1075. *Phosphonitrilic Derivatives. Part IX.*[1] *The Crystal Structure of Octamethylcyclotetraphosphonitrile.*

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The *X*-ray crystal-structure analysis of octamethylcyclotetraphosphonitrile, $[PN(CH_3)_2]_4$, shows that four discrete molecules, with $\bar{4}$ symmetry, crystallise in a tetragonal cell, with dimensions $a = b = 15{\cdot}705$, $c = 6{\cdot}425$ Å, and space group $I4_1/a$. The crystallographically non-equivalent P–N bond lengths are found, by three-dimensional anisotropic refinement, to be equal (1·591 and 1·601 Å; S.D. 0·003 Å). The average P–C bond length is 1·805 Å (S.D. 0·004 Å) and the ring angles are 119° 48′ (∠NPN) and 131° 57′ (∠PNP).

The crystal structures of four phosphonitriles have already been published; three of these are halides[2] and the fourth is the dimethylamide derivative.[3] In each case phosphorus is bonded to an electronegative element and the P–N bond lengths within the ring are short and equal. The actual length depends on the substituent on phosphorus.

The present work was undertaken to provide an accurate structure determination of a simple phosphonitrile containing only light atoms and to observe the structural effect of replacing the strongly electronegative fluorine atom by the isoelectronic methyl group.

There is also interest in the abnormally high melting point of the methyl derivatives;[4] these are 195° and 163° for the trimer and tetramer respectively, whilst the analogous ethyl tetramer is a liquid at room temperature.[5]

Experimental

Crystals of octamethylcyclotetraphosphonitrile, recrystallised from light petroleum, were kindly prepared by Searle.[4] Small equant crystals of maximum dimension 0·30 mm. were sealed inside a thin-walled glass capillary tube, to prevent hydration.

The photographs were taken at 140° K, by cooling the crystals in a stream of cold, dry nitrogen, in the apparatus described by Robertson.[6] The cell dimensions were obtained from oscillation photographs in the Straumanis position. Multiple-film, equi-inclination Weissenberg photographs of the *a* and *c* axes were recorded for the layers 0*kl* to 10*kl* and *hk*0 to *hk*4. A total of 817 of the possible 886 reflections gave measurable intensities; these were estimated visually by comparison with a calibration strip. Lorentz polarisation factors were calculated and applied on the Leeds University Pegasus computer by a method devised by Dr. F. M. Lovell. No correction was made for absorption.

The three-dimensional refinement was carried out on the Leeds University Pegasus[7] computer by the method of least squares, using the SFLS programme. The scattering factor used for phosphorus was that of Tomiie and Stam,[8] and for carbon, nitrogen, and hydrogen those of Berghuis *et al.*[9] were used; $1/F_0$ was used throughout as the weighting factor.[7] Calculation of the molecular dimensions and analysis of the thermal motion were carried out on the Pegasus computer.[7]

Crystal Data.—$[PN(CH_3)_2]_4$, $M = 300{\cdot}2$, m. p. 163°, tetragonal prisms, $a = b = 15{\cdot}705 \pm 0{\cdot}010$, $c = 6{\cdot}425 \pm 0{\cdot}005$ Å, $U = 1584{\cdot}7$ Å^3, $D_m = 1{\cdot}19$ g./c.c. (measured by flotation in a liquid in which the crystals are slightly soluble), $Z = 4$, $D_c = 1{\cdot}258$ g./c.c., $F(000) = 640$. Space group $I4_1/a$ (C^6_{4h}, No. 88), origin at $\bar{1}$, molecular symmetry $\bar{4}$, Cu-K_α radiation, $\mu = 39{\cdot}4$ cm.$^{-1}$.

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[1] Part VIII, Chapman and Paddock, *J.*, in the press.

[2] (*a*) Ketelaar and de Vries, *Rev. Trav. chim.*, 1939, **58**, 1081; (*b*) Wilson and Carroll, *J.*, 1960, 2548; (*c*) McGeachin and Tromans, *J.*, 1961, 4777.

[3] Bullen, *Proc. Chem. Soc.*, 1960, 425.

[4] Searle, *Proc. Chem. Soc.*, 1959, 7.

[5] Bilbo, *Z. Naturforsch.*, 1960, **15*b***, 330.

[6] Robertson, *J. Sci. Instr.*, 1960, **37**, 41.

[7] Cruickshank, Pilling, Bujosa, Lovell, and Truter, "Symposium on Computer Methods," Pergamon Press Ltd., London, 1961.

[8] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

[9] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendall, *Acta Cryst.*, 1955, **8**, 478.

TABLE 1.

Observed and calculated structure factors (× 10) (Reflections which are too weak to be measured are not included.)

