Acta Cryst. (1964). **17**, 1134

The Crystal and Molecular Structure of Phosphorus Tricyanide

By Kenneth Emerson*

Gates and Crellin Laboratories of Chemistry,† California Institute of Technology, Pasadena, California, U.S.A.

and Doyle Britton

School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.

(*Received* 3 *September* 1963)

Phosphorus tricyanide, $P(CN)_3$, forms tetragonal crystals, space group $I\bar{4}2d$ (D_{2d}^{12}) with 16 molecules in a unit cell of dimensions $a = 14{\cdot}00$, $c = 10{\cdot}81$ Å. The molecules are pyramidal and exhibit C_{3v} symmetry. The average bond distances are P–C, 1·78 Å and $C \equiv N$, 1·15 Å; average bond angles C–P–C, 93° and $P\text{–}C \equiv N$, 172°. All three nitrogen atoms are appreciably closer to neighboring phosphorus atoms than the sum of the van der Waals radii would predict.

Introduction

The determination of the crystal structure of phosphorus tricyanide was undertaken as part of a general study of the Group V tricyanides. The dissimilarity in physical properties between the known tricyanides and the corresponding trihalides is striking, and it was felt that crystallographic studies might shed some light on the reasons for these differences. The structure of arsenic tricyanide has recently been reported (Emerson & Britton, 1963); the structure of phosphorus tricyanide is closely related.

Experimental

Phosphorus tricyanide was prepared as described by Emerson (1960). Reagent-grade phosphorus trichloride was refluxed with commercial silver cyanide for 24 hours. The excess of phosphorus trichloride was distilled off at 75 °C; the residue was transferred to a sublimation apparatus, evacuated and warmed to 100–150 °C. The $P(CN)_3$ deposited in the receiver as colorless, rather flat needles elongated along **a**. No sample with clearly developed faces was ever obtained.

The compound is very hygroscopic and can be handled only in a dry-box. Crystals suitable for X-ray diffraction studies were transferred to thin walled glass capillaries, which were then sealed with Apiezon wax.

Weissenberg photographs of the first crystals mounted suggested monoclinic symmetry and a very large unit cell. These crystals were soon found to be rotation twins, the twin axis being [101]. This twinning was very common, and a number of such twins were examined and rejected before a truly single crystal was found.

Duplicate photographs were prepared from two different crystals by both precession and Weissenberg methods. Weissenberg photographs (Cu $K\alpha$ radiation) were taken of the 0th through 6th layer lines about the a axis; precession photographs (Mo $K\alpha$ radiation) were taken of the 001, 100, and 110 zones. Relative intensities were estimated by comparison with a standard intensity strip. Lorentz and polarization corrections were applied with the aid of programs available on the Univac Scientific 1103 computer (Rossman, Jacobson, Hirshfeld & Lipscomb, 1959). One of the crystals had an appreciable absorption but gave readable values for many of the very weak reflections; for this crystal an approximate correction was applied to the measured intensities on the assumption that the needle-like crystal was roughly cylindrical (*International Tables for X-ray Crystallography*, 1959). The corrected data for this crystal were compared with those obtained from the other crystal, for which absorption was negligible; good agreement was observed. The 418 independent reflections obtained were then correlated with each other on an arbitrary scale.

Space group and unit cell

Systematic extinctions occurred for $h+k+l$ odd and for $h+h+l=4n+2$, indicating a body-centered unit cell and a diamond glide. The space group must therefore be $I4_1md$ and $I\bar{4}2d$. Our successful refinement of the structure has shown the correct space group to be $I\bar{4}2d$.

In order to determine the cell dimensions a powder photograph of a mixture of $P(CN)_3$ and NaCl was measured and indexed. A two-parameter least-squares determination of the cell constant a_0 of NaCl and a coefficient, A, for the correction term for absorption was then calculated. The absorption effect was assumed to have the following functional dependence (Buerger, 1942).

$$\Delta(\sin^2\theta) = A\cos^2\theta\sin 2\theta\ .$$

---

* Present address: Chemistry Department, Montana State College, Bozeman, Montana, U.S.A.

† Contribution No. 2779.

The observations were weighted by sin 2θ. The resulting parameters were $A=0{\cdot}0032\pm0{\cdot}0007$ and $a_0=5{\cdot}6393\pm0{\cdot}0013$. This value agrees well with the value of 5·6402 reported by Swanson & Fuyat (1953). Absorption corrections indicated were then applied to the $P(CN)_3$ data, and the cell constants for this compound were determined by least squares.

As a cross check on this procedure a second least-squares determination of the $P(CN)_3$ cell constants was computed from the uncorrected data with the absorption factor A included as an additional parameter. The value for A obtained by this calculation did not differ significantly from zero, and the cell parameters obtained differed by about three standard deviations from those calculated by the first procedure. This difference in fit reflects primarily the fact that no $P(CN)_3$ reflections in the back reflection region appeared on the film. Without such back reflections determination of A becomes very uncertain, and hence one would expect the results of these two procedures to differ slightly. In view of these experimental uncertainties we are reporting as cell constants the average of these two determinations: $a=14{\cdot}00\pm0{\cdot}03$, $c=10{\cdot}81\pm0{\cdot}03$ Å. The quoted limits of error are equal to twice the standard deviation of the calculation.

