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The Crystal Structure of Compounds with $(N-P)_n$ Rings.

III. $(NH)_4P_4O_8H_4.2H_2O$, Tetrametaphosphimic Acid Dihydrate.

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The crystal structure of $(NH)_4P_4O_8H_4.2H_2O$ has been determined by three-dimensional X-ray methods. The compound crystallizes in the orthorombic space group $P2_12_12$. The cell dimensions are $a=13·98$, $b=8·32$, $c=5·04$ Å. There are two formula units on special positions with symmetry 2 in the unit cell. Anisotropic least-squares refinement was carried out with 482 independent reflexions. R is 0·064. Hydrogen atoms could not be found in the three-dimensional difference map, but comparison of the bond lengths and angles with those in $Na_3(NHPO_2)_3.4H_2O$ and in the phosphonitrilic derivatives strongly indicates that the nitrogen atoms of the ring are linked to hydrogen atoms. The values observed for P–O are best explained by considering the compound as an acid salt $2(H_3O)^+[(NH)_4P_4O_8H_2]^{2-}$. Neighbouring anions are linked by short O · · · H · · · O bonds of 2·46 Å to two-dimensional sheets perpendicular to the c axis. The hydrogen atom of the O · · · H · · · O bond is either in the centre of the bond or statistically distributed between two possible positions. The sheets are connected to a three-dimensional network by N–H · · · O bonds of 2·79 and 2·81 Å. The anions have the tub configuration with approximate symmetry $\bar{4}$. The P–N bonds are equal within experimental error. The average value is 1·66 Å. There are two kinds of P–O bond. The oxygen atoms of two independent P–O bonds of 1·52 Å are involved in the short O · · · H · · · O bonds. The oxygen atoms of the two remaining P–O bonds of $1·48_5$ Å are not directly linked to hydrogen. The standard deviation in the individual bond lengths is 0·01 Å. Average values for the angles are P–N–P = 125·6, N–P–N = 107·3, O–P–O = 116·1°, s.d. 0·5°.

Introduction

As was mentioned in the introduction to the previous paper on $Na_3(NHPO_2)_3.4H_2O$ (Olthof, Migchelsen & Vos, 1965), a study of the structure of $(NH)_4P_4O_8H_4.2H_2O$ is interesting in connexion with the position of the hydrogen atoms. A preliminary X-ray study was carried out by Corbridge (1953). Infrared spectroscopic work by Steger & Lunkwitz (1961) suggests that the nitrogen atoms in the $(N-P)_4$ ring are linked to hydrogen atoms.

Experimental

Tetrametaphosphimic acid dihydrate was prepared by hydrolysis of $(NPCl_2)_4$ (Stokes, 1896) and recrystallized from water. Although many attempts were made to grow crystals of reasonable dimensions, only very thin long needles along the c axis were obtained. Finally crystals with diameters of about 0·04 mm were grown by very slow evaporation of water from saturated aqueous solutions. The crystals were not of good quality, however. Preliminary photographs were taken of a great number of crystals, but in all cases Weissenberg exposures with strongly extended spots in the φ-direction were obtained. This indicates that the crystals show distortion around the c axis. Because of this effect and the small cross-section of the available crystals, long exposure times were required. Therefore only little use was made of integrated Weissenberg photographs.

Most intensities were estimated visually from equi-inclination Weissenberg photographs about the c axis, taken with nickel-filtered Cu radiation. The intensities on the upper layer Weissenberg photographs were corrected for the variation in spot shape by taking the harmonic mean of the values estimated for extended and contracted reflexion spots (Phillips, 1956); reflexions with low values of ξ for which this method is not valid were measured on integrated Weissenberg photographs. Intensities from different l-levels were put on the same relative scale by recording side by side on one film small parts of integrated equi-inclin-

Table 1. *Crystallographic data*

Orthorombic, spacegroup $P2_12_12$

a = 13·98, s.d. 0·03 Å
b = 8·32, s.d. 0·02
c = 5·04, s.d. 0·01

Table 2. *Observed and calculated structure factors*

In order to obtain F on the absolute scale, the values in the Table must be divided by 10

