	667	657	48
3	2	110	127	94
3	3	437	422	65
3	4	352	362	71
3	5	286	278	80
3	6	-55	34	
3	7	164	188	90
3	8	165	177	91
3	9	89	95	97
3	10	91	86	98
3	11	249	234	87
3	12	185	190	91
3	13	230	225	88
4	0	337	309	77
4	1	-76	112	96
4	2	122	118	95
4	3	287	285	80
4	4	203	201	88
4	5	352	347	74
4	6	101	47	99
4	7	-59	80	98
4	8	447	431	69
4	9	212	219	88
4	10	95	88	98
4	11	147	132	95
4	12	312	293	82
5	0	193	206	88
5	1	291	286	80
5	2	108	106	96
5	3	358	352	74
5	4	143	160	93
5	5	-0	33	
5	6	115	99	97
5	7	138	86	98
5	8	215	223	88
5	9	196	188	91
5	10	252	252	86
5	11	113	50	99
5	12	201	180	92
6	0	-72	56	99
6	1	320	341	76
6	2	-0	59	99
6	3	94	110	96
6	4	-49	152	94
6	5	139	137	95
6	6	124	165	93
6	7	119	112	97
6	8	144	154	94
6	9	176	145	95
6	10	211	199	90
6	11	82	101	97
7	0	315	304	80
7	1	126	145	94
7	2	-39	41	
7	3	-0	81	98
7	4	219	200	90
7	5	132	141	95
7	6	151	178	92
7	7	107	69	99
7	8	134	111	97
7	9	87	87	98
7	10	178	172	92
8	0	238	243	86
8	1	110	112	97
8	2	-0	24	
8	3	194	207	90
8	4	135	144	95
8	5	209	171	93
8	6	-51	96	97
8	7	215	208	90
8	8	158	167	93
9	0	535	539	61
9	1	150	157	94
9	2	171	169	93
9	3	142	162	93
9	4	375	348	77
9	5	-0	64	99
9	6	-0	51	99
10	0	169	195	90
10	1	309	291	82
10	2	-0	65	99
10	3	183	160	93
*** H = 5 ***				
0	1	137	136	94
0	2	83	26	
0	3	440	423	66
0	4	105	70	98
0	5	-0	46	99
0	6	-25	65	99
0	7	-56	40	99
0	8	91	44	99
0	9	-0	65	99
0	10	234	221	88
0	11	177	165	93
0	12	278	301	81
1	0	393	393	68
1	1	104	106	96
1	2	143	137	94
1	3	367	380	70
1	4	201	215	87
1	5	168	184	90
1	6	321	320	77
1	7	88	77	98
1	8	163	158	93
1	9	108	81	98
1	10	169	174	92
1	11	253	246	86
1	12	163	164	93
2	0	159	157	92
2	1	579	588	54
2	2	320	319	76
2	3	272	276	81
2	4	117	129	95
2	5	85	129	95
2	6	296	281	82
2	7	199	212	88
2	8	96	93	98
2	9	174	148	94
2	10	113	106	97
2	11	195	227	88
2	12	110	96	97
3	0	226	215	87
3	1	160	151	93
3	2	308	307	78
3	3	368	382	71
3	4	128	109	96
3	5	117	13	
3	6	261	257	84
3	7	108	114	96
3	8	118	82	98
3	9	130	127	96
3	10	306	300	81
3	11	257	256	85
3	12	159	180	92
4	0	-57	30	
4	1	206	211	88
4	2	257	256	84
4	3	135	147	94
4	4	148	177	92
4	5	176	168	92
4	6	236	232	87
4	7	278	283	83
4	8	170	158	94
4	9	75	58	99
4	10	253	248	86
4	11	144	150	94
5	0	-29	14	
5	1	274	255	84
5	2	114	141	94
5	3	-63	108	97
5	4	132	125	96
5	5	120	126	96
5	6	94	68	99
5	7	219	208	90
5	8	168	153	94
5	9	-44	29	
5	10	104	87	98
6	0	275	275	83