The density of the solid was determined by flotation to be approximately 1·35 g.cm^{-3}. The density calculated for a unit cell containing 16 molecules of $P(CN)_3$ is 1·37 g.cm^{-3}. The asymmetric unit therefore contains 1 molecule of $P(CN)_3$ regardless of the choice of space group.

Determination of structure

A preliminary choice of space group was made on the basis of the statistical distribution of intensities in the $hk0$ and $0kl$ zones (Howells, Phillips & Rogers, 1950). These distributions are shown in Fig. 1. These indicate that the crystal is centric in projection along [001] and acentric along [100], and therefore belongs in space group $I4_1md$ rather than $I\bar{4}2d$.

The positions of the phosphorus atoms were readily determined from a three-dimensional Patterson map. These positions have approximately the symmetry $I4_1/amd$, and do not discriminate between the two possible space groups.

A great deal of fruitless effort was then expended in attempting to locate the cyanide groups by conventional methods on the assumption that the space group was $I4_1md$. When crystals of $As(CN)_3$ became available, the study of $P(CN)_3$ was put aside in the hope that the crystal structure of the former would prove simpler and would throw some light on that of the latter. This did indeed prove to be the case.

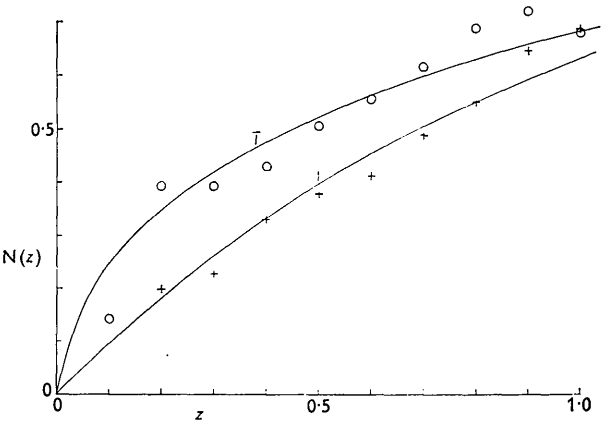

Fig. 1. Statistical distribution of intensities. Solid lines indicate theoretical distributions for centric and acentric cases, ○, calculated distribution for $hk0$; +, calculated distribution for $0kl$.

From the known structure of $As(CN)_3$ (Emerson & Britton, 1963) it was possible to deduce an analogous structure for $P(CN)_3$ in space group $I\bar{4}2d$ but not in $I4_1md$. Fourier syntheses using phases based on the known phosphorus atom positions supported this deduced structure. Least-squares refinement using a Burroughs 220 digital computer was accordingly begun with full three-dimensional data at an R value of 0·28. (The agreement index $R=\Sigma|F_o-F_c|/\Sigma F_o$.) After 5 cycles R had dropped to 0·21 and the structure was refining extremely slowly. A three-dimensional Fourier synthesis was calculated, and showed several carbon and nitrogen atoms displaced 0·1 to 0·2 Å from their least-squares positions. These positions were corrected, and 5 more cycles of least squares reduced R to 0·14. Anisotropic temperature factors were then introduced and in 9 more cycles R was reduced to 0·11. At this point the indicated shifts in all the parameters were less than half the corresponding standard deviations, and the refinement was considered complete. The final values of the parameters are given in Table 1.

Table 1. *Final parameters*

All values are multiplied by 10^4. Standard deviations (σ) are given in parentheses.
The anisotropic temperature factor has the form $\exp\{-(\beta_1h^2+\beta_2k^2+\beta_3l^2+\beta_4hk+\beta_5hl+\beta_6kl)\}$

	x/a	y/b	z/c	β_1	β_2	β_3	β_4	β_5	β_6
P	2381(2)	4939(2)	1021(3)	42(1)	43(1)	73(2)	12(5)	−8(3)	12(5)
C(1)	3037(10)	4110(10)	1974(13)	47(6)	58(8)	97(11)	3(16)	−3(17)	13(17)
C(2)	3344(9)	5773(9)	0934(11)	55(7)	56(6)	88(10)	22(17)	−31(15)	1(17)
C(3)	1850(9)	5513(9)	2310(12)	50(7)	54(7)	91(11)	10(15)	−9(16)	−6(15)
N(1)	3429(9)	3522(9)	2468(13)	73(8)	76(8)	124(12)	34(17)	−33(18)	50(18)
N(2)	3978(9)	6282(9)	0733(12)	68(8)	75(7)	130(13)	−37(18)	36(19)	22(17)
N(3)	1402(9)	5896(9)	3073(12)	69(6)	60(8)	120(12)	29(16)	−4(17)	6(18)

Table 2. *Observed and calculated structure factors*

All values are multiplied by 10. Unobserved reflections are indicated by u in the second column