h	k	l	F_o	F_c	A_c	B_c
0	2	0	592	623	-623	0
0	4	0	430	412	412	0
0	6	0	142	149	-149	0
0	10	0	147	166	166	0
1	1	0	577	571	571	0
1	2	0	430	427	-427	0
1	3	0	258	283	-283	0
1	6	0	238	251	251	0
1	9	0	207	193	193	0
2	0	0	400	415	415	0
2	2	0	592	560	-560	0
2	3	0	718	736	-736	0
2	4	0	121	116	116	0
2	7	0	304	311	311	0
2	9	0	202	207	-207	0
2	10	0	152	155	155	0
3	1	0	212	226	-226	0
3	2	0	187	185	-185	0
3	3	0	218	176	-176	0
3	4	0	86	64	-64	0
3	5	0	379	397	397	0
3	6	0	390	414	414	0
3	7	0	111	86	-86	0
3	9	0	137	140	-140	0
4	0	0	1007	987	-987	0
4	1	0	830	788	788	0
4	2	0	556	503	-503	0
4	3	0	298	283	-283	0
4	4	0	223	202	202	0
4	5	0	455	494	494	0
4	8	0	132	110	-110	0
5	1	0	319	319	-319	0
5	2	0	470	460	460	0
5	4	0	202	197	-197	0
5	8	0	212	208	-208	0
5	9	0	228	230	-230	0
6	0	0	501	472	472	0
6	1	0	293	285	285	0
6	3	0	197	198	198	0
6	7	0	253	257	-257	0
6	10	0	96	123	-123	0
7	1	0	106	87	87	0
7	3	0	162	141	141	0
7	5	0	435	471	-471	0
7	6	0	298	327	-327	0
7	7	0	268	276	276	0
8	0	0	157	130	130	0
8	2	0	410	412	412	0
8	3	0	218	228	-228	0
8	4	0	420	451	-451	0
8	5	0	162	175	-175	0
8	6	0	127	124	124	0
8	7	0	111	117	-117	0
8	8	0	132	132	132	0
9	1	0	207	208	208	0
9	2	0	430	462	-462	0
9	4	0	324	346	346	0
9	5	0	157	166	-166	0
9	7	0	212	207	207	0
9	8	0	233	224	224	0
10	0	0	243	278	-278	0
10	1	0	243	253	-253	0
10	5	0	233	250	250	0
10	7	0	121	110	110	0
10	8	0	96	102	102	0
11	2	0	268	283	-283	0
11	4	0	278	288	288	0
11	5	0	258	263	263	0
11	8	0	207	253	253	0
12	1	0	349	349	-349	0
12	3	0	319	325	325	0
12	4	0	258	256	256	0
13	1	0	157	144	-144	0
13	4	0	127	120	120	0
13	5	0	212	224	224	0
13	6	0	253	271	-271	0
13	7	0	172	222	-222	0
14	0	0	162	150	150	0
14	2	0	157	148	-148	0
14	5	0	142	151	-151	0
15	3	0	238	233	-233	0
16	0	0	253	270	270	0
16	1	0	121	137	137	0
16	2	0	142	136	-136	0
16	3	0	86	105	-105	0
16	4	0	76	94	-94	0
17	1	0	182	203	203	0
17	2	0	71	71	-71	0
17	3	0	96	123	-123	0
0	1	1	263	328	0	328
0	2	1	860	898	-898	0
0	3	1	212	181	0	-181
0	5	1	218	203	0	-203
0	10	1	187	208	208	0
1	1	1	486	542	495	-221
1	2	1	298	314	-267	164
1	3	1	354	353	-241	-258
1	4	1	364	372	2	-372
1	5	1	202	194	187	-52
1	6	1	197	202	193	58
1	7	1	172	175	-168	48
1	9	1	248	247	247	-22
2	0	1	233	267	267	0
2	1	1	172	169	167	-26
2	2	1	541	555	102	-545
2	3	1	258	214	-50	-208
2	4	1	91	82	6	-82
2	5	1	268	284	263	106
2	6	1	91	90	73	-53
2	7	1	445	439	439	-16
2	8	1	142	142	-136	41
2	9	1	131	141	-140	9
2	10	1	127	131	96	-88
3	0	1	364	401	0	-401
3	1	1	511	497	-192	-459
3	2	1	111	108	-93	54
3	3	1	288	278	-277	12
3	4	1	228	216	-201	80
3	5	1	298	305	297	-66
3	6	1	435	404	383	130
3	7	1	212	198	-190	54
3	8	1	137	136	-126	-51
4	0	1	465	464	-464	0
4	1	1	334	347	338	-79
4	2	1	228	229	225	39
4	3	1	445	461	-453	-80
4	4	1	218	223	185	121
4	5	1	379	389	104	374
4	7	1	177	169	-123	-116
4	8	1	162	149	-146	28
4	10	1	91	94	-93	-15
5	1	1	425	408	-304	-271
5	2	1	455	448	440	81
5	3	1	496	475	51	472
5	4	1	324	312	-278	143
5	6	1	187	173	135	108
5	8	1	238	246	-189	-156
5	9	1	167	166	-136	95
6	0	1	298	309	-309	0
6	1	1	263	242	-13	242
6	2	1	339	333	-202	265
6	3	1	197	184	181	-33
6	4	1	142	157	-127	94
6	5	1	248	243	-206	128
6	7	1	263	250	-215	-128
6	8	1	101	93	89	-27
7	0	1	476	460	0	460
7	1	1	167	152	121	-92
7	2	1	238	223	161	-156
7	3	1	288	291	224	187
7	5	1	425	370	-360	-84
7	6	1	167	146	-146	-10
7	7	1	273	273	261	-82
7	8	1	127	106	-97	-43
7	9	1	86	80	-22	77
8	1	1	121	123	-73	99
8	2	1	379	383	376	-75
8	3	1	349	325	216	-243
8	4	1	415	414	-411	-53
8	7	1	96	85	81	-26
8	8	1	101	104	87	-56
8	9	1	127	131	17	130
9	0	1	142	130	0	130
9	1	1	238	232	177	-150
9	2	1	430	423	-355	-230
9	4	1	197	193	171	-91
9	5	1	248	223	-223	5
9	7	1	192	179	153	93
9	8	1	121	127	111	62
10	0	1	86	90	90	0
10	1	1	359	363	-354	-82
10	2	1	233	236	197	-129
10	3	1	157	152	-68	-136
10	6	1	202	203	-55	195
10	8	1	76	72	39	-61
11	1	1	172	166	-127	-107
11	2	1	253	230	-229	-15
11	4	1	212	194	160	110
11	5	1	197	185	169	73
12	0	1	167	169	-169	0
12	1	1	430	401	-399	-37
12	2	1	263	259	-256	41
12	3	1	298	298	243	172
12	4	1	243	229	221	-62
12	5	1	147	135	-118	66
13	1	1	111	115	-113	15
13	2	1	132	125	120	31
13	4	1	197	190	134	135
13	5	1	177	179	173	-46
13	6	1	157	162	-161	15
14	0	1	172	167	167	0
14	1	1	116	106	106	0
14	2	1	238	238	-223	81
14	3	1	233	231	195	124
14	5	1	86	90	-27	-86
14	6	1	111	127	28	-124
15	1	1	147	142	141	14
15	3	1	172	173	-138	104
15	4	1	91	80	7	-80
16	0	1	395	415	415	0
16	1	1	132	128	127	18
16	2	1	91	87	-79	-35
16	3	1	116	139	-128	-55
16	4	1	101	126	16	124
17	1	1	137	152	112	-102
17	2	1	71	83	-84	1
0	0	2	809	654	654	0
0	2	2	187	177	-177	0
0	3	2	187	189	0	-189
0	4	2	157	160	160	0
0	5	2	506	517	0	-517
0	7	2	369	317	0	317
1	2	2	192	177	13	-176
1	3	2	268	260	-188	-179
1	4	2	309	307	63	-300
1	5	2	162	160	110	116
1	6	2	182	165	164	4
1	7	2	233	193	-155	113
1	8	2	127	115	-20	113
1	9	2	192	195	190	-40
2	0	2	238	214	-214	0
2	2	2	476	505	82	-498
2	3	2	152	154	-147	47
2	4	2	283	282	-72	273
2	5	2	137	125	-92	-84
2	7	2	172	151	125	83
2	8	2	172	181	-41	177
2	9	2	192	189	-149	-117
2	10	2	157	193	64	-182
3	1	2	384	403	161	-370
3	2	2	96	91	84	35
3	3	2	127	115	33	-110
3	4	2	349	358	-165	318
3	5	2	172	150	150	-7
3	6	2	278	260	258	-26
3	7	2	137	120	-101	64
3	8	2	177	169	-130	-107
4	0	2	460	484	-484	0
4	1	2	344	330	318	85
4	2	2	268	257	109	-232
4	3	2	263	256	-192	169
4	4	2	86	81	-25	78
4	5	2	420	427	170	392