6	1	92	117	96
6	2	125	151	94
6	3	-25	13	
6	4	223	225	88
6	5	-42	15	
6	6	171	147	94
6	7	134	130	96
6	8	202	189	91
6	9	-72	77	98
7	0	-30	35	
7	1	130	118	96
7	2	205	215	89
7	3	-67	87	98
7	4	168	155	94
7	5	165	180	92
7	6	166	122	96
7	7	85	81	98
7	8	-47	68	99
8	0	216	222	88
8	1	132	149	94
8	2	224	242	87
8	3	108	111	97
8	4	169	150	94
8	5	173	144	95
8	6	112	75	98
9	0	120	103	97
9	1	103	126	96
9	2	162	172	92
9	3	85	119	96
*** H = 6 ***				
0	0	229	231	86
0	1	345	358	74
0	2	98	95	97
0	3	-64	19	
0	4	118	116	96
0	5	-0	42	99
0	6	82	61	99
0	7	345	360	75
0	8	-28	33	
0	9	137	116	96
0	10	243	223	88
0	11	180	156	93
1	0	207	214	88
1	1	393	377	72
1	2	116	98	97
1	3	312	323	78
1	4	285	265	83
1	5	198	220	88
1	6	112	123	96
1	7	-75	64	99
1	8	210	210	89
1	9	133	157	93
1	10	137	133	95
1	11	156	175	92
2	0	170	163	93
2	1	116	120	96
2	2	313	306	79
2	3	134	113	96
2	4	89	90	98
2	5	121	137	95
2	6	245	240	86
2	7	195	101	97
2	8	141	110	97
2	9	182	188	91
2	10	273	274	83
3	0	-0	2	
3	1	105	102	97
3	2	-62	127	95
3	3	78	100	97
3	4	122	143	94
3	5	247	221	88
3	6	261	244	86
3	7	191	191	91
3	8	161	165	93
3	9	173	168	93
3	10	137	143	95
4	0	-0	8	
4	1	269	254	85
4	2	231	259	85
4	3	133	87	98
4	4	-68	76	98
4	5	89	37	
4	6	142	103	97
4	7	-49	78	98
4	8	97	26	
4	9	101	91	98
5	0	152	108	97
5	1	164	153	94
5	2	221	253	85
5	3	236	255	85
5	4	189	188	91
5	5	-66	50	99
5	6	154	133	95
5	7	-69	72	99
5	8	179	169	93
6	0	176	209	89
6	1	-50	34	
6	2	-34	94	98
6	3	264	253	86
6	4	-72	45	99
6	5	174	181	92
6	6	105	72	99
6	7	142	125	96
7	0	247	248	86
7	1	161	141	95
7	2	251	256	85
7	3	107	137	95
7	4	129	132	95
7	5	131	135	95
8	0	99	111	97
8	1	115	143	95
8	2	207	209	89
*** H = 7 ***				
0	1	127	112	96
0	2	384	406	71
0	3	89	88	98
0	4	180	186	91
0	5	-45	53	99
0	6	330	351	76
0	7	297	308	80
0	8	149	139	95
1	0	268	235	86
1	1	-0	101	97
1	2	301	321	79
1	3	88	101	97
1	4	161	156	93
1	5	101	104	97
1	6	110	15	
1	7	151	130	95
1	8	83	77	98
2	0	77	69	99
2	1	-41	78	98
2	2	346	346	77
2	3	266	274	83
2	4	87	62	99
2	5	153	151	94
2	6	166	177	92
2	7	237	245	86
2	8	114	56	99
3	0	260	267	84
3	1	118	85	98
3	2	142	132	95
3	3	84	55	99
3	4	258	235	87
3	5	-57	70	99
3	6	191	212	89
3	7	-0	89	98
4	0	-38	88	98
4	1	253	235	87
4	2	144	124	96
4	3	187	207	90
4	4	-0	92	98
4	5	-0	86	98
4	6	107	105	97
4	7	174	190	91
5	0	87	58	99
5	1	80	93	98
5	2	158	157	94
5	3	119	139	95
5	4	-33	85	98
5	5	139	149	94