	$\lvert F_o \rvert$	F_c
	0,0,*l*	
4	495	−481
	0,1,*l*	
1	1668	−1816
3	664	−666
5	82	78
7	46	25
	0,2,*l*	
0	1133	−1199
2	91	−87
4	227	240
6	236	−227
8	48	46
	0,3,*l*	
1	122	116
3	469	−456
5	360	−359
7	229	216
	0,4,*l*	
0	1764	−1961
2	1153	−1060
4	477	473
6	218	204
	0,5,*l*	
1	321	335
3	1171	1108
5	44	−37
7	63	−66
	0,6,*l*	
0	1318	1325
2	410	397
4	245	−246
6	110	119
	0,7,*l*	
1	750	−763
3	151	152
5	374	365
7	180	−162
	0,8,*l*	
0	76	81
2	658	657
4	112	−124
6	434	−440
	0,9,*l*	
1	50	−39
3	614	−612
5	492	−496
7	282	272
	0,10,*l*	
0	449	−396
2	466	−476
4	161	−162
6	382	368
	0,11,*l*	
1	69	−88
3	138	128
5	44	41
	0,12,*l*	
0	521	−546
2	112	125
4	115	109
6	261	249
	0,13,*l*	
1	296	319
3	361	365
5	361	315
	0,14,*l*	
0	202	195
2	355	357
4	45	37
	0,15,*l*	
1	164	160
3	126	−128
5	256	−249
	0,16,*l*	
0	357	353
2	70	−72
4	383	−348
	0,17,*l*	
1	243	−266
3	509	−456
	0,18,*l*	
0	390	−372
2	198	−191
	0,19,	
1	140	150
	0,20,*l*	
0	41	−35
	1,1,*l*	
2	1039	−1033
4	250	264
8	145	−134
	1,2,*l*	
1	500	−524
3	216	226
5	388	−423
7	248	−226
	1,3,*l*	
2	286	279
4	811	−826
8	312	318
	1,4,*l*	
1	495	−478
3	287	−268
5	450	417
7	293	272
	1,5,*l*	
2	429	442
4	326	317
6	73	76
8	70	−91
	1,6,*l*	
1	125	111
3	171	180
5	174	175
	1,7,*l*	
2	90	−85
4	513	533
6	61	−54
	1,8,*l*	
1	193	168
3	357	354
5	489	−511
7	293	−268
	1,9,*l*	
2	93	79
4	669	−711
6	33	−19
	1,10,*l*	
1	293	277
3	687	−690
5	177	200
7	174	187
	1,11,*l*	
2	551	−540
4	178	178
6	114	101
	1,12,*l*	
1	515	−492
3	370	369
5	167	178
	1,13,*l*	
2	515	522
4	165	160
	1,14,*l*	
1	115	114
3	96	91
5	107	−104
	1,15,	
2	187	183
4	95	−105
	1,16,*l*	
1	349	342
3	316	−276
5	104	−126
	1,17,*l*	
2	648	−551
	1,18,*l*	
1	339	−316
3	213	198
	1,19,*l*	
2	202	215
	2,1,*l*	
1	615	−659
3	535	−552
5	234	236
7	168	−148
	2,2,*l*	
0	56	53
2	411	−414
4	107	105
6	394	−397
8	34	28
	2,3,*l*	
1	603	595
3	292	−370
5	533	−534
7	304	299
	2,4,*l*	
0	531	570
2	542	−532
4	69	43
6	557	541
8	70	91
	2,5,*l*	
1	225	199
3	220	275
5	387	367
7	91	−88
	2,6,*l*	
0	74	51
2	145	−143
4	469	468
6	226	−218
	2,7,*l*	
1	215	−211
3	548	551
5	85	−80
7	146	−135
	2,8,*l*	
0	144	143
2	392	374
4	187	−183
6	352	−368
	2,9,*l*	
1	63	38
3	375	−378
5	288	−317
7	172	184
	2,10,*l*	
0	551	581
2	398	−401
4	191	−198
6	333	325
	2,11,*l*	
1	755	−778
3	75	−61
5	223	243
	2,12,*l*	
0	983	−1037
2	119	131
4	269	282
	2,13,*l*	
1	517	546
3	391	396
5	141	−163
	2,14,*l*	
0	307	292
2	133	139
4	190	−181
	2,15,*l*	
1	56	46
3	50	28
5	50	−51
	2,16,*l*	
0	304	300
2	106	117
4	213	−201
	2,17,*l*	
1	321	−367
3	291	−288
	2,18,*l*	
0	673	−591
2	48	45
	2,19,*l*	
1	306	331
	2 20*l*,	
0	151	177
	3,1,*l*	
2	138	−120
4	114	−110
6	69	−62
8	128	−122
	3,2,*l*	
1	926	968
3	174	−189
5	263	−273
7	156	−151
	3,3,*l*	
2	661	−623
4	492	−536
8	323	356
	3,4,*l*	
1	466	−440
3	492	−474
5	316	304
7	450	378
	3,5,*l*	
2	82	−73
4	311	306
6	219	230
	3,6,*l*	
1	736	−679
3	561	541
5	247	232
7	210	−187
	3,7,*l*	
2	971	1003
4	170	158
6	297	−317
	3,8,*l*	
1	741	707
5	349	−362
7	28	−32
	3,9,*l*	
2	281	−275
4	235	−225
6	62	58
	3,10,*l*	
1	150	152
3	316	−360
5	61	−46
	3,11,*l*	
2	804	−780
4	36	23
6	216	192
	3,12,*l*	
1	697	−693
3	321	345
5	230	219
	3,13,*l*	
2	730	706
4	66	−56
6	93	−103
	3,14,*l*	
1	323	315
3	160	−159
5	69	60
	3,15,*l*	
2	88	95
4	206	171
	3,16,*l*	
1	239	244
	3,17,*l*	
2	398	−348
4	80	−82
	3,18,*l*	
1	287	−255
3	109	116
	3,19,*l*	
2	81	94
	4,1,*l*	
1	1415	1398
3	208	196
5	209	−177
7	173	−167
	4,2,*l*	
0	1636	1707
2	141	−120
4	449	−455
6	141	−146
	4,3,*l*	
1	461	−460
3	423	−404
5	78	82
7	118	111
	4,4,*l*	
0	56	55
2	343	−303
4	330	−338
6	125	119
	4,5,*l*	
1	106	−133
3	548	−550
5	289	342
7	63	56
	4,6,*l*	
0	704	−617
2	67	−73
4	802	792
6	18	−15
	4,7,*l*	
1	937	893
3	528	551
5	347	−382
7	63	−54
	4,8,*l*	
0	915	851
2	96	−101
4	193	−186
6	57	50
	4,9,*l*	
1	278	−277
3	59	54
5	149	167
7	141	−155
	4,10,*l*	
0	106	109
2	68	−54
4	154	−169
6	358	−346
	4,11,*l*	
1	404	−404
3	351	−362
	4,12,*l*	
0	378	−309
2	98	−98
4	264	303
6	61	70
	4,13,*l*	
1	113	116
3	188	196
5	210	−210
	4,14,*l*	
0	190	158
2	47	−28
4	59	−51
	4,15,*l*	
1	59	−42
3	219	217
5	132	160
	4,16,*l*	
0	83	−76
2	120	112
4	61	−48
	4,17,*l*	
1	41	−25
3	41	23
	4,18,*l*	
0	63	−59
2	115	116
	5,1,*l*	
2	1037	1035
4	326	−318
6	190	−181
	5,2,*l*	
1	224	235
3	786	−789
5	216	−204
	5,3,*l*	
2	811	−812
4	289	301
6	128	138
	5,4,*l*	
1	258	−237
3	54	39
5	110	−122
7	41	−41
	5,5,*l*	
2	300	−298
4	109	−108
6	116	125
	5,6,*l*	
1	117	−113
3	467	465
5	322	316
7	94	91
	5,7,*l*	
2	823	825
4	207	−215
6	155	−163
	5,8,*l*	
1	278	272
3	522	−509
7	83	82
	5,9,*l*	
2	325	−324
4	363	385
6	45	−40
	5,10,*l*	
1	214	−198
3	328	315
5	338	−384
	5,11,*l*	
4	291	−296
6	111	108
	5,12,*l*	
1	86	90
5	255	236
	5,13,*l*	
2	50	−48
	5,14,*l*	
3	106	−115
5	119	127
	5,15,*l*	
4	196	178
	5,16,*l*	
1	84	−93
3	141	127
	5,17,*l*	
2	225	221
4	118	−140
	5,18,*l*	
1	198	201
3	97	−123
	5,19,*l*	
2	174	−233
	6,1,*l*	
1	1103	1136
3	571	551