ℓ	$10F_o$	$10F_c$	10A	10B
	h = 0		k = 0	
4	569	493	493	0
8	134	113	113	0
12	120	134	134	0
	h = 0		k = 1	
1	u	94	0	-94
3	328	303	0	303
5	756	648	0	648
7	783	689	0	-689
9	405	428	0	428
11	282	302	0	-302
13	96	119	0	119
	h = 0		k = 2	
0	164	152	152	0
2	1943	2302	2302	0
4	238	215	-215	0
6	545	549	549	0
8	71	64	64	0
10	129	136	136	0
12	u	3	-3	0
	h = 0		k = 3	
1	301	190	0	190
3	679	597	0	597
5	435	419	0	-419
7	246	235	0	235
9	389	400	0	-400
11	131	132	0	132
13	93	106	0	-106
	h = 0		k = 4	
0	668	598	-598	0
2	181	170	170	0
4	1336	1194	1194	0
6	126	112	-112	0
8	471	453	453	0
10	u	40	-40	0
12	u	10	10	0
	h = 0		k = 5	
1	107	102	0	102
3	482	451	0	-451
5	110	106	0	106
7	394	386	0	-386
9	60	73	0	73
11	142	139	0	-139
13	142	146	0	146
	h = 0		k = 6	
0	192	192	-192	0
2	985	975	975	0
4	367	304	304	0
6	553	477	477	0
8	238	235	-235	0
10	63	9	9	0
12	u	35	35	0
	h = 0		k = 7	
1	493	526	0	-526
3	68	44	0	-44
5	534	380	0	-380
7	140	118	0	118
9	208	231	0	-231
11	131	143	0	143
	h = 0		k = 8	
0	756	733	733	0
2	257	255	-255	0
4	933	761	761	0
6	85	54	54	0
8	123	112	112	0
10	u	17	17	0
12	u	47	-47	0
	h = 0		k = 9	
1	164	177	0	-177
3	613	572	0	-572
5	u	15	0	-15
7	337	298	0	-298
9	101	115	0	115
11	120	147	0	-147
	h = 0		k = 10	
0	u	45	-45	0
2	526	455	455	0
4	211	207	-207	0
6	567	487	487	0
8	162	120	120	0
10	38	10	10	0
	h = 0		k = 11	
1	411	364	0	-364
3	107	112	0	-112
5	452	376	0	-376
7	u	5	0	5
9	156	181	0	-181
	h = 0		k = 12	
0	640	636	636	0
2	u	25	-25	0
4	498	404	404	0
6	58	49	-49	0
8	118	116	116	0
10	u	34	-34	0
	h = 0		k = 13	
1	216	217	0	-217
3	296	272	0	-272
5	u	32	0	-32
7	208	179	0	-179
9	115	153	0	153
	h = 0		k = 14	
0	142	130	-130	0
2	457	421	421	0
4	96	72	-72	0
6	137	132	132	0
8	u	26	-26	0
	h = 0		k = 15	
1	170	168	0	-168
3	46	53	0	-53
5	249	200	0	-200
7	96	78	0	78
	h = 0		k = 16	
0	156	172	172	0
2	120	97	-97	0
4	142	135	135	0
6	u	72	-72	0
	h = 0		k = 17	
1	101	97	0	-97
3	175	168	0	-168
	h = 1		k = 1	
2	605	594	590	69
6	430	401	347	200
10	u	32	-31	-7
	h = 1		k = 2	
1	230	226	179	138
3	1207	1266	-1260	-124
5	495	430	165	-398
7	487	454	47	-452
9	438	441	132	-420
11	205	222	76	-209
13	104	127	-39	-121
	h = 1		k = 3	
0	93	74	0	74
2	241	200	95	-176
4	279	250	-244	-55
6	318	326	301	-125
8	131	112	-77	82
10	u	31	-31	4
12	52	45	42	18
	h = 1		k = 4	
1	640	793	774	171
3	394	384	-235	-304
5	501	462	-436	-152
7	307	283	30	-281
9	222	236	7	-236
11	200	185	-69	-171
13	126	140	31	-137
	h = 1		k = 5	
0	501	459	0	-459
2	471	434	-408	-119
4	285	254	-194	164
6	457	437	-426	-97
8	u	60	-52	-29
10	u	75	-24	71
12	u	36	35	11
	h = 1		k = 6	
1	476	473	-124	-456
3	621	596	572	-167
5	312	295	-202	-215
7	230	218	-90	-199
9	189	184	-98	-155
11	170	180	40	-176
13	79	98	-2	-98
	h = 1		k = 7	
0	u	6	0	6
2	112	117	-16	116
4	298	261	25	-260
6	386	358	-340	112
8	208	193	-191	-26
10	u	53	-1	-53
12	88	112	-108	30
	h = 1		k = 8	
1	320	298	-208	-213
3	608	485	-110	-473
5	402	362	291	-215
7	192	166	-100	-133
9	192	144	56	-132
11	126	120	-27	-116
	h = 1		k = 9	
0	224	246	0	246
2	134	124	-54	-112
4	246	184	-139	120
6	263	248	-167	-182
8	150	145	-145	1
10	156	149	-149	-3
12	u	89	-85	-28
	h = 1		k = 10	
1	u	40	-23	-32
3	318	273	148	-230
5	364	310	-97	-294
7	170	132	93	-94
9	186	158	-96	-125
11	96	109	63	-90
	h = 1		k = 11	
0	192	189	0	-189
2	186	184	-84	164
4	383	343	-330	-96
6	140	126	-82	95
8	134	115	-107	-44
10	170	149	-148	-15
	h = 1		k = 12	
1	74	85	73	-43
3	142	132	-83	-103
5	181	156	89	-129
7	255	213	-113	-180
9	164	148	92	-115
	h = 1		k = 13	
0	224	232	0	232
2	172	179	-110	-141
4	93	107	-55	92
6	u	28	-27	8
8	140	101	-101	-1
	h = 1		k = 14	