Computer programs. The calculations were carried out on the CDC 3600 computer in Uppsala. The following programs were used:

DATAPH. Lorentz factor and absorption correction. Modification of a program originally written by Coppens *et al.*[5] The program also calculates the extinction components necessary for isotropic or anisotropic extinction refinement in the program LINUS.

DRF. Fourier calculations. Local modification of a program written by A. Zalkin, Berkeley, Calif.

LINUS. Full matrix, least-squares refinement with options for isotropic and anisotropic extinction refinement. This program is a modification due to Coppens and Hamilton[3] of the Brookhaven National Laboratory version of the program ORFLS, originally written by Busing *et al.*[6]

ORFFE. Crystallographic function and error program written by Busing *et al.*[7]

ORTEP. A thermal-ellipsoid plot program for crystal structure illustrations written by Johnson.[8]

WAL. A program for analysing the weighting scheme following the least-squares refinement written by one of the authors (P.-G. J.).

Table 4. Covalent bond lengths and angles.

A. Bond lengths (Å). Distances within brackets are corrected for thermal riding motion.[15]

	Neutron		X-Ray[1]
P-O(1)	1.561 (6)	[1.567]	1.573 (4)
P-O(2)	1.522 (7)	[1.528]	1.506 (5)
P-O(3)	1.540 (6)	[1.555]	1.550 (5)
P-O(4)	1.510 (6)	[1.519]	1.505 (5)
O(1)-H(6)	1.023 (10)		
O(3)-H(7)	1.072 (10)		
N(1)-N(2)	1.436 (4)		1.438 (8)
N(1)-H(1)	1.002 (12)	[1.036]	
N(1)-H(2)	1.024 (11)	[1.061]	
N(2)-H(3)	1.033 (9)	[1.055]	
N(2)-H(4)	1.052 (10)	[1.070]	
N(2)-H(5)	1.048 (9)	[1.069]	

B. Angles (degrees).

	Neutron	X-Ray[1]
O(1)-P-O(2)	109.7 (0.4)	109.7 (0.3)
O(1)-P-O(3)	104.9 (0.4)	104.3 (0.3)
O(1)-P-O(4)	110.7 (0.4)	110.7 (0.3)
O(2)-P-O(3)	107.8 (0.4)	107.7 (0.3)
O(2)-P-O(4)	112.4 (0.4)	112.9 (0.3)
O(3)-P-O(4)	111.0 (0.4)	111.2 (0.3)
P-O(1)-H(6)	113.2 (0.7)	
P-O(3)-H(7)	116.2 (0.6)	
N(2)-N(1)-H(1)	107.1 (0.8)	
N(2)-N(1)-H(2)	106.3 (0.8)	
H(1)-N(1)-H(2)	106.2 (1.1)	
N(1)-N(2)-H(3)	111.9 (0.7)	
N(1)-N(2)-H(4)	108.1 (0.6)	
N(1)-N(2)-H(5)	109.4 (0.6)	
H(3)-N(2)-H(4)	109.5 (0.8)	
H(3)-N(2)-H(5)	107.7 (0.8)	
H(4)-N(2)-H(5)	110.3 (0.8)	

COMPARISON OF NEUTRON AND X-RAY PARAMETERS

A comparison of the positional and thermal parameters of the heavy atoms with the X-ray results of Liminga[1] is included in Table 1. The table gives the difference Δ (defined as X-ray parameter minus neutron parameter), followed by $|\Delta|/\sigma$, where σ is the combined standard deviation defined as

$$\sigma = (\sigma^2_{\text{X-ray}} + \sigma^2_{\text{neutron}})^{1/2}$$

The agreement between the positional parameters is very satisfactory; no error is greater than twice the combined standard deviation. Bond lengths and angles for the heavy atoms are compared in Table 4. The hydrogen atoms bonded to the hydrazinium ion could be localized in the X-ray study by combining information obtained from the difference Fourier maps with chemical evidence. As is to be expected, these hydrogen positions are not accurately determined; they differ from those obtained in the present neutron study by 0.08 – 0.14 Å.