TABLE 1. (*Continued.*)

	$\lvert F_o\rvert$	F_c
	6.1,*l*	
5	342	−290
7	132	−119
	6,2,*l*	
0	417	441
2	228	−196
4	797	−811
6	63	−60
	6,3,*l*	
1	765	−769
3	284	−291
5	508	492
7	80	−72
	6,4,*l*	
0	172	−157
2	521	492
4	183	185
6	260	−257
	6,5,*l*	
1	34	−32
3	463	−446
5	127	−124
7	216	208
	6,6,*l*	
0	332	−325
4	226	228
6	375	375
	6,7,*l*	
1	664	633
3	54	33
5	62	−50
7	104	−105
	6,8,*l*	
0	352	329
2	511	−507
4	177	−166
6	93	86
	6,9,*l*	
1	200	−196
3	288	286
5	232	247
7	154	−249
	6,10,*l*	
0	166	−153
2	421	409
6	475	−490
	6,11,*l*	
1	330	328
3	300	−269
5	235	−196
	6,12,*l*	
0	549	548
2	227	−220
4	74	67
6	150	170
	6,13,*l*	
1	416	−443
3	150	−149
5	89	85
	6,14,*l*	
0	409	−412
2	187	−188
4	03	170
	6,15,*l*	
1	70	63
3	292	244
	6,16,*l*	
2	76	68
	6,17,*l*	
1	214	227
3	166	166
	6,18,*l*	
0	502	493
	6,19,*l*	
1	298	−375
	7,1,*l*	
2	676	695
4	154	156
6	216	−218
	7,2,*l*	
1	67	−28
3	282	−282
5	186	−176
7	51	46
	7,3,*l*	
2	83	−77
4	435	451
6	116	122
	7,4,*l*	
1	453	444
3	518	534
5	313	−291
7	339	−309
	7,5,*l*	
2	252	−259
4	433	−429
6	45	−4
	7,6,	
3	245	−239
5	178	169
7	252	244
	7,7,*l*	
2	312	−311
4	77	−80
6	70	74
	7,8,*l*	
1	459	−455
3	113	−116
5	291	282
7	39	38
	7,9,*l*	
2	385	401
4	389	418
6	182	−145
	7,10,*l*	
1	138	149
3	336	335
5	298	−343
	7,11,*l*	
2	358	361
4	252	−263
	7,12,*l*	
1	411	427
3	372	−338
5	66	−52
	7,13,*l*	
2	711	−735
	7,14,*l*	
1	442	−465
3	256	231
5	174	192
	7,15,*l*	
2	227	215
4	44	39
	7,16,*l*	
1	47	−50
	7,17,*l*	
2	372	369
	7,18,*l*	
1	336	349
	8,1,*l*	
1	393	−357
3	276	268
5	56	40
7	136	−127
	8,2,*l*	
0	733	−671
2	326	307
6	63	61
	8,3,*l*	
1	329	345
3	393	387
5	164	185
7	76	−77
	8,4,*l*	
0	145	121
2	460	440
6	382	−388
	8,5,*l*	
3	154	−140
5	300	−305
7	190	186
	8,6,*l*	
0	210	196
2	66	−39
4	372	−385
6	266	294
	8,7,*l*	
1	452	−441
3	495	−493
5	284	290
7	81	−98
	8,8,*l*	
0	710	−685
2	86	−83
4	332	349
6	126	101
	8,9,*l*	
1	444	449
3	343	360
	8,10,*l*	
0	155	137
2	109	106
4	132	−132
6	78	−88
	8,11,*l*	
1	332	329
3	63	50
5	57	−48
	8,12,*l*	
0	556	561
4	242	−225
	8,13,*l*	
1	387	−410
3	386	−395
5	166	164
	8,14,*l*	
0	431	−427
2	38	−30
4	408	373
	8,15,*l*	
1	145	143
3	83	87
	8,16,*l*	
2	166	−147
	8,17,*l*	
1	127	122
3	108	148
	8,18,*l*	
0	351	343
	9,1,*l*	
2	304	−295
4	481	449
6	57	−36
	9,2,*l*	
1	427	−409
3	378	370
5	68	−36
	9,3,*l*	
2	851	822
4	110	107
	9,4,*l*	
1	463	436
3	76	−60
5	338	−320
7	187	−209
	9,5,*l*	
2	283	−268
4	273	−262
6	29	−20
	9,6,*l*	
1	222	211
3	169	−163
5	107	99
7	81	105
	9,7,*l*	
2	762	−797
4	87	91
6	89	82
	9,8,*l*	
1	720	−691
3	411	399
5	213	212
	9,9,*l*	
2	706	718
6	92	−89
	9,10,*l*	
1	255	249
3	387	−375
5	85	−85
	9,11,*l*	
2	44	46
4	179	157
	9,12,*l*	
1	329	344
3	76	62
5	221	−204
	9,13,*l*	
2	382	−402
4	188	−155
	9,14,*l*	
1	276	−301
3	297	255
	9,15,*l*	
2	195	168
4	92	−101
	9,16,*l*	
1	117	−106
3	210	−220
	9,17,*l*	
2	63	69
	10,1,*l*	
1	679	−683
3	58	24
5	216	209
7	70	−79
	10,2,*l*	
0	1275	−1265
2	109	−131
4	343	333
6	44	−30
	10,3,*l*	
1	849	871
3	769	753
5	216	−208
	10,4,*l*	
0	827	851
2	139	152
4	417	−412
6	98	−105
	10,5,*l*	
1	269	−245
3	83	−73
	10,6,*l*	
0	402	389
2	283	289
4	71	−61
6	57	−51
	10,7,*l*	
1	654	−689
3	427	−457
	10,8,*l*	
0	1226	−1238
4	262	273
6	76	70
	10,9,*l*	
1	558	567
3	200	209
5	131	−126
	10,10,*l*	
0	369	385
2	248	−251
4	233	−231
	10,11,*l*	
1	74	−68
3	272	296
5	245	258
	10,12,*l*	
0	285	270
2	425	460
4	114	−102
	10,13,*l*	
1	57	45
3	369	−344
	10,14,*l*	
0	129	−134
2	71	−79
4	63	66
	10.15,*l*	
3	174	−160
	10,16,*l*	
0	211	−180
2	243	−253
	11,1,*l*	
2	547	−549
	11,2,*l*	
1	713	−756
3	166	163
5	175	179
	11,3,*l*	
2	849	842
6	121	−106
	11,4,*l*	
1	595	638
3	262	−265
	11,5,*l*	
2	97	−95
4	150	152
	11,6,*l*	
1	227	217
3	171	167
5	171	−178
	11,7,*l*	
2	408	−425
4	205	−212
6	60	−62
	11,8,*l*	
1	499	−527
3	73	74
	11,9,*l*	
2	177	194
4	116	−106
	11,10,*l*	
1	88	96
3	245	−269
5	266	308
	11,11,*l*	
4	507	459
	11,12,*l*	
1	158	159
3	337	299
	11,13,*l*	
2	141	150
4	258	−264
	11,14,*l*	
1	55	65
3	216	−196
	11,15,*l*	
2	215	−218
	11,16,*l*	
1	173	−182
	12,1,*l*	
1	104	−105
3	280	−251
5	47	−32
	12,2,*l*	
0	301	−295
2	350	−341
4	271	279
6	148	146
	12,3,*l*	
1	283	272
3	427	444
5	44	−45
	12,4,*l*	
0	801	779
2	87	96
4	153	−161
6	145	174
	12,5,*l*	
1	173	−173
3	73	49
5	187	168
	12,6,*l*	
0	70	−50
2	141	115
6	363	−406
	12,7,*l*	
1	110	−107
3	144	−138
5	404	−372
	12,8,*l*	
0	320	−318
2	121	−106
4	89	−78
	12,9,*l*	
1	80	−50
5	91	97
	12,10,*l*	
2	66	−51
4	157	140
	12,11,*l*	
1	89	−108
3	320	277
	12,12,*l*	
0	76	−79
2	281	259
4	63	−54
	12,13,*l*	
1	196	233
3	65	−59
	12,14,*l*	
0	287	268
2	46	−43
	12,15,*l*	
1	158	−170
	12,16,*l*	
0	269	−272
	13,1,*l*	
2	89	−78
4	421	−429
6	86	83
	13,2,*l*	
1	150	−150
3	95	−83
5	447	393
	13,3,*l*	
2	116	111
4	268	264
	13,4,*l*	
1	108	111
3	76	−70
5	72	58
	13,5,*l*	
2	140	122
4	222	211
	13,6,*l*	
1	132	126
3	87	89
5	352	−333
	13,7,*l*	
2	76	81
4	417	−407
	13,8,*l*	
1	109	110
3	213	−220
5	75	74
	13,9,*l*	
2	327	−377
4	82	68
	13,10,*l*	
1	310	−354
3	240	210