1	u	44	-42	-14
3	134	90	-82	-35
5	140	112	-60	-94
7	219	185	141	-121
	h = 1		k = 15	
0	148	157	0	-157
2	123	139	-43	132
4	u	39	32	-22
6	93	80	-71	-37
	h = 1		k = 16	
1	u	65	-62	18
3	u	12	8	9
	h = 1		k = 17	
0	u	65	0	65
2	u	75	0	-75
	h = 2		k = 2	
0	2080	2883	2883	0
4	1166	1218	1033	646
8	320	306	278	127
12	u	79	-49	62
	h = 2		k = 3	
1	71	72	-51	-52
3	991	1003	-991	-149
5	427	413	-64	408
7	479	486	-50	-483
9	235	254	-118	225
11	224	241	45	-237
13	150	133	-10	133
	h = 2		k = 4	
0	u	39	39	0
2	1506	1770	1452	1014
4	164	144	-127	68
6	553	535	522	114
8	u	63	17	-61
10	88	68	67	10
12	u	11	8	-7
	h = 2		k = 5	
1	427	476	107	-463
3	413	435	-325	289
5	427	425	-149	-398
7	276	259	163	202
9	348	346	-161	-306
11	126	150	-72	132
13	82	80	18	-78
	h = 2		k = 6	
0	567	666	666	0
2	u	62	4	62
4	799	770	763	99
6	u	62	-62	8
8	361	326	313	-90
10	u	28	-21	-19
12	u	60	-48	36
	h = 2		k = 7	
1	164	193	-145	-128
3	583	576	95	-569
5	200	192	158	109
7	380	332	-44	-329
9	203	129	-88	94
11	115	129	-31	-125
	h = 2		k = 8	
0	u	16	-16	0
2	550	603	585	-147
4	110	91	-16	90
6	630	534	528	-76
8	u	56	-51	23
10	u	33	9	32
	h = 2		k = 9	
1	367	407	-157	-376
3	189	129	-4	-129
5	427	428	-148	-402
7	238	233	-230	38
9	238	214	99	-190
11	197	170	60	159
	h = 2		k = 10	
0	553	612	612	0
2	u	120	-118	-22
4	766	615	614	-35
6	u	58	9	57
8	u	68	68	8
10	u	53	-17	-51
	h = 2		k = 11	
1	216	222	80	-207
3	427	376	32	-374
5	167	149	-119	-90
7	235	232	-17	-232
9	216	181	70	167
	h = 2		k = 12	
0	170	162	-162	0
2	534	544	540	-71
4	u	103	-68	-78
6	211	220	214	52
8	u	18	8	16
	h = 2		k = 13	
1	222	237	61	-229
3	u	92	2	-92
5	285	280	41	-277
7	137	136	119	65
9	159	146	-27	-144
	h = 2		k = 14	
0	348	366	366	0
2	u	71	-68	-17
4	200	220	220	-2
6	u	77	-74	-22
8	126	117	92	71
	h = 2		k = 15	
1	145	130	8	-130
3	282	231	-82	-215
5	u	27	24	13
7	172	148	-4	-148
	h = 2		k = 16	
0	u	14	-14	0
2	203	170	168	20
4	u	90	-89	10
	h = 2		k = 17	
1	175	179	-94	-152
3	u	58	13	-57
	h = 3		k = 3	
2	753	806	690	-417
6	498	557	-557	-20
10	u	88	7	88
	h = 3		k = 4	
1	668	810	467	-661
3	241	254	-248	-55
5	465	452	-300	-338
7	334	377	-133	-353
9	279	318	-75	-309
11	208	212	84	-194
13	112	94	1	-94
	h = 3		k = 5	
0	427	496	0	-496
2	391	393	371	-128
4	249	218	157	-150
6	175	105	95	-44
8	235	242	-237	49
10	u	15	14	-2
12	159	132	-131	20
	h = 3		k = 6	
1	268	294	160	247
3	624	609	218	-569
5	331	309	-267	-157
7	238	253	-124	-220
9	230	219	21	-218
11	137	138	-56	-126
	h = 3		k = 7	
0	159	160	0	-160
2	457	466	-457	-88
4	200	178	-167	62
6	216	178	-79	-160
8	u	40	-30	-26
10	233	248	-246	-31
12	u	17	15	7
	h = 3		k = 8	
1	205	231	-200	-115
3	326	292	281	78
5	389	359	-134	-333
7	145	153	74	-134
9	197	150	-37	146
11	142	149	30	-146
	h = 3		k = 9	
0	u	26	0	-26
2	205	197	-170	100
4	334	353	-321	-148
6	u	103	-75	71
8	227	208	-162	-130
10	u	92	-81	-43
	h = 3		k = 10	
1	u	133	92	-96
3	271	248	-145	-201
5	263	244	242	-35
7	257	246	-114	-219
9	148	137	33	-133
11	90	104	-35	-98
	h = 3		k = 11	
0	241	246	0	246
2	162	177	-130	-120
4	181	143	61	129
6	u	114	-111	-28
8	156	148	-145	-27
10	98	92	-92	4
	h = 3		k = 12	
1	u	42	-42	2
3	126	124	-42	-117
5	219	196	-2	-196
7	u	115	101	-56
9	115	117	-85	-80
	h = 3		k = 13	
0	u	105	0	-105
2	186	195	26	193
4	126	128	-124	-33
6	175	166	-166	-2
8	u	60	-60	5
	h = 3		k = 14	
1	156	160	-158	-26
3	u	66	-54	-38
5	u	44	36	-25
7	u	84	-31	-78
	h = 3		k = 15	
0	u	132	0	132
2	u	86	-33	-79
4	131	140	-137	28
6	131	107	-97	-45
	h = 3		k = 16	
1	u	91	-82	-40
3	u	25	14	20
	h = 3		k = 17	
0	u	108	0	-108
2	u	73	-60	40
	h = 4		k = 4	
0	1667	2535	2535	0
4	865	894	761	470
8	170	170	168	23