The agreement between the X-ray and neutron thermal parameters (for the heavy atoms) is less satisfactory than that between the positional param-

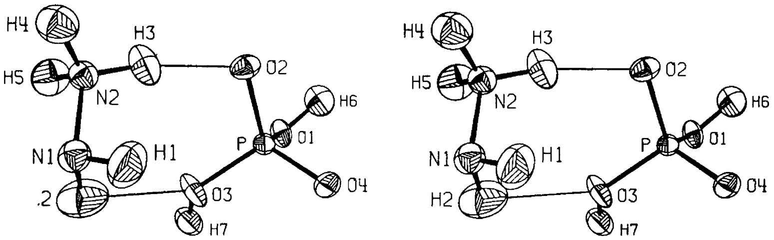

Fig. 1. Stereoscopic illustration of an asymmetric unit of $N_2H_5H_2PO_4$. The ellipsoids are scaled to include 50 % probability.

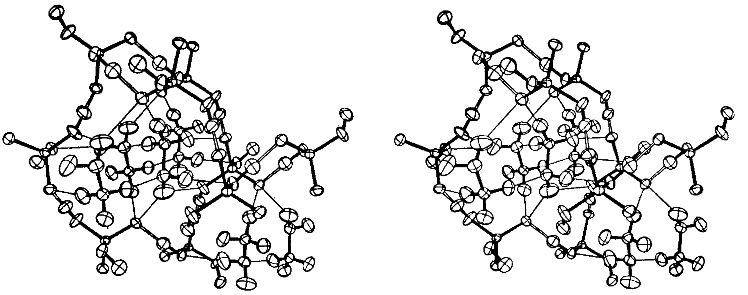

Fig. 2. Stereoscopic pair of figures showing part of the three-dimensional structure. Covalent bonds are filled, H···O distances shorter than 1.6 Å (part of O – H···O bonds) are open and the H···N and H···O contacts which are part of N – H···N and N – H···O bonds are drawn as single lines.

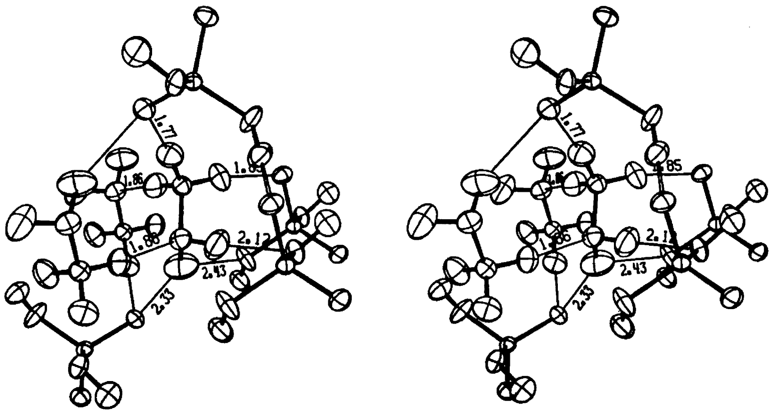

Fig. 3. Stereoscopic illustration of the hydrogen bond contacts around an $N_2H_5^+$ ion. All contacts where the H···O or H···N distances are less than 2.5 Å are included.

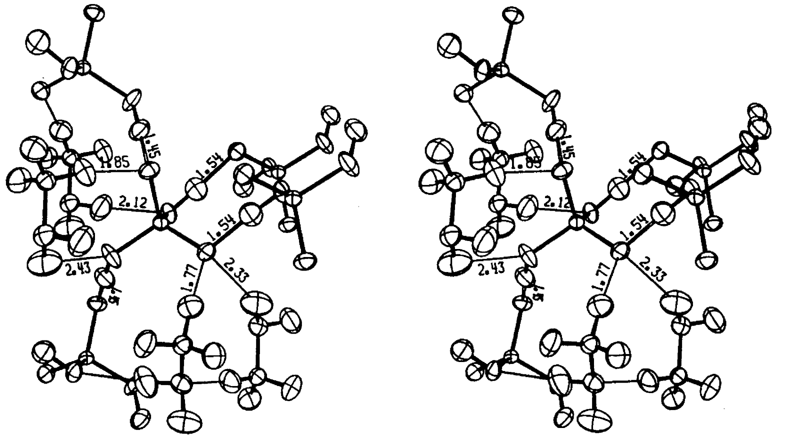

Fig. 4. Stereoscopic view of the environment of an $H_2PO_4^-$ ion. All contacts where the H···O or H···N distances are less than 2.5 Å are included.