TABLE 1. (*Continued.*)

	$\lvert F_o \rvert$	F_c
	13,11,l	
2	266	235
4	187	200
	13,12,l	
1	78	77
	13,13,l	
2	181	187
	13,14,l	
1	313	322
	14,1,l	
1	276	272
3	348	−343
5	193	−179
	14,2,l	
0	325	291
2	257	−264
4	73	70
	14,3,l	
1	349	−354
3	76	−68
5	291	240
	14,4,l	
0	384	−398
2	115	−116
4	250	225
	14,5,l	
1	213	209
3	238	253

	$\lvert F_o \rvert$	F_c
	14,6,l	
0	279	286
2	85	75
4	83	−77
	14,7,l	
1	209	211
5	203	−229
	14,8,l	
0	532	545
2	125	−121
4	222	−206
	14,9,l	
1	454	−498
3	202	−194
	14,10,l	
0	632	−682
2	50	25
4	287	308
	14,11,l	
1	178	204
3	176	164
	14 ,12,l	
0	134	111
	14,14,l	
0	320	292
	15,1,l	
2	99	101
4	300	−273

	$\lvert F_o \rvert$	F_c
	15,2,l	
1	70	40
3	231	−247
5	82	77
	15,3,l	
2	430	−444
4	198	174
	15,4,l	
1	346	−358
3	353	327
5	109	139
	15,5,l	
2	330	336
4	44	40
	15,6,l	
1	227	237
3	102	−90
	15,7,l	
2	112	112
4	104	−103
	15,8,l	
1	180	198
3	313	−285
	15,9,l	
2	403	−385
4	57	53

	$\lvert F_o \rvert$	F_c
	15,10,l	
1	336	−316
3	370	344
	15,11,l	
2	316	296
	15,12,l	
1	97	94
	16,1,l	
3	187	−176
	16,2,l	
0	54	18
2	38	−31
4	96	−86
	16,3,l	
1	242	−251
3	306	−261
	16,4,l	
0	508	−516
2	64	64
4	414	431
	16,5,l	
1	301	335
3	255	228
	16,6,l	
0	345	303
2	86	−85
4	271	−222