12	101	125	-93	83
	h = 4		k = 5	
1	427	474	396	-261
3	438	503	-161	-476
5	443	419	-89	409
7	419	421	-203	-368
9	263	246	-133	207
11	197	201	42	-196
	h = 4		k = 6	
0	u	19	19	0
2	750	813	777	240
4	219	221	-203	87
6	657	628	628	26
8	98	95	82	-47
10	u	86	55	66
	h = 4		k = 7	
1	268	313	-56	-308
3	85	97	79	56
5	493	537	-282	-457
7	290	276	-238	139
9	214	241	35	-238
11	150	135	-6	135
	h = 4		k = 8	
0	613	673	673	0
2	u	60	60	-7
4	556	643	642	32
6	90	99	-81	57
8	205	192	185	-50
10	68	74	-40	-62
	h = 4		k = 9	
1	192	236	-108	-210
3	301	344	-17	-344
5	u	38	-34	-16
7	263	258	-28	-257
9	192	173	-13	172
11	178	133	-18	-131
	h = 4		k = 10	
0	u	110	-110	0
2	668	741	732	-120
4	u	53	53	3
6	178	172	168	-37
8	93	109	-108	12
10	u	13	-2	13
	h = 4		k = 11	
1	194	224	-70	-214
3	150	144	-57	-132
5	318	288	68	-280
7	112	108	50	95
9	203	162	-17	-162
	h = 4		k = 12	
0	339	406	406	0
2	145	126	-126	-1
4	304	298	294	-53
6	u	30	-30	0
8	150	124	71	102
	h = 4		k = 13	
1	123	139	68	-121
3	244	260	-63	-253
5	u	47	14	-45
7	249	212	7	-212
	h = 4		k = 14	
0	u	4	-4	0
2	192	211	210	5
4	79	98	-88	-43
6	205	192	137	134
	h = 4		k = 15	
1	189	205	-62	-196
3	66	94	28	-90
5	172	175	-34	-172
	h = 4		k = 16	
0	181	221	221	0
2	u	38	-29	-25
4	137	131	117	60
	h = 4		k = 17	
1	u	127	47	-118
	h = 5		k = 5	
2	337	410	295	-284
6	98	95	-26	-91
10	244	273	-272	-23
	h = 5		k = 6	
1	279	304	49	-300
3	214	205	-180	98
5	512	518	-297	-425
7	315	269	140	-230
9	235	234	18	-234
11	159	169	36	-165
	h = 5		k = 7	
0	380	440	0	-440
2	266	227	212	-81
4	298	287	-286	-26
6	u	61	61	-2
8	255	242	-223	-95
10	u	11	-4	-10
12	115	124	-107	62
	h = 5		k = 8	
1	315	364	316	180
3	293	280	-51	-275
5	131	113	-104	44
7	304	269	-76	-258
9	192	221	17	-220
11	170	146	-59	-134
	h = 5		k = 9	
0	85	85	0	-85
2	255	251	-201	-151
4	140	107	69	82
6	244	189	-186	36
8	79	60	-50	-32
10	153	112	-112	-10
	h = 5		k = 10	
1	123	111	-80	-77
3	85	63	-23	59
5	214	210	37	-207
7	79	93	53	-77
9	214	147	-62	-133
	h = 5		k = 11	
0	u	18	0	18
2	107	112	15	111
4	148	119	-105	-54
6	142	118	-118	-2
8	112	78	-74	-26
	h = 5		k = 12	
1	227	203	-194	-62
3	85	93	-59	-72
5	131	138	128	51
7	153	144	-42	-138
9	52	51	20	-47
	h = 5		k = 13	
0	137	149	0	149
2	159	159	-152	-48
4	112	105	-97	41
6	260	160	-137	-82
8	131	100	-94	36
	h = 5		k = 14	
1	131	119	-119	-11
3	79	81	78	20
5	170	126	-77	-100
7	u	34	28	-20
	h = 5		k = 15	
0	u	91	0	-91
2	118	106	-67	82
4	268	177	-142	-106
6	u	99	-76	64
	h = 5		k = 16	
1	u	69	-5	69
3	u	134	-101	-88
5	85	71	27	-66
	h = 5		k = 17	
0	u	81	0	81
2	u	80	2	-80
	h = 6		k = 6	
0	900	1286	1286	0
4	832	872	847	206
8	u	67	55	39
12	u	70	-32	63
	h = 6		k = 7	
1	260	278	134	-243
3	331	348	-201	-284
5	252	221	-162	150
7	353	332	-126	-307
9	233	254	-81	241
11	203	191	15	-190
	h = 6		k = 8	
0	131	131	-131	0
2	865	971	970	44
4	u	51	-44	26
6	197	187	187	1
8	u	38	9	-37
10	u	77	30	71
	h = 6		k = 9	
1	230	217	-40	-214
3	156	135	135	11
5	318	293	45	-290
7	211	184	-25	182
9	246	224	-63	-215
	h = 6		k = 10	
0	569	603	603	0
2	u	10	-4	-9
4	241	217	206	-69
6	u	81	-80	7
8	211	225	194	114
	h = 6		k = 11	
1	167	155	80	-133
3	241	208	-40	-204
5	u	63	54	32
7	266	246	-15	-246
	h = 6		k = 12	
0	u	72	72	0
2	238	233	233	-6
4	u	59	-59	-6
6	252	206	147	143
	h = 6		k = 13	
1	227	214	-97	-190
3	148	140	-6	-140
5	222	189	-62	-179
	h = 6		k = 14	
0	224	228	228	0
2	u	67	-60	-30
4	197	204	176	103
	h = 6		k = 15	
1	u	142	33	-138
3	153	169	-28	-167
	h = 6		k = 16	
0	148	113	-113	0
2	148	160	160	12
	h = 6		k = 17	
1	u	114	-46	-104
	h = 8		k = 8	
0	739	840	840	0
	h = 8		k = 12	
0	370	293	293	0
	h = 10		k = 10	
0	397	354	354	0