eters. This is not surprising, since it is an accepted phenomenon that the systematic errors introduced by the assumption of a spherical electron distribution greatly prejudice thermal parameters determined using X-rays.[9,10]

DISCUSSION OF THE STRUCTURE

The structure is illustrated in Figs. 1 – 4. A more detailed stereoscopic view of the heavy atom structure has been given by Liminga.[11] The structure is composed of $N_2H_5^+$ and $H_2PO_4^-$ ions. Relatively short O – H···O hydrogen bonds link the $H_2PO_4^-$ ions to form a three-dimensional framework. Six-membered puckered rings of phosphate * groups stacked above one another are present in the structure. The $N_2H_5^+$ ions are linked by N – H···N bonds, giving rise to infinite zig-zag chains which are connected to the phosphate framework by N – H···O bonds. Two $N_2H_5^+$ ions can be regarded as lying inside each six-membered phosphate ring (*cf.* Fig. 2).

The hydrazinium(+) ion

The N – N distance of 1.436(4) Å agrees with the X-ray value of 1.438(8) Å.[1] Earlier reported N – N distances for the $N_2H_5^+$ ion in a number of different compounds are in the range 1.42 to 1.46 Å.[12,13]

The conformation of the hydrazinium ion is shown in Fig. 5. The H(1) – N(1) – N(2) – H(3) torsion angle is 38.1(1.1)°. It thus deviates considerably from the staggered conformation, which is probably the most stable form in the free ion. In the two compounds containing $N_2H_5^+$ ions, earlier studied by neutron diffraction, a perfect staggered conformation was found in $N_2H_5HC_2O_4$ (required by symmetry)[13] and a nearly staggered one in $LiN_2H_5SO_4$.[14]

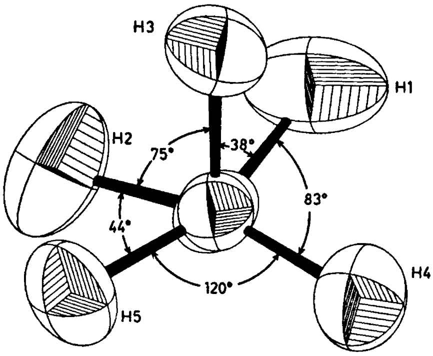

Fig. 5. The conformation of the $N_2H_5^+$ ion viewed down the N(2) – N(1) bond.

The mean apparent N(1) – H bond length is 1.013(8) Å, whereas the mean apparent N(2) – H bond length is 1.044(5) Å. In the neutron diffraction study of $N_2H_5HC_2O_4$ [13] it was also found that the uncorrected N – H distances were slightly longer at the NH_3^+ end than at the NH_2 end. If a correction for thermal riding motion [15] is applied, the differences become smaller for both structures. The observed differences are then no longer significant. However, it is not at all certain that the riding model is appropriate in this case.

Hydrogen bonding. Fig. 3 illustrates the hydrogen bond contacts around a hydrazinium ion; all contacts where the H···O or H···N distances are less than 2.5 Å have been included. Table 5 gives numerical values for the N – H···O and N – H···N bond lengths and angles.

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* Phosphate is used as an abbreviated form for dihydrogen phosphate in this discussion.

Table 5. Hydrogen bond distances and angles.[a]

A. N – H···O and O – H···O bonds.

X	H	O	X···O	X – H	H···O	∠X – H···O	∠H···O – P
N(1)	H(1)	O(1) *	3.123 (6)	1.002 (12)	2.122 (13)	175.7 (1.2)	109.1 (0.5)
N(1)	H(2)	O(4) *	3.252 (6)	1.024 (11)	2.335 (13)	148.5 (1.1)	123.7 (0.5)
N(1)	H(2)	O(3)	3.078 (6)	1.024 (11)	2.429 (14)	120.5 (1.0)	126.1 (0.5)
N(2)	H(3)	O(2)	2.865 (6)	1.033 (9)	1.845 (10)	168.9 (0.9)	111.1 (0.5)
N(2)	H(4)	O(4) *	2.812 (5)	1.052 (10)	1.769 (10)	170.6 (0.9)	114.8 (0.4)
O(1)	H(6)	O(4) *	2.561 (7)	1.023 (10)	1.542 (10)	173.9 (1.0)	113.4 (0.5)
O(3)	H(7)	O(2) *	2.517 (7)	1.072 (10)	1.446 (10)	176.9 (0.9)	112.7 (0.5)

