The Structure of *N*-Methyltrichlorophosphinimine Dimer

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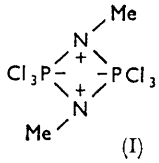
The structure of *N*-methyltrichlorophosphinimine dimer, $(CH_3NPCl_3)_2$, has been determined by three-dimensional Fourier synthesis and full-matrix least-squares refinement of *X*-ray diffraction data. The structure is composed of discrete centrosymmetric dimeric molecules with a planar four-membered ring of alternate phosphorus and nitrogen atoms (P–N–P = 99·5° ± 0·4° and N–P–N = 80·5° ± 0·4°). The co-ordination of each phosphorus atom is approximately a trigonal bipyramid of three chlorine atoms and two nitrogen atoms, one apical and one equatorial. The apical bond distances are P–Cl = 2·133 ± 0·003 Å and P–N = 1·769 ± 0·007 Å; the equatorial are P–Cl = 2·026 ± 0·004 Å and P–N = 1·635 ± 0·007 Å. The co-ordination of the nitrogen is trigonal with a N–C bond distance of 1·475 ± 0·010 Å. The shortness of the P–N bonds and the planar co-ordination of the nitrogen atoms suggest some $d\pi$–$p\pi$ bonding between the phosphorus and nitrogen atoms.

ANY elucidation of the nature of bonding in phosphonitriles is rendered difficult by the dearth of accurate structural data. Detailed crystallographic data are available only for cyclic polymers. The P–N bond distances within the $(P–N)_n$ ring are equal for any given compound of the type $(X_2PN)_n$, but are not necessarily equal if the exocyclic ligands on the phosphorus atoms are not equivalent. A summary of these studies is given in Table 1.[1–7]

In all previous stucture determinations of molecular cyclophosphonitriles, the nitrogen and phosphorus atoms were found to be two- and four-co-ordinate, respectively. Recently, Chapman *et al.*[8] prepared *N*-methyltrichlorophosphinimine dimer and the molecular configuration (I) has been proposed. We have carried



(I)

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TABLE 1
Molecular structures of cyclophosphonitriles as determined by *X*-ray analyses

Compound	P–N length (ring) (Å)	Conformation of ring	Ref.
$(F_2PN)_4$	1·51 ± 0·02	Planar	1
$(Cl_2PN)_3$	1·59$_5$ ± 0·017	Virtually planar	2,3
$(Cl_2PN)_4$	1·570 ± 0·009	Slightly puckered	8
$[(CH_3)_2N]_6P_4N_4$ ...	1·59	Puckered	5
$[(CH_3)_2PN]_4$	1·596 ± 0·005	Puckered	6
$(C_6H_5)_2Cl_4P_3N_3$ *...	1·555 1·578 1·615	Slight chair form	7

* 1,1,3,3-Tetrachloro-5,5-diphenyltriphosphinimine.

out a detailed crystal and molecular structure determination of this compound.

EXPERIMENTAL

Single crystals of *N*-methyltrichlorophosphinimine dimer were prepared using the method of Chapman *et al.*[8] Methylammonium chloride (0·11 mole) and phosphorus pentachloride (0·10 mole) were refluxed in 1,1,2,2-tetrachloroethane (0·1 l.) for 5 hr. The insoluble salts were filtered off, and the solvent was distilled off *in vacuo*. The product was recrystallised from carbon tetrachloride and sublimed at 150°/0·5 torr. Monoclinic needles of dimeric *N*-methyltrichlorophosphinimine were formed, m. p. 160° (decomp.).

Suitable single crystals for *X*-ray analysis were selected by microscopic examination and mounted in 0·3 mm. diameter Lindemann glass capillaries. Selection and mounting of the crystals were done in a dry-box since the compound is hygroscopic.

Crystal Data.—$(CH_3NPCl_3)_2$, $M = 332·7$, monoclinic, space group $P2_1/n$, $a = 6·95 \pm 0·02$, $b = 14·06 \pm 0·03$, $c = 6·02 \pm 0·02$ Å, $\beta = 99·3 \pm 0·2°$, $D_m = 1·93 \pm 0·03$ (by flotation), $Z = 4$ units of (CH_3NPCl_3), $D_c = 1·90$. The space group and lattice parameters were determined using single-crystal precession techniques.