4	6	2	304	270	-28	-268
4	7	2	142	138	-14	-138
4	8	2	127	119	15	118
4	9	2	192	191	-8	-191
5	1	2	207	194	-96	-169
5	2	2	253	229	183	-138
5	3	2	283	286	105	265
5	4	2	440	465	-347	310
5	5	2	167	132	-50	-121
5	6	2	177	151	102	110
5	7	2	243	223	50	-216
5	8	2	258	237	-169	-166
5	9	2	172	164	-46	158
6	2	2	293	298	162	250
6	3	2	192	206	137	-153
6	4	2	192	186	-6	186
6	5	2	182	166	-52	157
6	6	2	324	294	-16	-293
6	8	2	106	86	71	48
6	9	2	106	97	-25	93
7	0	2	516	536	0	536
7	1	2	304	301	-156	258
7	2	2	374	384	121	-364
7	3	2	248	235	130	196
7	5	2	329	287	-272	91
7	7	2	233	217	178	-124
7	9	2	101	105	-20	103
8	0	2	202	187	-187	0
8	1	2	248	231	-105	205
8	2	2	304	281	281	17
8	3	2	344	342	59	-337
8	4	2	329	311	-229	209
8	5	2	177	153	-126	-86
9	0	2	379	366	0	366
9	1	2	91	81	62	51
9	2	2	152	158	-83	-134
9	3	2	319	289	118	-264
9	4	2	187	177	126	-125
9	5	2	212	195	-152	122
9	7	2	177	171	112	130
10	0	2	127	117	-117	0
10	1	2	177	174	-149	90
10	2	2	329	302	-14	-301
10	3	2	157	128	42	-121
10	4	2	187	161	4	-161
10	5	2	121	117	-3	116
10	6	2	187	191	-68	178
10	7	2	111	115	30	-111
10	8	2	71	73	65	-34
11	0	2	344	306	0	-306
11	2	2	147	117	-105	51
11	3	2	374	338	21	-337
11	6	2	121	117	-94	69
12	1	2	349	314	-234	-209
12	2	2	127	105	-103	21
12	3	2	273	255	206	150
12	4	2	207	200	135	-148
12	5	2	182	185	-78	167
13	0	2	253	235	0	-235
13	1	2	192	185	-72	171
13	4	2	111	106	19	103
13	6	2	106	122	-79	93
14	0	2	197	190	130	0
14	2	2	253	251	-106	227
14	3	2	162	138	26	136
14	4	2	157	148	49	140
14	5	2	96	120	-45	-111
15	2	2	202	197	62	187
15	3	2	177	185	-64	174
15	4	2	167	189	2	-189
16	0	2	182	193	193	0
16	1	2	182	197	130	148
16	2	2	167	164	-142	-83
16	3	2	91	109	-96	-53
0	2	3	288	330	-330	0
0	3	3	137	123	0	123
0	4	3	233	234	234	0
0	5	3	415	518	0	-518
0	6	3	142	141	-141	0
0	7	3	278	263	0	263
1	1	3	111	129	-46	-121
1	2	3	116	127	-21	126
1	3	3	228	250	136	-210
1	4	3	314	349	-129	-324
1	6	3	132	124	-122	-16
1	7	3	116	106	-61	86
1	8	3	147	144	-92	111
2	1	3	162	179	152	-94
2	2	3	496	543	-36	-542
2	4	3	106	111	52	98
2	5	3	172	169	-106	-132
2	7	3	142	129	-32	125
2	8	3	137	142	25	139
2	9	3	76	86	-50	-70
3	0	3	223	256	0	-256
3	1	3	354	391	-124	-371
3	2	3	116	104	96	38
3	4	3	243	257	-104	235
3	5	3	142	136	-131	-35
3	7	3	152	146	118	85
3	8	3	101	104	-104	-9
4	1	3	334	363	328	-157
4	2	3	111	126	104	-70
4	3	3	218	231	-218	74
4	4	3	207	217	-13	217
4	5	3	304	324	128	298
4	6	3	182	188	-68	-175
4	8	3	197	208	130	164
4	9	3	106	113	-32	-108
5	1	3	192	197	105	-167
5	2	3	91	91	85	-34
5	3	3	354	391	122	372
5	4	3	228	245	23	244
5	5	3	182	189	-160	-99
5	6	3	212	197	189	55
5	7	3	111	176	93	-149
5	8	3	167	166	50	-158
6	1	3	152	140	44	132
6	2	3	253	266	67	258
6	3	3	152	151	-147	-34
6	4	3	157	159	7	158
6	5	3	157	157	76	137
6	6	3	238	240	-80	-226
6	7	3	182	187	109	-152
6	8	3	106	96	69	67
7	0	3	460	509	0	509
7	1	3	177	172	-13	173
7	2	3	273	300	-100	-283
7	3	3	223	241	223	93
7	7	3	101	117	44	-109
8	0	3	349	381	-381	0
8	1	3	187	177	70	162
8	2	3	132	124	115	-47
8	3	3	288	286	-47	-282
8	7	3	91	94	45	-82
9	0	3	228	240	0	240
9	1	3	233	237	-223	78
9	2	3	197	193	10	-193
9	3	3	228	234	26	-233
9	6	3	162	150	-129	-77
9	7	3	167	179	61	168
10	1	3	162	147	144	-33
10	2	3	162	146	13	-145
10	3	3	177	152	44	-146
10	4	3	167	152	2	-155
10	5	3	101	99	-12	99
10	6	3	238	270	-28	269
10	7	3	101	108	-81	-72
11	0	3	268	244	0	-244
11	2	3	142	137	99	101
11	3	3	268	255	-61	-248
11	4	3	157	144	102	102
11	5	3	121	117	-34	111
12	0	3	157	140	140	0
12	1	3	127	114	-47	-104
12	2	3	137	118	47	108
12	3	3	197	211	36	207
12	4	3	172	169	-53	-160
12	5	3	116	115	-67	93
12	6	3	111	137	-42	130
13	0	3	187	192	0	-192
13	1	3	228	238	162	174
13	2	3	137	137	-59	123
13	4	3	81	92	-44	81
14	2	3	162	174	20	173
14	3	3	182	198	-116	161
15	1	3	71	69	-45	52
15	2	3	121	129	-35	125
0	3	4	142	144	0	144
0	4	4	197	194	194	0
0	5	4	354	351	0	-351
0	7	4	212	193	0	193
1	0	4	212	234	0	-234
1	1	4	248	277	-260	-94
1	2	4	379	395	213	332
1	4	4	258	263	71	-253
1	8	4	101	104	-49	92
2	0	4	81	78	-78	0
2	1	4	96	115	105	-46
2	2	4	258	264	73	-254
2	3	4	233	242	212	116
2	4	4	167	157	-50	168
2	5	4	207	190	-152	-114
2	7	4	207	178	-155	89
2	8	4	116	123	-9	122
3	0	4	354	328	0	-328
3	1	4	395	415	259	-325
3	2	4	172	184	161	89
3	3	4	147	135	53	125
3	5	4	197	177	-154	-88
3	6	4	142	121	-114	-43
3	8	4	96	96	-78	55
4	0	4	263	270	270	0
4	2	4	132	125	112	-56
4	3	4	121	111	-104	37
4	4	4	207	208	-171	119
4	5	4	197	158	10	158
4	6	4	172	153	-51	-144
4	8	4	121	163	117	113
5	1	4	263	268	140	-229
5	2	4	197	196	-195	-8
5	3	4	309	325	-31	323
5	4	4	162	131	-100	85
5	5	4	167	144	-108	-95
5	7	4	96	86	76	-42
6	1	4	142	136	-134	25
6	2	4	152	136	13	135
6	3	4	142	149	-124	-82
6	5	4	182	140	99	99
6	7	4	243	246	200	-142
7	0	4	349	371	0	371
7	1	4	207	210	-204	49
7	2	4	192	189	-75	-174
7	5	4	132	98	82	-55
7	6	4	207	186	183	-32
8	0	4	309	311	-311	0
8	3	4	197	159	47	-152
8	4	4	162	121	91	-80
8	6	4	116	106	54	89
9	0	4	197	188	0	188
9	1	4	132	115	-92	68
9	2	4	263	231	171	-156
9	3	4	172	168	91	-142
9	6	4	81	73	-42	-61
10	1	4	172	154	153	14
10	4	4	212	191	3	-190
10	5	4	121	130	-110	69
11	0	4	172	165	0	-165
11	1	4	182	158	93	128
11	3	4	167	152	-58	-140
11	4	4	101	87	-73	47
11	5	4	101	112	-84	74
12	0	4	182	176	176	0
12	2	4	152	139	19	137
12	3	4	147	141	-1	141
12	4	4	192	218	-118	-184
13	1	4	167	175	84	154
13	2	4	111	116	-78	86
14	1	4	66	77	-57	-51