B. N – H···N bond.

N(2)···N(1) *	2.907 (4)	N(2) – H(5)···N(1) *	173.6 (0.8)
N(2) – H(5)	1.048 (9)	H(5)···N(1)* – N(2)*	121.1 (0.4)
H(5)···N(1) *	1.863 (9)	H(5)···N(1)* – H(1)*	109.3 (0.9)
		H(5)···N(1)* – H(2)*	105.9 (0.9)

[a] Atoms marked with asterisks indicate atoms not in the asymmetric unit (*cf.* Table 6).

The $N_2H_5^+$ ions are hydrogen bonded to one another to form infinite zig-zag chains. As has been pointed out by Liminga,[11] there are two possible ways of linking $N_2H_5^+$ ions to form infinite chains by N – H···N hydrogen bonds. In one type, the NH_2 group acts both as donor and acceptor for the N – H···N bond. In the other, the NH_2 end accepts one hydrogen bond donated by the NH_3^+ end. Only one example of the first type has been found, namely in $LiN_2H_5SO_4$,[14] whereas the present structure is one among several instances of the second type.

The N(2) – H(5)···N(1) hydrogen bond has an H···N separation of 1.863(9) Å, and the N···N distance is 2.907(4) Å. The bond is nearly linear with an N – H···N angle of 173.6(0.8)°. These values correspond closely to those found in the neutron diffraction study of $N_2H_5HC_2O_4$ [1.837(11), 2.872(5) Å, and 176.1(1.2)°].[13]

The hydrogen atoms H(1) – H(4) of the $N_2H_5^+$ ion are involved in hydrogen bonds with oxygen atoms belonging to the surrounding phosphate groups (see Fig. 3). These bonds are much shorter at the NH_3^+ end than at the NH_2 end. The atoms H(1), H(3), and H(4) each take part in a slightly bent N – H···O hydrogen bond; the N – H···O angles are 176, 169, and 171°. The remaining hydrogen atom, H(2), may be regarded as taking part in a very weak bifurcated hydrogen bond $\mathrm{N(1)-H(2)}\begin{smallmatrix}\cdot\cdot\,\mathrm{O(4)}\\ \cdot\cdot\,\mathrm{O(3)}\end{smallmatrix}$. The H···O distances are as long as 2.34 and 2.43 Å. The latter contact could equally well be regarded as a short van der Waals contact especially since the possible N(1) – H(2)···O(3) hydrogen bond is severely bent with an N – H···O angle of 120°.

The dihydrogen phosphate ion

The geometry of the $H_2PO_4^-$ ion shows a significant departure from a regular tetrahedron (Table 4). The hydrogen atoms of the $H_2PO_4^-$ ion could not be directly located in the X-ray study.[1] The assignment of hydrogen atoms to this group was therefore based on the observed differences in the P – O bond lengths; the two longer bonds were assumed to be P – OH bonds. The present neutron results confirm these predictions. The P – O and P – OH bond distances are in good agreement with earlier reported values. A summary of such values has been given by Liminga.[1]

The conformation of the dihydrogen phosphate ion is shown in Fig. 6. The disposition of the two O – H bonds is very different, so no specific conformation seems to be favoured. This is to be expected, if the conformation is determined primarily by van der Waals repulsion between the atoms of the ion. The shortest H···O contacts within the ion are H(6)···O(4), H(6)···O(2), and H(7)···O(1). These are 2.844(1), 2.760(11), and 2.540(9) Å, respectively, of which only the latter distance is close to 2.6 Å, the sum of the van der Waals radii for hydrogen and oxygen atoms.