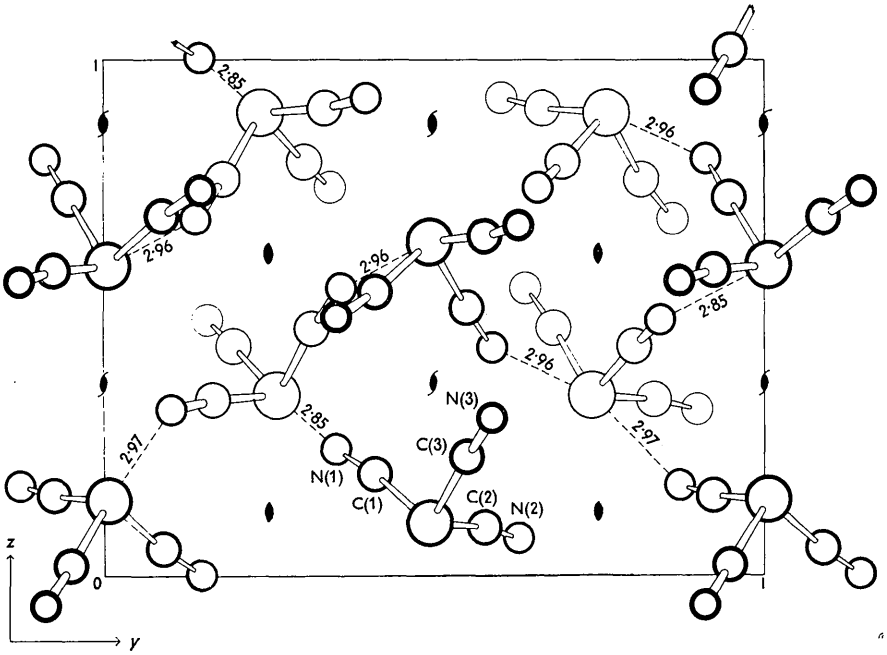

Fig. 2. Diagram showing two layers of molecules when viewed along *a*. This comprises approximately one-half the contents of the unit cell. Close intermolecular approaches are indicated by dashed lines with the distances marked in Å. (The distances given as 2·96 and 2·97 are all in error and should all be 0·01 Å larger.)

Table 2 gives the values of the observed and calculated structure factors. Fig. 2 is a drawing of a segment of the unit cell, with the intermolecular distances marked in Å.

The least-squares routine used for the refinement has been described by Hybl (1961). The quantity minimized in the calculation is $w(F_o^2-F_c^2)^2$. In this refinement the weighting function was of the form

$$\sqrt{w}=\sqrt{w_e}\,\frac{1}{1+SF_o+TF_o^2}\,,$$

where $\sqrt{w_e}$ is an externally assigned weight and S and T are variable parameters. The external weight was taken as 0 for unobserved reflections, as ½ for those reflections which had been corrected for absorption, and as 1 for all others except 202, 404, 240, and 440. These four were suspected of reading errors and were given weights of 0·1 to 0·01. Initially S was set equal to 0·1 and T equal to 0. After the introduction of anisotropic temperature factors S was gradually decreased and T increased until in the final cycle S was 0 and T was 0·01.

Discussion of the structure

The bond distances and bond angles for the molecule are given in Table 3. The average P–C bond length is 1·78 Å and the average C–N bond 1·15 Å. The values are in good agreement with the calculated values of 1·79 and 1·15 Å obtained using bond radii given by Pauling (1959) and Bent (1961). The bond angles at the phosphorus average 93°, and those at the carbon 172°. The deviations from these averages do not appear to be significant; in no case is the variance greater than one standard deviation. The molecule has C_{3v} symmetry to within two standard deviations of the parameters. The significant deviation of the P–C–N angle from 180° is surprising; there does not appear to be any ready explanation for it. A similar deviation from 180° was observed in As(CN)$_3$, but in that case the uncertainty was considerably greater, and the significance of the deviation was considered doubtful.