	$\lvert F_o \rvert$	F_c
	16,8,l	
0	295	299
2	94	−84
	16,9,l	
1	221	−220
3	146	−145
	16,10,l	
0	284	−243
2	104	109
	16,11,l	
1	190	204
	16,12,l	
0	102	99
	17,1,l	
2	165	−150
4	142	139
	17,2,l	
1	160	180
3	153	123
	17,3,l	
2	297	−271
4	171	−171
	17,4,l	
1	228	−259
3	294	279

	$\lvert F_o \rvert$	F_c
	17,5,l	
2	255	239
4	44	−53
	17,6,l	
1	72	−70
3	265	−267
	17,8,l	
1	148	148
3	49	62
	17,9,l	
2	32	−28
	17,10,l	
1	108	111
	18,1,l	
1	219	−221
3	121	116
	18,2,l	
0	80	73
2	357	359
	18,3,l	
1	70	68
3	215	−220
	18,4,l	
0	196	−162
2	44	−49

	$\lvert F_o \rvert$	F_c
	18,5,l	
1	44	44
3	32	−28
	18,6,l	
0	196	−176
2	164	−172
	18,7,l	
1	46	−36
	18,8,l	
0	42	31
	19,1,l	
2	88	−93
	19,2,l	
1	150	165
	19,3,l	
2	28	29
	19,4,l	
1	50	−42
	19,5,l	
2	86	−121
	19,6,l	
1	148	−206
	20,2,l	
0	158	135

TABLE 2.

Atomic co-ordinates in Å (σ is the standard deviation in Å).

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
P	1·7646	0·0006	2·9019	0·0006	1·0113	0·0008
N	0·541	0·002	2·212	0·003	0·264	0·003
C_1	3·200	0·003	2·528	0·004	−0·011	0·004
C_2	2·140	0·004	2·122	0·004	2·599	0·004
H_1	4·07	0·04	2·92	0·04	0·49	0·04
H_2	3·07	0·04	3·12	0·05	−0·97	0·05
H_3	3·27	0·04	1·60	0·04	−0·19	0·05
H_4	3·05	0·05	2·47	0·05	3·00	0·05
H_5	1·35	0·05	2·23	0·05	3·35	0·06
H_6	2·32	0·05	1·07	0·05	2·48	0·06

TABLE 3.

Thermal parameters (units in 10^{-4} Å^2).

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{13}	σ	U_{23}	σ
P	199	3	193	3	294	4	7	4	−23	5	−67	5
N	191	10	285	12	385	14	23	18	−195	21	−27	20
C_1	234	12	438	18	473	18	6	24	−247	30	−6	26
C_2	513	20	324	16	407	17	10	28	136	28	−229	28

	U	σ		U	σ		U	
H_1	157	99	H_3	170	105	H_5	375	142
H_2	343	135	H_4	337	144	H_6	348	142

TABLE 4.

Magnitude and direction of the principal axes of the ellipsoids of thermal motion with respect to the crystallographic axes. (l, m, and n are direction cosines.)

	Å^2	l	m	n		Å^2	l	m	n
P	0·0188	−0·951	−0·041	−0·306	C_1	0·0234	−1·000	+0·010	−0·007
	0·0306	−0·301	−0·106	+0·948		0·0580	−0·012	−0·656	+0·755
	0·0192	−0·072	+0·994	+0·088		0·0331	+0·003	+0·755	+0·656
N	0·0190	−0·995	+0·101	−0·018	C_2	0·0271	+0·270	−0·751	+0·603
	0·0446	−0·069	−0·521	+0·851		0·0593	−0·814	+0·157	+0·559
	0·0226	+0·077	+0·848	+0·525		0·0380	+0·514	+0·642	+0·569

STRUCTURE DETERMINATION

The position of the phosphorus atom was found from the Patterson synthesis projected down [*c*]. Fourier methods were used to locate the positions of the nitrogen and the carbon atoms; these four atoms (and six hydrogen atoms) in the 16-fold general positions are sufficient to define the structure. Two-dimensional refinement, by alternate structure-factor and difference Fourier calculations, was discontinued at $R(hk0) = 0{\cdot}16$.

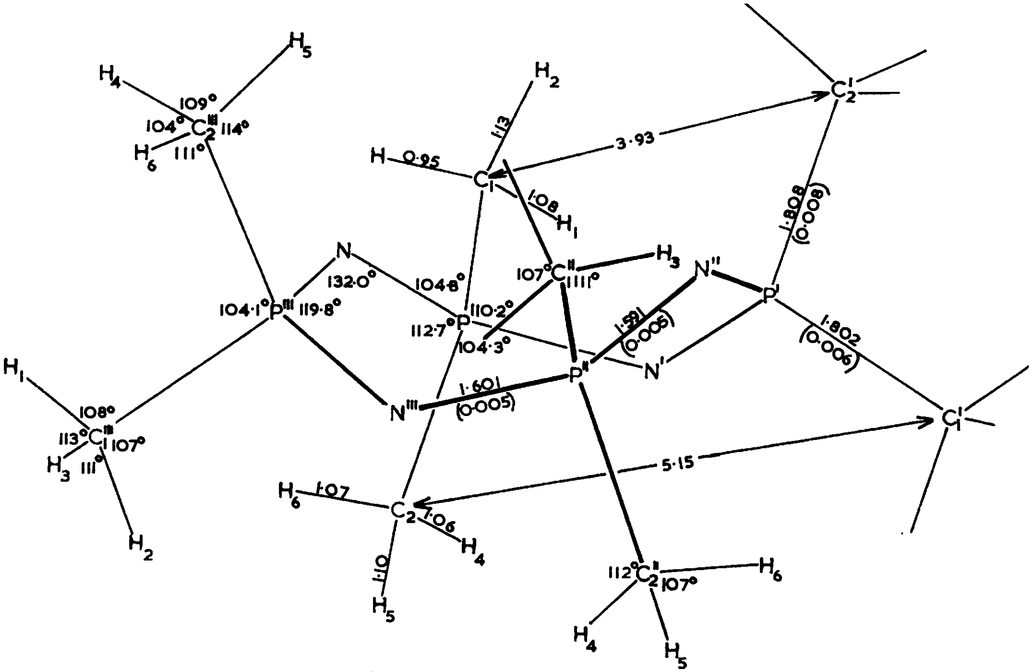

FIG. 1. The bond lengths (Å) and angles in the $[PN(CH_3)_2]_4$ molecule. The sum of the standard deviation and thermal motion correction is shown in Å in parentheses; for the angles at the phosphorus atom this value is 0·2° and 0·3° for the angle NPN'.[10]

The *z*-co-ordinate of the phosphorus atom was obtained from the 0*kl* Patterson synthesis. The *x*, *y*, and *z* parameters were refined simultaneously in this projection to $R(0kl) = 0{\cdot}13$. Individual isotropic temperature factors were applied in the last two calculations.