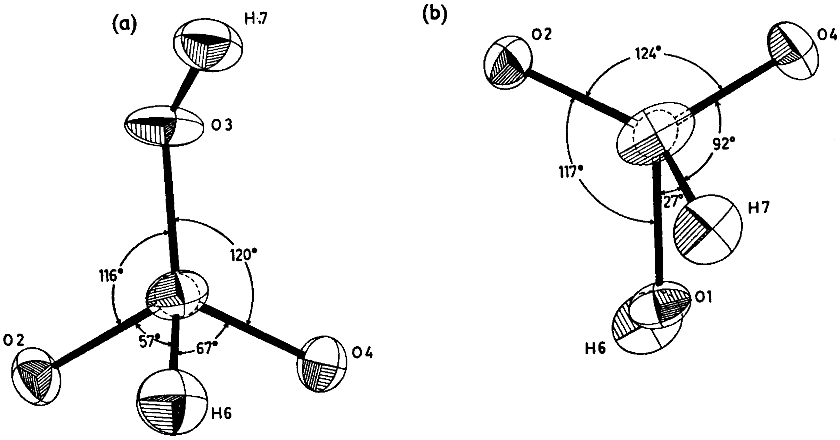

Fig. 6. (a) The conformation of the $H_2PO_4^-$ ion viewed down the O(1) – P bond. (b) The conformation of the $H_2PO_4^-$ ion viewed down the O(3) – P bond.

Hydrogen bonding. The environment of a dihydrogen phosphate ion is illustrated in Fig. 4. Table 5 A gives bond lengths and angles for those hydrogen bonds where the oxygen atoms of the phosphate group act as acceptor atoms. It is clear from Fig. 4 that the oxygen atoms, which have covalently attached hydrogen atoms, are much weaker acceptors of hydrogen bonds than the other two oxygen atoms.

The two approximately linear O – H···O bonds have O···O distances of 2.517(7) and 2.561(7) Å. The difference in strength between these two bonds is evident on comparing the corresponding H···O distances of 1.446(10) and 1.542(10) Å. The covalent O – H bond distances are 1.072(10) and 1.023(10) Å, the longer O – H bond being associated with the shorter H···O contact.

All short intermolecular distances are listed in Table 6. An examination of this table reveals three short N···O contacts (3.082, 3.033, and 3.136 Å)

Table 6. Short intermolecular distances. All intermolecular distances involving hydrogen atoms ≤ 2.9 Å, and not involving hydrogen atoms ≤ 3.4 Å, are listed. Atoms not in the asymmetric unit are accompanied by a subscript. The four-digit subscript indicates how the atomic parameters can be derived from the corresponding atom in the asymmetric unit. The first three digits code a lattice translation, *e.g.* 564 means a translation of $(5-5)a+(6-5)b+(4-5)c$ or (b − c). The fourth digit specifies one of the following operations:

1: x,y,z
2: $1/2-x,\ -y,\ 1/2+z$
3: $1/2+x,\ 1/2-y,\ -z$
4: $-x,\ 1/2+y,\ 1/2-z$

$\mathrm{P\cdots H(7)_{5554}}$	2.470 (9)	$\mathrm{O(3)\cdots H(3)_{5551}}$	2.690 (12)
$\mathrm{P\cdots H(6)_{5553}}$	2.551 (10)	$\mathrm{O(3)\cdots H(4)_{6454}}$	2.854 (11)
$\mathrm{P\cdots H(4)_{6454}}$	2.765 (10)	$\mathrm{O(3)\cdots H(1)_{4551}}$	2.881 (15)
$\mathrm{P\cdots H(3)_{5551}}$	2.782 (11)	$\mathrm{O(3)\cdots N(1)_{5551}}$	3.078 (6)^a
$\mathrm{O(1)\cdots H(1)_{4551}}$	2.122 (13)^a	$\mathrm{O(3)\cdots N(2)_{5551}}$	3.136 (6)
$\mathrm{O(1)\cdots O(4)_{4553}}$	2.561 (7)^a	$\mathrm{O(3)\cdots O(4)_{5552}}$	3.298 (6)
$\mathrm{O(1)\cdots H(7)_{5554}}$	2.625 (10)	$\mathrm{O(4)\cdots H(6)_{5553}}$	1.542 (10)^a
$\mathrm{O(1)\cdots H(3)_{5454}}$	2.718 (12)	$\mathrm{O(4)\cdots H(4)_{6454}}$	1.769 (10)^a
$\mathrm{O(1)\cdots N(2)_{5454}}$	3.082 (6)	$\mathrm{O(4)\cdots H(2)_{5542}}$	2.335 (13)^a
$\mathrm{O(1)\cdots N(1)_{4551}}$	3.123 (6)^a	$\mathrm{O(4)\cdots N(2)_{6454}}$	2.812 (5)^a
$\mathrm{O(1)\cdots O(3)_{5554}}$	3.205 (8)	$\mathrm{O(4)\cdots N(1)_{5542}}$	3.252 (6)^a
$\mathrm{O(1)\cdots O(2)_{5454}}$	3.209 (7)	$\mathrm{N(1)\cdots H(5)_{5563}}$	1.863 (9)^a
$\mathrm{O(2)\cdots H(7)_{5554}}$	1.446 (10)^a	$\mathrm{N(1)\cdots N(2)_{5563}}$	2.907 (4)^a
$\mathrm{O(2)\cdots H(3)_{5551}}$	1.845 (10)^a	$\mathrm{N(2)\cdots H(5)_{5563}}$	2.880 (10)
$\mathrm{O(2)\cdots O(3)_{5554}}$	2.517 (7)^a	$\mathrm{H(1)\cdots H(5)_{5563}}$	2.390 (14)
$\mathrm{O(2)\cdots H(1)_{6554}}$	2.693 (13)	$\mathrm{H(1)\cdots H(7)_{6551}}$	2.542 (15)
$\mathrm{O(2)\cdots H(2)_{6554}}$	2.832 (13)	$\mathrm{H(1)\cdots H(6)_{6551}}$	2.800 (14)
$\mathrm{O(2)\cdots H(6)_{5553}}$	2.833 (10)	$\mathrm{H(1)\cdots H(3)_{6454}}$	2.897 (15)
$\mathrm{O(2)\cdots N(2)_{5551}}$	2.865 (6)^a	$\mathrm{H(2)\cdots H(5)_{5563}}$	2.359 (15)
$\mathrm{O(2)\cdots N(1)_{6554}}$	3.033 (5)	$\mathrm{H(3)\cdots H(7)_{5554}}$	2.577 (13)
$\mathrm{O(3)\cdots H(2)_{5551}}$	2.429 (14)^a	$\mathrm{H(4)\cdots H(6)_{5652}}$	2.810 (12)
		$\mathrm{H(6)\cdots H(7)_{5554}}$	2.602 (12)

[a] Distances corresponding to hydrogen bonds.

which do not represent hydrogen bonds. On the other hand, one of the N − H···O bonds has an N···O separation as long as 3.252 Å. It is thus clear that deductions made only on the basis of short N···O contacts can be misleading; an accurate determination of the hydrogen positions is often essential in revealing the true hydrogen bonding scheme.

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REFERENCES

1. Liminga, R. *Acta Chem. Scand.* **19** (1965) 1629.
2. Liminga, R. *Acta Chem. Scand.* **20** (1966) 2483.
3. Coppens, P. and Hamilton, W. C. *Acta Cryst.* **A 26** (1970) 71.

4. Zachariasen, W. H. *Acta Cryst.* **23** (1967) 558.
5. Coppens, P., Leiserowitz, L. and Rabinovich, D. *Acta Cryst.* **18** (1965) 1035.
6. Busing, W. R., Martin, K. O. and Levy H. A. *ORNL-TM-305*, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1962.
7. Busing, W. R., Martin, K. O. and Levy, H. A. *ORNL-TM-306*, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1964.
8. Johnson, C. K. *ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1965.
9. Coppens, P. *Acta Cryst.* **A 25** (1969) 180.
10. Hamilton, W. C. *Acta Cryst.* **A 25** (1969) 194.
11. Liminga, R. *Arkiv Kemi* **28** (1968) 483.
12. Liminga, R. and Lundgren, J.-O. *Acta Chem. Scand.* **19** (1965) 1612.
13. Nilsson, Å., Liminga, R. and Olovsson, I. *Acta Chem. Scand.* **22** (1968) 719.
14. Padmanabhan, V. M. and Balasubramanian, R. *Acta Cryst.* **22** (1967) 532.
15. Busing, W. R. and Levy, H. A. *Acta Cryst.* **17** (1964) 142.

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