Table 3. *Bond distances and bond angles*

Distances		Angles	
P–C(1)	1·803 ± 0·029 Å	C(2)–P–C(1)	93·7 ± 2°
P–C(2)	1·786 ± 0·027	C(3)–P–C(1)	93·2 ± 2
P–C(3)	1·774 ± 0·027	C(2)–P–C(3)	93·6 ± 2
C(1)–N(1)	1·124 ± 0·047	P–C(1)–N(1)	170·7 ± 3
C(2)–N(2)	1·158 ± 0·044	P–C(2)–N(2)	172·2 ± 3
C(3)–N(3)	1·165 ± 0·044	P–C(3)–N(3)	171·9 ± 3

The intermolecular interactions in this crystal are apparently more complex than was the case in As(CN)$_3$. In the latter compound there is one N–As intermolecular distance which is appreciably shorter than the normal van der Waals distance; this was interpreted as a weak interaction with a bond order of approximately 0·03. In P(CN)$_3$ three P–N intermolecular distances, 2·85, 2·98, and 2·97 Å, are substantially shorter than the predicted van der Waals distance of 3·4 Å. If one calculates partial bond orders from these distances (Pauling, 1959) one obtains 0·02, 0·01 and 0·01 respectively. The individual intermolecular interactions thus appear to be weaker in $P(CN)_3$ than in $As(CN)_3$, but since there are three of them the net intermolecular forces might be comparable in the two systems. The C–N–P angles for these atoms are 116°, 122°, and 116°, in contrast again to $As(CN)_3$, for which the C–N–As angle at the interacting nitrogen is very close to 180°.

There are, then, two features of this structure which were unexpected, first that the P–C–N groups are not linear, and second that the C–N · · · P external interaction is not even approximately linear. However, both of these features have been observed before in the structure of $Se(SeCN)_2$ (Aksnes & Foss, 1954) in which were found Se–C–N angles of 164° and short, 3·04 Å, C–N · · · Se distances which were not close to the C–N direction. The structure of the isomorphic compound $Se(SCN)_2$ has also been studied (Ohlberg & Vaughan, 1954), and found to have the same nonlinear, short, 2·98 Å, C–N · · · Se distance. However, in this study the S–C–N angle was assumed to be 180° and the structure was not refined with respect to this detail. Preliminary studies have been made on another apparently isostructural compound, $S(SCN)_2$ (Foss, 1956), but no details of the structure have been reported. It is a likely possibility that nonlinearity at the carbon atom is a consequence of a nonlinear external interaction.

The principal axes of the ellipsoids represented by the anisotropic temperature factors are given in Table 4. The phosphorus atom and the carbon atoms are nearly isotropic. The vibrations of the nitrogen atoms are larger, as expected, and also more anisotropic. The angle between the shortest principal axis for each nitrogen and the vector connecting its bonded carbon and the phosphorus atom in the nearest adjoining molecule varies from 15° to 45°, suggesting that there is some hindrance to vibration in this direction.

Table 4. *Principal axes of vibrational ellipsoids*

q_i are the direction cosines relative to the unit cell axes

Atom	B	q_a	q_b	q_c
P	3·8	0·54	0·75	0·39
	3·6	0·62	−0·04	−0·78
	2·6	−0·57	0·66	−0·49
C(1)	4·7	−0·33	0·31	0·89
	4·6	0·93	0·25	0·26
	3·5	−0·15	0·92	−0·37
C(2)	5·6	0·74	0·48	−0·48
	4·2	−0·05	0·75	0·66
	3·0	0·67	−0·46	0·58
C(3)	4·8	0·69	0·46	−0·56
	4·0	0·49	0·28	0·83
	3·6	−0·54	0·85	0·03
N(1)	7·4	0·34	0·78	0·54
	6·8	0·78	0·09	−0·62
	3·2	−0·52	0·63	−0·58
N(2)	7·3	0·78	−0·41	0·47
	6·4	−0·13	0·62	0·77
	3·5	0·61	0·67	−0·43
N(3)	6·3	0·58	0·81	0·12
	5·6	−0·15	−0·03	0·99
	3·9	0·80	−0·59	0·11

The relation between the structure of $As(CN)_3$ and $P(CN)_3$ is very interesting. The arrangement of the arsenic and phosphorus atoms in their respective compounds is essentially the same. The unit cells have closely related dimensions, the approximate conversion relations being

$$\mathbf{a} = 2\mathbf{B}$$
$$\mathbf{a} = \mathbf{A} - \mathbf{C}$$
$$\mathbf{c} = \mathbf{A} + \mathbf{C}$$

where lower case letters refer to $P(CN)_3$ and capitals to $As(CN)_3$. In the $As(CN)_3$ structure chains of molecules held together by weak external bonds were found. The molecules in any chain were related to each other by translation, and chains were related one to another by twofold axes. In the $P(CN)_3$ structure similar chains may be found, based on the shortest external interaction. However, only the second nearest neighbors in any chain are related by translation, while the nearest neighbors are related by the operation of a *d*-glide plane, and the chains are related by the $\bar{4}$ axis. The $P(CN)_3$ molecule therefore is in a somewhat different environment and has a roughly octahedral set of cyanide neighbors, three bonded directly and three bonded loosely, rather than the three direct bonds and the one loose bond in the $As(CN)_3$.