TABLE 5.

Magnitudes and directions of the principal axes of translational and oscillational ellipsoids.

Å²	*l*	*m*	*n*	*θ*	*l*	*m*	*n*
0·0188	+0·5209	−0·8536	−0·0014	1·50°	+0·0003	+0·0001	+1·0000
0·0197	−0·0014	−0·0006	+1·0000	2·97	−0·8599	−0·5105	+0·0003
0·0188	+0·8763	+0·4818	+0·0010	2·79	−0·5105	+0·8599	+0·0000

Corrections to the atomic co-ordinates due to the thermal motion (Å).

	x	*y*	*z*		*x*	*y*	*z*
P	+0·0027	−0·0017	+0·0005	C_1	+0·0044	−0·0021	−0·0018
N	+0·0009	−0·0027	−0·0013	C_2	+0·0030	−0·0027	+0·0040

The initial cycle of three-dimensional refinement was computed with isotropic temperature factors, individual anisotropic temperature factors being used thereafter. During five cycles of refinement, *R* decreased from 0·262 to 0·077. Examination of the low-order reflections revealed that extinction alone could not account for the discrepancy between the observed and

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[10] Darlow, *Acta Cryst.*, 1960, **13**, 683.

the calculated structure factors. The contributions of the six hydrogen atoms were consequently included. The hydrogen atoms were placed in the staggered orientation with respect to the other ligands on the phosphorus atom, and the co-ordinates were chosen to make the C–H bond length equal to 1·09 Å. An isotropic temperature factor corresponding to a mean-square amplitude of vibration of 0·06 Å was used. After three further cycles, in which all the atoms were allowed to move, a final *R* of 0·057 was obtained (observed reflections only). The refinement was judged to be complete when the shifts in the atoms, excluding hydrogen atoms, were less than one-third of their estimated standard deviation. The validity of the hydrogen atom co-ordinates is indicated by the decrease of their thermal motion during the refinement (Table 3).

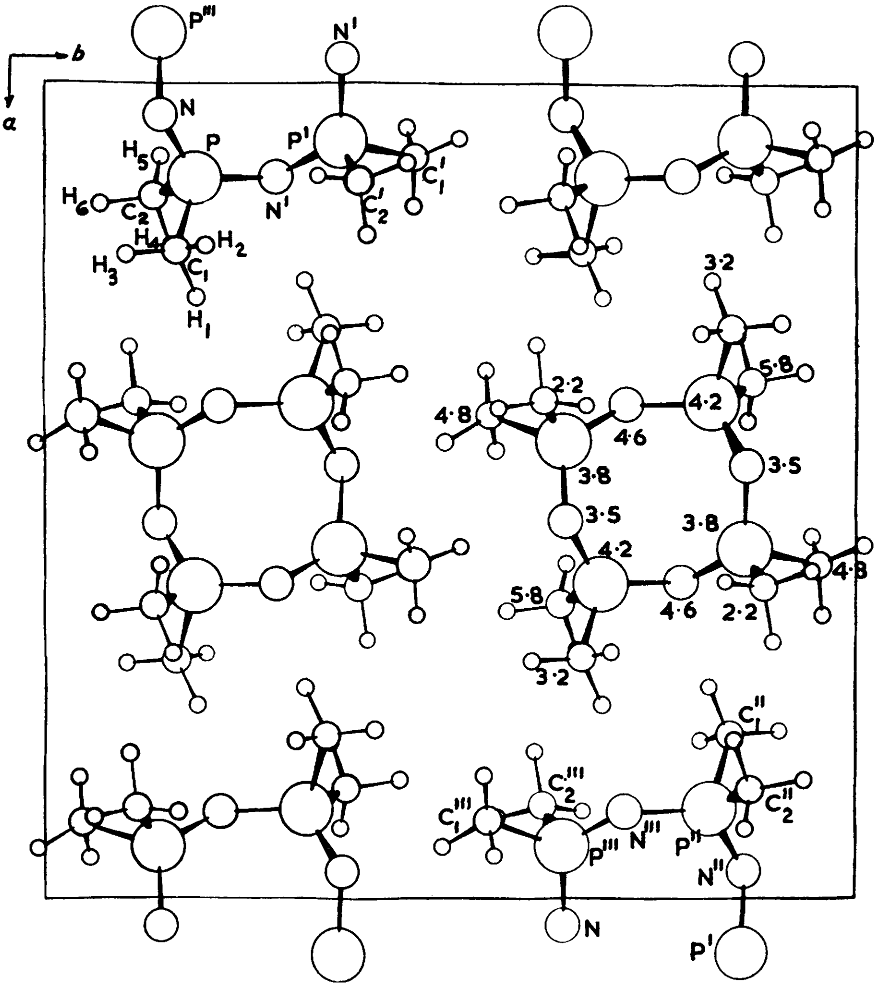

FIG. 2. Projection of the structure down the *c* axis. The heights of the atoms are in Å.

Results.—A list of observed and calculated structure factors for the observed reflections is given in Table 1. The final atomic co-ordinates with their standard deviations are given in Table 2; co-ordinates with four places of decimals were used to calculate the bond lengths and angles given in Fig. 1. The low values found for the standard deviations are partly due to the small thermal motion observed at this temperature.