Intensity Data.—Complete three-dimensional *X*-ray diffraction intensity data (up to $\sin\theta/\lambda = 0·7247$) were taken with zirconium-filtered molybdenum K_α radiation from a crystal approximately 0·32 mm. long and 0·17 mm. in diameter. A General Electric XRD-5 *X*-ray unit equipped with a single-crystal orienter and scintillation counter was used, and the data were collected using the stationary-crystal, stationary-counter technique.[9] A forty-second peak height intensity was recorded for each of 2005 reflections (including the systematically extinct reflections of the type $h0l$, $h + l = 2n + 1$). The background intensity, found to be independent of ϕ and χ, was tabulated as a function of 2θ. Four standard reflections were measured periodically; the average decrease in their intensities compared with the number of reflections observed was used to correct for decomposition effects. The maximum decrease in intensity was 18%.

Streak corrections were made using the technique of Benson and Fitzwater,[10] a method essentially equivalent to that of Williams and Rundle.[11] A theoretical curve was used to convert from peak-height into integrated intensity data after the method of Alexander and Smith.[12] Intensities were corrected for Lorentz and polarisation factors. Because of the small absorption coefficient of the compound ($\mu/\rho = 8·9$ cm.^{2}/g.), no absorption correction was made.

Treatment of Errors and "Unobserved" Reflections.—The estimated error in each intensity measurement was calculated by the formula

$$(\Delta I)^2 = C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2 + (K_S C_S)^2 + (K_D D C_T)^2$$

where C_T, C_B, and C_S are the total, background, and streak counts, respectively, and D is the decomposition correction. In addition to the statistical errors, this formula assumes relative errors of K_T, K_B, K_S, and K_D in the total, background, and streak intensities, and in the decomposition correction, respectively. The relative errors assigned are 2% for K_S, and 5% for K_B, K_S, and K_D.

The finite difference method was used to derive the formula for the estimated standard error for each reflection:

$$\Delta F = (\mathrm{Lp})^{-\frac{1}{2}} [(I + \Delta I)^{\frac{1}{2}} - I^{\frac{1}{2}}]$$

where I is the calculated intensity and Lp is the Lorentz-polarisation correction. A reflection having an intensity less than three times its ΔF was considered to be "unobserved" and was not used in the refinement. The standard errors were used during refinement to weight the 801 observed structure factors.

Structure Determination.—The presence of dimeric molecules in a unit cell with space group symmetry of order 4 requires the dimer to be centrosymmetric. The positions of the phosphorus and the three chlorine atoms were obtained from an analysis of the Harker sections of a sharpened Patterson map, the data having been sharpened using a programme of Granoff and Jacobson.[13] Using these four atoms to determine the signs, an electron-density map was then computed which revealed the positions of the nitrogen and carbon atoms in the asymmetric unit. The hydrogen atoms were neglected for this structure determination. The Patterson and electron-density maps were computed using the programme of Ledet.[14] The HFS atomic scattering factors [15] were used in all structure-factor calculations. All computations were performed using an IBM 7074 computer.

A full-matrix least-squares refinement was initiated with all atoms isotropic, using the programme of Fitzwater.[16] When the residual factor $(R = \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ reached 0·233, anisotropic refinement was begun. The final *R*-factor was 0·0574; the weighed *R*-factor $\{R_{\mathrm{weighted}} = \Sigma||(F_o/\sigma)| - |(F_c/\sigma)||/\Sigma|(F_o/\sigma)|\}$ was 0·0561. A list of the calculated and observed structure factors is given in Table 2 on an absolute scale. The final positional and thermal parameters and their errors are given in Table 3. The interatomic distances and angles, and their errors, were

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TABLE 2

Observed and calculated structure factors for $(CH_3NPCl_3)_2$. (The first column contains the running index k, the second $10|F_o|$, and the third $10F_c$)