ation Weissenberg photographs of different layer lines. Allowance was made for the difference in path length of the X-rays through the film caused by the variation in the equi-inclination angle, while further experimental conditions were kept constant. The intensities of 482 reflexions were obtained in this way. No correction for absorption was applied as the errors due to absorption are small ($\mu = 65$ cm^{-1}).

The crystallographic data are listed in Table 1. The constants *a* and *b* were determined from back-reflexion photographs (λ(Cu $K\alpha_1$) = 1·54050 Å, λ(Cu $K\alpha_2$) = 1·54434 Å). The values obtained are not very accurate, however, as only reflexions with $\theta < 80°$ could be measured; *c* was obtained by measuring θ (00l) with Mo $K\alpha$ radiation (λ(Mo $K\alpha_1$) = 0·70926 Å) on a diffractometer. The observed density, 1·95 g.cm^{-3} (Corbridge, 1953), agrees with the calculated value, 2·00 g.cm^{-3}, for two formula units $(NH)_4P_4O_8H_4 . 2H_2O$ per cell.

Determination of the coordinates

The cell contains two $(NH)_4P_4O_8H_4$ units which are on special positions with symmetry 2 and one independent water molecule. The *x* and *y* coordinates of the two independent phosphorus atoms could be obtained from a Patterson synthesis of the centrosymmetric [001] projection. Nitrogen and oxygen atoms of the group $N_4P_4O_8$ were placed so that the shape of the 'molecule' in [001] projection was analogous to that in $(NPCl_2)_4$ (Hazekamp, Migchelsen & Vos, 1962). The position of the oxygen atom of the water molecule was clearly shown by a [001] electron density map of the observed reflexions. After isotropic refinement of the [001] projection, *z* coordinates of all atoms except hydrogen were obtained from a three-dimensional Patterson synthesis.

The coordinates and the temperature factors of the phosphorus, nitrogen and oxygen atoms were refined by anisotropic least-squares analysis (Rollett, 1961). The calculations were kindly carried out by Dr J. S. Rollett on the Mercury computer at Oxford. The weighting system was $w = [1 + (|F_o| - 20)^2/22·5^2)]^{-1}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). *R* decreased to 0·064 for the observed reflexions listed in Table 2. The final coordinates and thermal parameters are listed in Tables 3 and 4 respectively. For the reasons already mentioned in the discussion of the thermal motion of the trimeric salt (Olthof, Migchelsen & Vos, 1965), attempts to interpret the motion of the atoms of the group $N_4P_4O_8$ in terms of rigid body vibrations were not successful. No corrections for angular oscillations were therefore applied to the atomic coordinates.

Apart from the statistical errors given in Table 3, systematic errors of about the same magnitude as in $Na_3(NHPO_2)_3 . 4H_2O$ may occur in the atomic coordinates.

Description of the structure

The metaphosphimate group

The arrangement of the atoms in [010] and [001] projection is shown in Fig. 1. Fig. 2 and Table 5 give the intra- and intermolecular distances smaller than 3 Å and the values of the valence angles. The e.s.d. in the bond lengths and angles are 0·01 Å and 0·5° respectively. The group $(NH)_4P_4O_8$, shown in Fig. 3 has the tub configuration. Within experimental error the atoms are related by a fourfold inversion axis although only a twofold axis is required by crystallographic symmetry. The P–N bond lengths are equal within experimental error.