Table 3 shows the parameters of anisotropic thermal motion for the four heavy atoms, and the isotropic thermal motion for the hydrogen atoms. The U_{ij} values, which give the magnitudes and orientation of the vibration ellipsoids with respect to the crystallographic axes, were used to calculate the principal axes of the vibration ellipsoids for each atom and their direction cosines with respect to the tetragonal axes (Table 4).[11] The direction of the maximum amplitude of vibration for the phosphorus atom almost coincides with the normal to the plane containing the phosphorus atom and the two adjacent nitrogen atoms. No simple correlation can be found relating a molecular axis with the ellipsoid of vibration for the nitrogen atom. The assumption was made that the molecule behaves as a rigid body in order that the anisotropic thermal parameters could be analysed into translational and oscillational motion.[12] The results are given in Table 5, which also includes the corrections to the co-ordinates due to the rotational oscillations. The effects of these corrections [13] on the bond lengths and angles are very small (0·003 Å and less than 0·1°), because the intensity data were recorded at 140° K; they are not exact since the agreement between the observed and the calculated values of U_{ij} indicate some internal vibrations. Since the corrections increase the uncertainty of the molecular dimensions they have been added to the standard deviations; the sum is shown in Fig. 1.

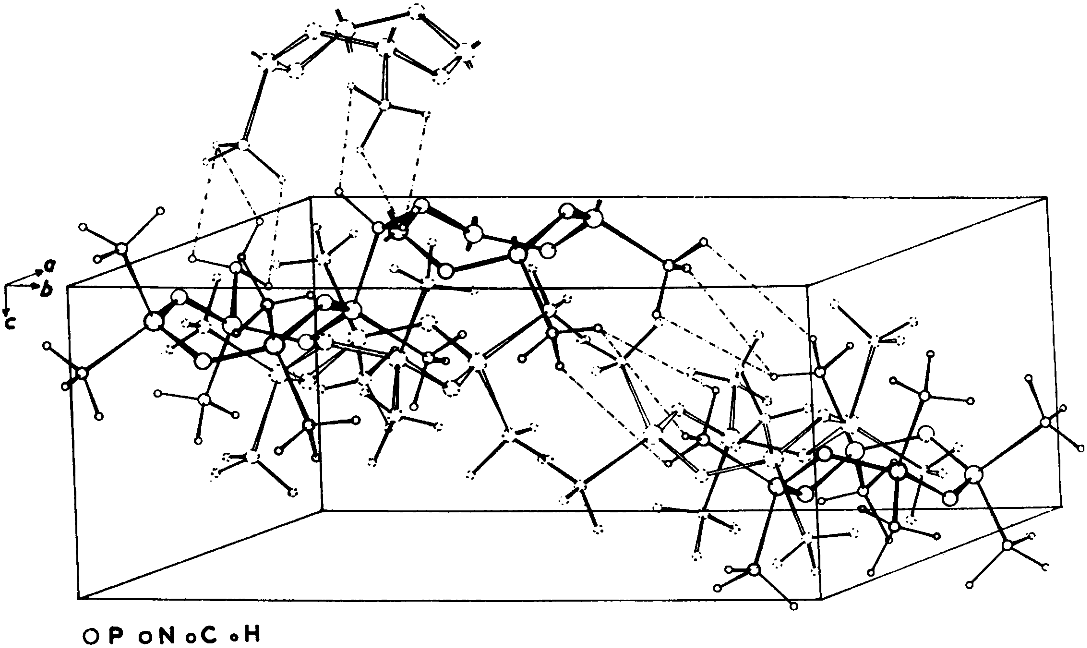

FIG. 3. A clinographic drawing of the structure. Molecules are shown whose centres are at 0, $\frac{1}{4}$, $\frac{1}{8}$; 1, $\frac{1}{4}$, $\frac{1}{8}$; 1, $\frac{3}{4}$, $\frac{7}{8}$ (drawn with solid lines), and $\frac{1}{2}$, $\frac{1}{4}$, $\frac{3}{8}$; $\frac{1}{2}$, $\frac{1}{4}$, $-\frac{5}{8}$; $\frac{1}{2}$, $\frac{3}{4}$ $\frac{5}{8}$ (drawn with open bonds and dotted circles). Chain lines show the short H · · · H distances between interlocking methyl groups.

Description of the Structure.—The structure is composed of discrete molecules of $[PN(CH_3)_2]_4$, forming puckered eight-membered rings whose mean planes are parallel to the *ab* plane and related to each other by glide planes (Figs. 2 and 3). The ring consists of alternate phosphorus and nitrogen atoms related by $\bar{4}$ symmetry. The departure of the ring from planarity may be assessed by the difference in *z* co-ordinates of adjacent phosphorus (0·42 Å) and nitrogen atoms (1·08 Å).

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[11] Cruickshank, *Acta Cryst.*, 1956, **9**, 747.
[12] Cruickshank, *Acta Cryst.*, 1956, **9**, 754.
[13] Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

The molecular dimensions are shown in Fig. 1. The difference of $0{\cdot}009_6$ Å between the two P–N bond lengths ($1{\cdot}591_1$ and $1{\cdot}600_7$ Å) is not significant;[14]

$$\begin{aligned}&\sigma^2(\Delta l) = \\ &\sigma^2(P) + \sigma^2(N) - \sigma^2(P)\cos\angle\,NPN - \sigma^2(N)\cos\angle PNP \text{ in the direction } P\text{–}N\ + \\ &\sigma^2(P) + \sigma^2(N) - \sigma^2(P)\cos\angle NPN - \sigma^2(N)\cos\angle PNP \text{ in the direction } P'\text{–}N = \\ &0{\cdot}0049\ \text{Å}\end{aligned}$$

The P–C bond lengths ($1{\cdot}808_2$ and $1{\cdot}801_8$ Å) are not significantly different; $\sigma(\Delta l) = 0{\cdot}0055$ Å.

Although the bisectors of the angles NPN′ and C_1PC_2 are almost collinear, the dihedral angle between the plane containing NPN′ and C_1PC_2 is 94° 46′.

Intermolecular distances are found to be greater than the sum of the van der Waals radii of the methyl groups (4·0 Å) with the exception of C_1xyz . . . $C_2(\frac{1}{4} + y, \frac{1}{4} - x, -\frac{3}{4} + z)$, which is 3·68 Å.