The fact that on sublimation the crystals grow as needles in the direction of one of the two equivalent axes is rather surprising. We have made several examinations of powdered $P(CN)_3$ and of the sublimed needles under a petrographic microscope. Excellent uniaxial figures were obtained with convergent polarized light from a number of fragments. No complete figures were obtained from any of the needles, but from the positions of the isogyres observed it was clear that the *c* axis is perpendicular to the needle axis. The possibility that the crystal is only pseudotetragonal, and that the *a* and *b* axes are not exactly equivalent, exists; but we can find no evidence in support of this suggestion other than the peculiar crystal habit*. A second and perhaps more likely explanation is that the crystals grow at the sublimation temperature in a monoclinic form, and transform on cooling to the tetragonal form.

The authors wish to thank the computing center at the University of Minnesota for making time available on the Univac Scientific 1103 computer. One of us (K.E.) expresses his appreciation to the Eastman

---

* In a private communication Dr J. J. Daly of Monsanto Research S.A., Zürich, has informed us that he has observed needles elongated along **a**, hexagonal plates, and tetragonal prisms in crystals grown by Dr L. Maier. These all appeared to be different habits of the same structure reported here.

Kodak Company for a fellowship during the academic year 1959–60, and to the National Science Foundation for a summer fellowship during 1960. Some of the work described was also supported by a grant from the National Science Foundation. We are indebted to Dr Richard E. Marsh of the California Institute of Technology for help and advice in the course of the refinement.

References

AKSNES, O. & FOSS, O. (1954). *Acta Chem. Scand.* **8**, 1787.
BENT, H. A. (1961). *J. Inorg. Nucl. Chem.* **19**, 43.
BUERGER, M. J. (1942). *X-ray Crystallography.* p. 427. New York: Wiley.
EMERSON, K. (1960). Thesis, Univ. of Minnesota.
EMERSON, K. & BRITTON, D. (1963). *Acta Cryst.* **16**, 113.
FOSS, O. (1956). *Acta Chem. Scand.* **10**, 136.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
HYBL, A. (1961). Thesis, California Institute of Technology
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
OHLBERG, S. M. & VAUGHAN, P. A. (1954). *J. Amer. Chem. Soc.* **76**, 2649.
PAULING, L. (1959). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
ROSSMAN, M. G., JACOBSON, R. A., HIRSHFELD, F. & LIPSCOMB, W. N. (1959). *Acta Cryst.* **12**, 530.
SWANSON, H. E. & FUYAT, R. K. (1953). U.S. Nat. Bur. Stand. Circular 539. Vol. II, p. 41.

Acta Cryst. (1964). **17**, 1139

The Structure of the Triclinic Form of Sodium Tetrametaphosphate Tetrahydrate

BY HELEN M. ONDIK

National Bureau of Standards, Washington 25, D.C., U.S.A.

(*Received* 27 *August* 1963 *and in revised form* 17 *October* 1963)

The cell dimensions of triclinic sodium tetrametaphosphate tetrahydrate, $Na_4P_4O_{12}.4H_2O$, are

$$a=6{\cdot}652\pm0{\cdot}001,\ b=9{\cdot}579\pm0{\cdot}002,\ c=6{\cdot}320\pm0{\cdot}001\ \text{Å};$$
$$\alpha=103^\circ\ 24'\pm1',\ \beta=106^\circ\ 59'\pm1',\ \gamma=93^\circ\ 17'\pm1',$$

space group $P\bar{1}$, $Z=1$.

The structure was determined from a three-dimensional Patterson function, and refined by complete-matrix least-squares. The R value for 1335 observed non-zero reflections is 0·086.

The tetrametaphosphate ring is on the center of symmetry at the origin of the unit cell. One of the two crystallographically different Na ions is fivefold coordinated, and the other is sixfold coordinated.

The fivefold coordinated Na ion links the rings along **c**, the sixfold coordinated ion links the rings along **a**. There are some similarities between the structures of the monoclinic and triclinic forms of this salt but the differences are too great to permit a transition between the two forms in the solid state. Such a transition, reported by other workers, has not been confirmed by this investigator.

Introduction

Bell, Audrieth & Hill (1952), in reporting the two crystalline modifications of $Na_4P_4O_{12}.4H_2O$, described a transition in the solid state from the monoclinic to the triclinic form. The transition was not observed by workers at The Johns Hopkins University (Gross, 1955). Preliminary chemical evidence (Gross, Gryder & Donnay, 1955) had indicated the possible existence of stereoisomers of the tetrametaphosphate anion ring. To establish the relationship between the two forms and learn whether the polymorphism is attributable to different stereoisomers, structure determinations were undertaken. The structure of the triclinic form is now given and compared with the monoclinic structure previously reported (Ondik, Block & MacGillavry, 1961).

Preparation

Pure sodium tetrametaphosphate was kindly provided by Dr J. W. Gryder of The Johns Hopkins University. The tetrametaphosphate was produced both by cold hydrolytic cleavage of α-P_4O_{10} (Bell, Audrieth & Hill, 1952) and by the Warschauer (1903) process from H_3PO_4 and CuO. The product of the latter procedure was purified of other phosphates by the ion-exchange method of Barney & Gryder (1955). Great care must be taken to avoid precipitating a mixture of the two modifications from solution. Approximately 97% pure triclinic material (by volume, as estimated during microscopic examination with a polarizing microscope) may be obtained by slowly adding 95% ethanol with rapid stirring to a solution of the sodium tetrametaphosphate kept at about 50 °C. Single crystals suitable