Table 3. *Final coordinates and standard deviations as calculated from the least-squares residuals*

	x	s.d.	y	s.d.	z	s.d.
P(1)	0·1251	0·0002	0·1166	0·0004	0·1044	0·0007
P(2)	0·0694	0·0002	−0·2109	0·0004	−0·0616	0·0007
N(1)	0·0164	0·0006	0·1896	0·0012	0·1611	0·0022
N(2)	0·1141	0·0006	−0·0294	0·0012	−0·1200	0·0022
O(1)	0·1838	0·0005	0·2470	0·0010	−0·0306	0·0021
O(2)	0·1618	0·0005	0·0556	0·0011	0·3618	0·0021
O(3)	0·1446	0·0005	−0·3123	0·0010	0·0747	0·0021
O(4)	0·0320	0·0006	−0·2765	0·0011	−0·3156	0·0021
$(H_2O)_I$	0·3478	0·0007	−0·0401	0·0013	0·4783	0·0027

Table 4. *Thermal parameters* (*in* Å$^2 \times 10^4$)

Standard deviations calculated by the least-squares program are given in brackets

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
P(1)	65(7)	167(8)	74(12)	−51(25)	−13(5)	−3(4)
P(2)	98(7)	119(8)	107(12)	−48(27)	−6(5)	−7(4)
N(1)	165(34)	159(32)	203(48)	−324(85)	−30(16)	−8(17)
N(2)	102(27)	250(34)	203(45)	−94(90)	−28(18)	−24(17)
O(1)	159(21)	191(29)	256(43)	−136(70)	22(15)	0(12)
O(2)	94(21)	324(32)	290(46)	−81(82)	38(15)	34(15)
O(3)	140(21)	184(27)	453(38)	457(82)	−26(16)	−16(14)
O(4)	223(27)	185(32)	378(45)	−153(88)	−29(16)	−23(17)
$(H_2O)_I$	354(34)	343(39)	509(64)	−72(101)	28(23)	−10(21)

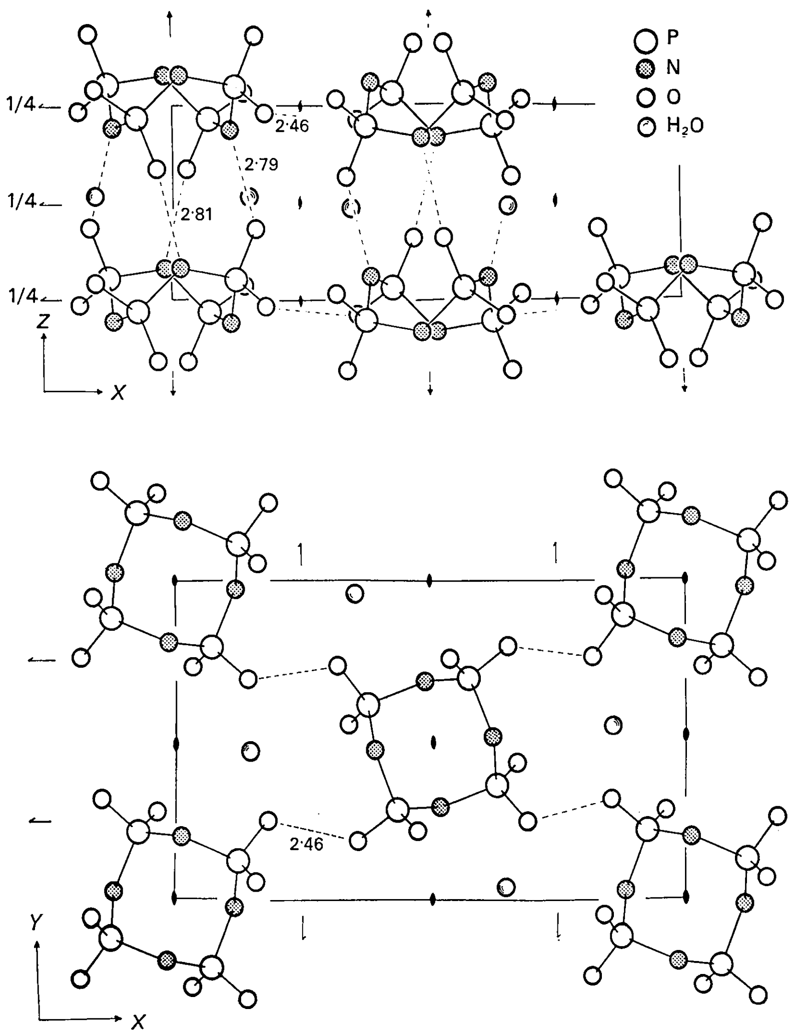


Fig. 1. The arrangement of the P, N and O atoms, in [010] projection (above) and in [001]-projection (below).

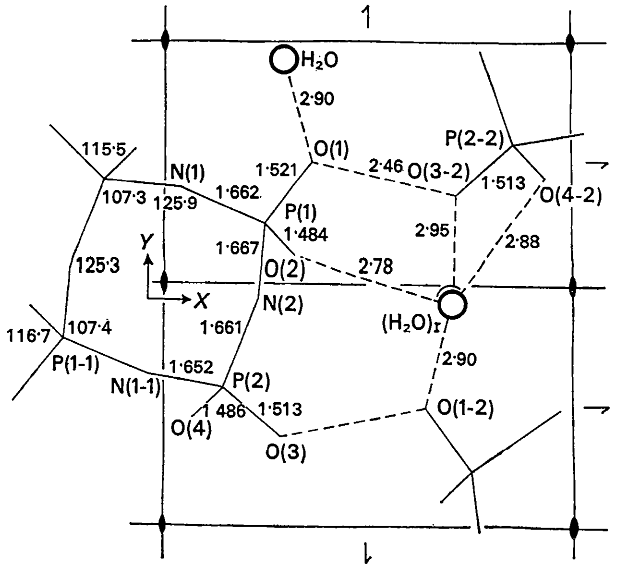


Fig. 2. [001] projection with bond lengths and angles.

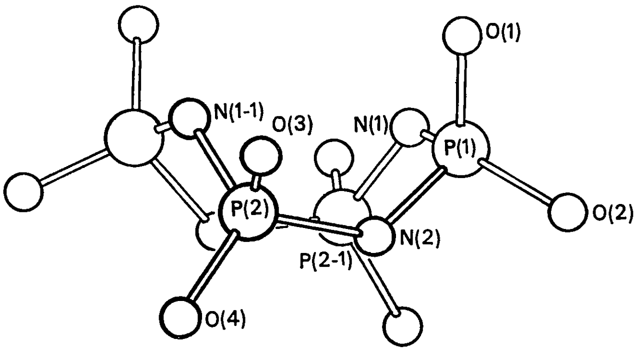


Fig. 3. The nitrogen, phosphorus and oxygen atoms of the tetrametaphosphimate group.

A measure of the shape of the ring in the tetrameric phosphonitrilic molecules with symmetry $\bar{4}$ is provided by the distance of the phosphorus atoms from the plane through the inversion centre of the axis and perpendicular to this axis (Bullen, 1962). For the tetrameric phosphonitrilic compounds this distance varies from 0·18 Å, in $[NP(NMe_2)_2]_4$, to 0·35 Å in $(NPCl_2)_4$ – *K* form. In the present structure the corresponding distance is 0·42 Å. It may thus be concluded that the (N–P)$_4$ ring in the investigated acid dihydrate is more puckered than in the tetrameric phosphonitrilic compounds. As in the tetrameric phosphonitrilics, the nitrogen atoms are further apart from the plane mentioned above than the phosphorus atoms. The distance observed is 0·71 Å.