DISCUSSION

The molecular geometry is unlikely to be greatly affected by van der Waals forces between molecules. Even within the molecule, distances between carbon atoms belonging to different phosphorus atoms can be varied without change of the ring angles at phosphorus and nitrogen. The distance C_1–C_2' (3·93 Å), although only slightly altered by twisting a model of the molecule, may be increased to a value greater than 4 Å. This distance would be less than 3·9 Å if the angle PNP were only 120°; presumably compensation could be achieved by a more puckered ring and greater C_1PN' and C_2PN angles. It is thought, therefore, that in such a flexible molecule the angles in the ring are not controlled by van der Waals forces within the molecule.

The two P–N bond lengths (1·591 and 1·601 Å) are equal within experimental error, and are appreciably shorter than the sum of the single covalent radii[15] (1·76 Å), the value found in sodium phosphoramidate[16] (Table 6). The average P–N bond length is close to that in the trimeric phosphonitrilic chloride (Wilson *et al.*[2]) and to that quoted by Bullen[3] in his preliminary report on the structure of octakisdimethylamidotetraphosphonitrile. The length indicates partial double-bond character, as expected theoretically,[17] though the amount is presumably less than in the tetrameric fluoride (McGeachin *et al.*[2]), which has a shorter P–N bond. The P–C bond is a little shorter than the sum of the covalent radii[15] and is close to those reported for other organic compounds of quinquevalent phosphorus (Table 7).

TABLE 6.

Bond lengths of P–N and P–C in other structures (Å).

P–N	σ		Ref.	P–C	σ		Ref.
1·76	0·02	NaH_3NPO_3	16	1·837	0·007	$[H_2BP(CH_3)_2]_3$	*b*
1·653	0·005	$(NH_2)_3PBH_3$	*a*	1·82, 1·84	0·015	$[(C_2H_5)_2PS]_2$	*c*
1·66, 1·69		$(PNCl_2)_4$	2*a*	1·82, 1·88		$[C_6H_5(CH_3)PS]_2$	*d*
1·57, 1·60, 1·61	0·017	$(PNCl_2)_3$	2*b*	1·813		$(CH_3)_2PO$	*e*
1·59 cyclic		$\{PN[N(CH_3)_2]_2\}$	3	1·87	0·02	$P(CH_3)_3$	*f*
1·75, 1·84 exocyclic				1·937	0·017	$P(CF_3)_3$	*g*
1·49, 1·51, 1·52	0·02	$(PNF_2)_4$	2*c*	1·906	0·02	$P(CF_3)_5$	*h*

References: (*a*) Nordman, *Acta Cryst.*, 1960, **13**, 535. (*b*) Hamilton, *Acta Cryst.*, 1955, **8**, 199. (*c*) Dutta and Wolfson, *Acta Cryst.*, 1961, **14**, 178. (*d*) Wheatley, *J.*, 1960, 523. (*e*) Wang, Forsvaretsforskningsinstitutt (Norway) Intern. Rapport IR–K–225 (1960). (*f*) Springall and Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 996. (*g*) Bowen, *Trans. Faraday Soc.*, 1954, **50**, 463. (*h*) Spencer and Lipscomb, *Acta Cryst.*, 1961, **14**, 250.

The angle at the nitrogen atom in the present structure (132°) is greater than the 120° expected on the simplest basis, though the difference is less than for the fluoride. Such

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[14] Cruickshank and Robertson, *Acta Cryst.*, 1953, **6**, 698.

[15] Pauling, " Nature of the Chemical Bond," Cornell University Press, 3rd edn., pp. 224, 229.

[16] Hobbs, Corbridge, and Raistrick, *Acta Cryst.*, 1953, **6**, 621; Cruickshank, unpublished work.

[17] Craig and Paddock, *Nature*, 1958, **181**, 1052; Craig, *J.*, 1959, 997; Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

an effect is common where chains and rings are formed from alternate first- and second-row elements, notably in octamethylcyclotetrasiloxane [18] (Si–O–Si = 143°), in octamethylcyclotetrasilazane [19] (Si–N–Si = 123°), and in ammonium [20] and sodium tetrametaphosphate [21] (P–O–P = 131° and 133°). The ring angle at phosphorus is almost the same in the octamethylcyclotetraphosphonitrile as in other tetrameric phosphonitriles. The exocyclic C–P–C angle is 104°; it is greater than the F–P–F angle in the fluoride (100°) because of the lower electronegativity of the methyl group.[22]

There is no indication of hydrogen bonding in the structure; all intermolecular C–N distances are greater than 3·59 Å, the sum of the van der Waals radii for the methyl group and nitrogen atom being 3·50 Å. However, a P–C bond of one molecule is directed towards a carbon atom on another to give the distance 3·68 Å; as a result two hydrogen atoms of $C_2(\frac{1}{4} + y, \frac{1}{4} - x, -\frac{3}{4} + z)$ fall in the spaces between the three hydrogen atoms on $C_1(x,y,z)$. Such interlocking of methyl groups has also been observed for sodium hydrogen diacetate,[23] and, aided by the high molecular symmetry, may account in part for the high melting point of the phosphonitrile.

It is a pleasure to thank Dr. M. R. Truter for her valuable advice and Dr. D. W. J. Cruickshank and Mr. N. L. Paddock for helpful discussion. I am grateful to the Directors and staff of the Computing Laboratory for carrying out the computations, to Albright and Wilson (Mfg.) Ltd. for financial support and to the Imperial Chemical Industries Limited for the loan of some of the equipment.

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[18] Steinfink, Post, and Fankuchen, *Acta Cryst.*, 1955, **8**, 420.
[19] Yokoi and Yamasaki, *J. Amer. Chem. Soc.*, 1953, **75**, 4139.
[20] Romers, Ketelaar, and MacGillavry, *Acta Cryst.*, 1951, **4**, 114; Cruickshank, unpublished work.
[21] Ondik, Block, and MacGillavry, *Acta Cryst.*, 1961, **14**, 555.
[22] Linnett and Mellish, *Trans. Faraday Soc.*, 1954, **50**, 657.
[23] Speakman and Mills, *J.*, 1961, 1164.