Location of the hydrogen atoms

The positions of the six independent hydrogen atoms could not be found from the final asymmetric three-dimensional difference map. It has, however, been possible to obtain rather strong indirect evidence for their location:

(1) Two hydrogen atoms belong to the water molecule. As will be shown below it is very likely that an additional proton is linked to the water molecule to give an H_3O^+ ion. Fig. 2 and Table 5 show that there are four $H_2O \cdots O$ distances smaller than 3 Å; no $H_2O \cdots N$ distances smaller than 3 Å were observed. Except for $O(1{-}2) \cdots (H_2O)_I \cdots O(3{-}2)(z+1) = 173°$ all angles $O \cdots (H_2O) \cdots O$ are between 73° and 109°. It is not certain to which extent each of the short $H_2O \cdots O$ distances coincides with a hydrogen bond.

(2) Comparison of the observed P–N bond lengths and the observed valence angles with those in phosphonitrilic derivatives and in sodium trimetaphosphimate (Table 6) strongly suggests that the compound is in the metaphosphimate form. This is in agreement with

Table 5. *Distances* (*smaller than* 3 Å) *and angles*

Distance	Value	Distance	Value
P(1)–N(1)	1·662 Å	P(1) ··· P(2)	2·955 Å
P(1)–N(2)	1·667	P(1) ··· P(2 – 1)	2·950
P(2)–N(2)	1·661	N(1) ··· O(1)	2·576
P(2)–N(1 – 1)*	1·652	N(1) ··· O(2)	2·529
P(1)–O(1)	1·521	N(2) ··· O(1)	2·538
P(1)–O(2)	1·484	N(2) ··· O(2)	2·615
P(2)–O(3)	1·513	O(1) ··· O(2)	2·558
P(2)–O(4)	1·486	N(1) ··· N(2)	2·682
		N(2) ··· O(3)	2·585
Angle	Value	N(2) ··· O(4)	2·553
N(1)–P(1)–N(2)	107·4°	N(1 – 1) ··· O(3)	2·509
N(2)–P(2)–N(1 – 1)	107·3	N(1 – 1) ··· O(4)	2·598
P(2 – 1)–N(1)–P(1)	125·9	O(3) ··· O(4)	2·536
P(1)–N(2)–P(2)	125·3	N(2) ··· N(1 – 1)	2·667
O(1)–P(1)–O(2)	116·7	N(2) ··· O(2)(*z* – 1)	2·787
O(3)–P(2)–O(4)	115·5	N(1 – 1) ··· O(4)(*z* + 1)	2·812
O(1)–P(1)–N(1)	108·0	O(1) ··· O(3 – 2)	2·460
O(1)–P(1)–N(2)	105·4	$(H_2O)_I$ ··· O(2)	2·782
O(2)–P(1)–N(1)	106·9	$(H_2O)_I$ ··· O(3 – 2)(*z* + 1)	2·946
O(2)–P(1)–N(2)	112·1	$(H_2O)_I$ ··· O(4 – 2)	2·882
O(3)–P(2)–N(2)	109·0	$(H_2O)_I$ ··· O(1 – 2)	2·902
O(3)–P(2)–N(1 – 1)	104·8		
O(4)–P(2)–N(2)	108·3		
O(4)–P(2)–N(1 – 1)	111·7		

* Atoms with an additional index 1 are related to those in Table 3 by the twofold axis [00*z*], those with the additional index 2 by the twofold screw axis [¼, *y*, 0].

Table 6. *Comparison of bond lengths and angles in the anions* $(NHPO_2)_3^{3-}$ *and* $[(NH)_4P_4O_8H_2]^{2-}$ *with those in phosphonitrilic derivatives*

Compound	P–N(Å)	P–O(Å)	Angle at P		Angle at N
			exo*	endo	
$(NHPO_2)_3{}^{3-}$	$1{\cdot}68_3$	$1{\cdot}49_5$	118·4°	104·5°	122·7°
$[(NH)_4P_4O_8H_2]^{2-}$	$1{\cdot}66_1$	$1{\cdot}51_7$ $1{\cdot}48_5$	116·1	107·3	125·6
$(NPCl_2)_3$	1·59		102	120	119
$(NPF_2)_3$	1·56		99	119	120
$(NPCl_2)_4$	1·57		103	121	131
$(NPMe_2)_4$	1·60		104	120	132
$[NP(NMe_2)_2]_4$	1·58		104	120	133
$(NPF_2)_4$	1·51		100	123	147

* Angle between the two exocyclic bonds

References: $(NPCl_2)_3$: Wilson & Carroll (1960); $(NPF_2)_3$: Dougill (1963); $(NPMe_2)_4$: Dougill (1961); $[NP(NMe_2)_2]_4$: Bullen (1962); $(NPF_2)_4$: McGeachin & Tromans (1961).

the infrared spectroscopic work mentioned in the introduction. Two independent hydrogen atoms are thus attached to the two independent nitrogen atoms. It is very likely that there are hydrogen bonds N(1–1) $\cdots$ O(4)($z+1$) = 2·81 Å and N(2)($z+1$) $\cdots$ O(2) = 2·79 Å between neighbouring molecules in the z direction (see Fig. 1). The angles P(1–1)–N(1–1) $\cdots$ O(4)($z+1$), P(2)–N(1–1) $\cdots$ O(4)($z+1$), P(1)($z+1$)–N(2)($z+1$) $\cdots$ O(2) and P(2)($z+1$)–N(2)($z+1$) $\cdots$ O(2) are between 116 and 119°, N(1–1) $\cdots$ O(4)($z+1$)–P(2)($z+1$) = 145° and N(2)($z+1$) $\cdots$ O(2)–P(1) = 143°. It is noteworthy that the atoms O(4)($z+1$) and O(2) lie in the planes P(1–1)–N(1–1)–P(2) and P(1)($z+1$)–N(2)($z+1$)–P(2)($z+1$) respectively.

(3) The fifth hydrogen atom, tentatively called H(5), will be situated between O(1) and O(3–2), thus forming a very short hydrogen bond O(1) $\cdots$ H(5) $\cdots$ O(3–2) of length 2·46 Å. The equal observed values P(1)–O(1) = $1{\cdot}52_1$ Å and P(2–2)–O(3–2) = $1{\cdot}51_3$ Å, e.s.d. 0·01 Å, indicate that the proton is either located in the centre of the bond or is statistically distributed between the potential minima near O(1) and O(3–2). The P–O length may be compared with the observed 'average' values for P–O, 1·538 Å, in the room temperature modification of KH_2PO_4 (Bacon & Pease, 1953) in which the hydrogen atoms are assumed to be disordered in hydrogen bonds of 2·49 Å. Symmetrical hydrogen bonds of about 2·50 Å have been observed in Type A acid salts (*e.g.* MHY_2, where M is a univalent metal and HY a monocarboxylic acid) (Shrivastava & Speakman, 1961; Calleri & Speakman, 1964).

(4) The remaining hydrogen atom may either combine with the water molecule to give an H_3O^+ ion, as has been suggested by Corbridge (1953), or may be linked to one of the oxygen atoms of the PO_2 groups. The latter possibility was preferred by Steger & Lunkwitz (1962) as a comparison of the infrared spectrum of the hydrated acid with that of the anhydrous compound did not indicate the presence of H_3O^+ ions. The observed P–O bond lengths are, however, best explained by the first possibility. Both P(1)–O(2) = $1{\cdot}48_4$ Å and P(2–2)–O(4–2) = $1{\cdot}48_6$ Å, e.s.d. 0·01 Å, are significantly smaller than the minimum observed value for P–O in P–O–H, 1·56 Å (Cruickshank, 1961). No hydrogen atom is thus attached to O(2) or O(4–2). The alternative possibility that O(1) and O(3–2) each have a hydrogen atom (with H(5) in a fixed position) is also not very probable, as this would make both P(1)–O(1) and P(2–2)–O(3–2) at least equal to the minimum value 1·56 Å. It is thus tentatively assumed that the elongation of 0·03 Å for P(1)–O(1) and P(2–2)–O(3–2) relative to P(1)–O(2) and P(2–2)–O(4–2) is due to the presence of H(5) only.

If the above assumption is correct $(NH)_4P_4O_8H_4 . 2H_2O$ has to be considered as an acid salt: $2(H_3O)^+ [(NH)_4P_4O_8H_2]^{2-}$. This would imply that bond lengths and angles in the anion are close to those in the anhydrous acid alkali salts $2M^+[(NH)_4P_4O_8H_2]^{2-}$ which Corbridge (1953) found to be isomorphous with the 'acid dihydrate'. An attempt will be made to obtain further indirect evidence for the positions of the hydrogen atoms in $(NH)_4P_4O_8H_4 . 2H_2O$ by determining the bond lengths and angles in one of the anhydrous acid alkali salts by X-ray diffraction. A direct determination of the positions of the hydrogen atoms in the 'acid dihydrate' by neutron diffraction cannot be carried out because of the small dimensions of the available crystals.

Intramolecular bond lengths and angles are discussed in a later section of this paper.

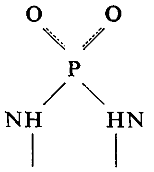
The three-dimensional network

Fig. 1 shows that the anions are connected to a three-dimensional network by hydrogen bonds. The short O $\cdots$ H $\cdots$ O bonds of 2·46 Å link the anions to firm two-dimensional sheets perpendicular to the c axis. Successive sheets are connected by N–H $\cdots$ O bonds of 2·80 Å. Except by these bonds the anions are held together by hydroxonium ions. Besides the usual electrostatic interaction there may be hydrogen bonding *via* ions. The contribution of the hydrogen atoms of H_3O^+ to the hydrogen bonding is, however, not a prerequisite for the formation of the crystal structure, as the H_3O^+ ions may be replaced by Rb^+ or K^+ ions.

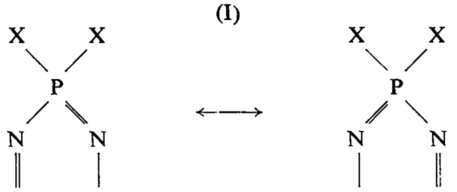
In view of the firm two-dimensional network perpendicular to the c axis it is remarkable that during our experiments only crystals could be obtained which are very thin perpendicular to **c** and very elongated along **c**.

Discussion of the bond lengths and angles

In Table 6 the bond lengths and angles in $Na_3(NHPO_2)_3 . 4H_2O$ described in a previous paper (Olthof, Migchelsen & Vos, 1965) and in $(NH)_4P_4O_8H_4 . 2H_2O$ are compared with those in the phosphonitrilic derivatives. The Table shows that there are striking differences between the two groups of 'molecules'. The endocyclic P–N bonds in the metaphosphimates are approximately 0·1 Å longer than those in the phosphonitrilics, which indicates that in the former compounds the double bond character of these bonds is relatively small. This is in agreement with formulae (I) and (II) for the metaphosphimates and the phosphonitrilics respectively.



(I)



(II)

The double bond character of the P–N bonds is also reflected by the values of the angles N–P–N. In agreement with the rule that a single bond repels other bonds less than a double bond (Gillespie & Nyholm, 1957), in the metaphosphimates the angle N–P–N is smaller than in the phosphonitrilics. As may be expected from the structural formulae, the reverse relation holds for the exocyclic angles: O–P–O is larger than X–P–X. The angles at nitrogen are more difficult to compare because of the large differences observed for the phosphonitrilics.

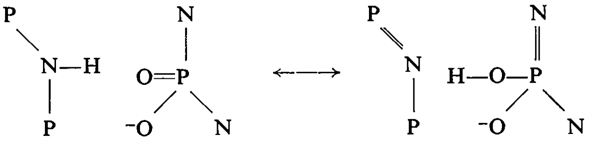
A thorough theoretical discussion of the endocyclic P–N bonds in the phosphonitrilic derivatives is given by Craig & Paddock (Craig & Paddock, 1962; Paddock, 1964). The authors showed that π-bonding in the ring may occur because of two effects: delocalization of the π-electrons of the double bonds in (II), and (partial) delocalization of the lone-pair electrons of the nitrogen atoms into the *d* orbitals of the phosphorus atoms. If both effects are important symmetrically non-equivalent bonds need not have different lengths. For molecules like $(NPCl_2)_4$ Craig & Paddock have made plausible that the *total* overlap of the two nitrogen orbitals involved in the π-bonding and the phosphorus *d* orbitals is (almost) equal for all bonds in the ring. In all phosphonitrilics investigated so far, equal lengths have been found for symmetrically non-equivalent bonds.

In molecules where, in contradistinction to the phosphonitrilic derivatives, only one of the effects is important, symmetrically non-equivalent bonds are expected to have different lengths. This is so for $(NSF)_4$ in which S–N bonds with lengths 1·66 and 1·54 Å alternate. (Wiegers, 1963; Wiegers & Vos, 1963). In this compound delocalization of the nitrogen lone pairs seems to be prevented by the lone-pair electrons on the sulphur atom.

In the metaphosphimates the shortening of the P–N bonds by some 0·1 Å relative to the value 1·77 Å accepted for a single bond (Cruickshank, 1964) has to be ascribed to delocalization of the nitrogen lone pairs only (for a similar shortening see the exocyclic P–N bonds in $[NP(NMe_2)_2]_4$ (Bullen, 1962). Unequal values might therefore be expected for the symmetrically non-equivalent bonds in the anion $[(NH)_4P_4O_8H_2]^{2-}$. Within experimental error, however, equal values are observed. For the trimeric anion the P–N bonds related by the pseudo mirror plane [best plane through N(1), P(3), O(3) and O(6)] are expected to be approximately equal. The observed differences 0·025, 0·017 and 0·003 Å, e.s.d. 0·01 Å, are not significant; the average values 1·681, 1·676 and 1·692 Å are just equal within experimental error. No significant differences in P–N bond lengths are thus observed due to the difference in location of the hydrogen atoms relative to N(1) and N(2) or N (3).

Comparison of Table 4 in the previous paper (Olthof, Migchelsen & Vos, 1965) and Table 5 in the present paper shows that the P–N bonds in the trimeric compound have a tendency to be longer, 0·02 Å on the average, than those in the tetrameric anion. It should be noted that the observed difference in P–N bond lengths may not be interpreted in the same way as the similar, although larger, difference between the P–N bond lengths in the trimeric and tetrameric phosphonitrilic compounds. In the phosphonitrilics where the total amount of π-bonding increases with increasing values of P–N–P, π-bonding in the trimeric compound is relatively weak, and thus P–N relatively long, because of the restricted value of P–N–P in the nearly planar six-membered rings. In the investigated metaphosphimates such a restriction does not occur as both the trimeric and the tetrameric anions are non-planar.

Although the observed difference between the P–N bond lengths in $Na_3(NHPO_2)_3 . 4H_2O$ and in $(NH)_4P_4O_8H_4 . 2H_2O$ is only just significant, it is interesting to show that this difference may be caused by intermolecular forces. In the tetrameric compound all nitrogen atoms of the ring are hydrogen bonded to oxygen atoms by means of hydrogen bonds of 2·80 Å. In the trimeric compound two of the nitrogen atoms are involved in hydrogen bonds of appr. 3 Å, whereas for the third atom the distance to the neighbouring oxygen atoms is still longer. The relatively strong interaction by N–H · · · O bonds in the tetrameric compound may be explained by assuming cooperative resonance, *e.g.* of type



(*A*) (*B*)

the phosphonitrilate form *B* being more important for the tetrameric than for the trimeric compound. A relatively large contribution of the phosphonitrilate form to the structure of the tetramer, is in agreement with the 'small' lengths observed for the P–N bonds. It is worth mentioning, however, that the present X-ray study cannot distinguish between resonance as mentioned above and tautomerism. The difference between the P–N bond lengths in the trimeric and tetrameric compound is equally well explained by assuming that a small number of the tetrameric molecules have the phosphonitrilate structure. This implies that a small number of the hydrogen atoms of the N · · · O bonds are directly linked to oxygen.

The P–O bonds in the two metaphosphimates have a slightly different character. In the trimeric salt the oxygen atoms of the PO_2^- groups are not directly linked to hydrogen atoms, whereas in the tetrameric acid salt H(5) is directly attached to O(1) or (and) O(3–2) (see previous paragraph). Table 6 shows that the observed differences in the P–O bond lengths are small, average values being $1{\cdot}49_5$ Å for $Na_3(NHPO_2)_3 . 4H_2O$ and 1·50 Å for $(NH)_4P_4O_8H_4 . 2H_2O$. The interdependence of the π-character of the four bonds at phosphorus (Cruickshank, 1961) makes it difficult to compare the observed values with the P–O bond lengths in other compounds. For phosphorus–oxygen compounds P–O bond lengths ranging from 1·40 to 1·69 Å have been observed; the P–O bonds of the PO_2^- groups in $RbPO_3$, $Na_5P_3O_{10}$ and in $Na_4P_4O_{12} . 4H_2O$ have a length of 1·49 Å (Cruickshank, 1961).

Inspection of Table 6 shows that the values of the valence angles in the metaphosphimates are closely related to the π character of the bonds. Relatively large values for O–P–O, N–P–N and P–N–P are found between relatively short bonds with large π character.

Calculations were carried out on the digital computer ZEBRA with programs devised by Dr D. W. Smits, Dr J. C. Schoone and Dr D. Rogers; the least-squares analysis was carried out by Dr J. S. Rollett on the Mercury Computer at Oxford. We wish to thank Professor E. H. Wiebenga for his interest throughout the course of this investigation and Professor N. L. Paddock for some interesting discussions. The work was supported by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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The Crystal Structure of the 1:1 Complex of 7,7,8,8-Tetracyanoquinodimethan, and *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine

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The crystal is monoclinic, probably $C2/m$, with $a = 9{\cdot}88$, $b = 12{\cdot}71$, $c = 7{\cdot}72$ Å, $\beta = 97{\cdot}34°$, $Z = 2$.

The structure was deduced from a three-dimensional Patterson synthesis, and refined by block-diagonal least squares. The constituent molecules partially overlap each other with an interplanar spacing of 3·27 Å. Other intermolecular distances are consistent with van der Waals interaction.

Introduction

Many molecular complexes involving 7,7,8,8-tetracyanoquinodimethan (TCNQ) have been described by Melby, Harder, Hertler, Mahler, Benson & Mochel (1962). The crystal-structure analysis of the 1:1 complex with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) was undertaken to assist further investigation (in the Division of Pure Chemistry) of its paramagnetic properties.

Experimental

Crystal data

Monoclinic

$a = \ 9{\cdot}88 \pm 0{\cdot}03$ Å

$b = 12{\cdot}71 \pm 0{\cdot}04$

$c = 97{\cdot}34 \pm 0{\cdot}05°$

$\beta = \ 7{\cdot}72 \pm 0{\cdot}03$

$V = 961{\cdot}5$ Å^3