0 k 0

4	1001	-1087
6	146	-163
8	61	-64
10	262	268
16	169	161
18	159	-136
20	125	-108

0 k 1

1	798	817
2	62	-115
3	245	-218
4	699	668
7	276	-265
8	100	-75
9	138	-128
10	176	181
11	207	189
12	80	-51
13	57	50
14	83	90
15	90	86
17	55	-49
18	55	-57
19	145	-133
20	66	55

0 k 2

0	597	-561
1	816	-798
3	247	-226
4	522	502
5	439	424
6	232	-236
7	75	74
8	402	-394
9	211	209
11	92	-85
12	272	259
14	159	167
15	144	143
16	93	-84
17	113	-97
18	74	-76

0 k 3

1	85	75
2	344	-326
3	315	318
5	473	-470
6	79	81
7	297	-290
8	168	166
10	94	74
13	239	230

0 k 4

0	135	138
1	342	347
2	213	205
3	224	215
4	259	-257
5	258	-249
6	374	-362
7	120	-92
9	107	86
11	144	136
12	103	105
14	148	130
15	122	-111

0 k 5

1	91	45
2	179	178
4	192	-188
5	98	-94
6	75	-64
7	97	-82
9	78	-75
12	67	60
13	130	121
14	93	-83

0 k 6

0	206	201
1	98	-97
3	232	-228
4	95	-85
7	130	124
8	81	-82
12	77	61

0 k 7

1	156	152
2	98	-100
3	75	-60
5	58	-53
7	67	-57
11	57	46

0 k 8

7	56	-39
8	56	-50

1 k 1

0	495	514
1	72	-69
2	113	-112
3	245	263
5	170	-168
7	266	-272
8	368	-373
9	475	486
10	225	220
11	257	267
12	133	143
17	84	-98

1 k 2

1	74	-84
2	70	99
3	190	178
4	143	133
6	510	-585
7	325	-346
8	165	187
9	159	-160
10	536	577
11	123	129
13	172	185
16	78	-74

1 k 3

0	62	65
1	324	-309
2	182	179
3	232	-226
4	289	-277
6	359	-359
7	68	77
8	90	102
9	230	235
12	55	69
14	163	162
17	72	-68

1 k 4

1	226	215
2	236	-237
3	119	-120
4	212	-205
5	475	-457
6	92	75
7	100	105
8	79	68
9	171	174
11	90	-95
13	65	66
16	76	-71

1 k 5

3	193	-190
5	171	-162
11	93	97
12	67	59
15	127	-113

1 k 6

2	119	-110
3	70	92
4	191	-174
5	110	96
7	124	-126
8	55	52
9	123	-112
11	90	84
12	56	33
14	57	-56

1 k 7

0	108	98
3	85	-82
6	72	-19

1 k 8

1	64	51
6	58	-50

2 k 1

1	804	751
2	482	-467
3	834	-860
4	205	-231
5	351	-337
6	88	98
8	356	350
9	141	152
10	350	351
11	77	81
13	158	-168
15	104	99
16	71	-73
17	59	88

2 k 2

0	360	358
1	355	-345
2	116	-109
4	390	-388
6	88	-85
7	167	-181
9	321	324
11	99	104
16	56	59
17	119	-131

2 k 3

1	434	-403
2	580	-554
3	244	232
4	67	-62
5	91	83
8	61	61
9	84	-88
13	131	148
16	75	-84
18	61	-72

2 k 4

0	329	-301
1	250	-239
2	98	89
3	394	-379
4	122	116
5	106	-95
6	99	-93
7	98	102
15	66	-68
17	63	-66

2 k 5

1	55	57
2	72	68
4	229	-210
5	96	-86
6	139	-121
10	113	107
12	76	70
14	106	-100

2 k 6

1	87	87
5	149	-139
9	68	67
11	90	78

2 k 7

2	111	-98
4	91	-81
5	58	47
8	69	56

2 k 8

1	61	-54
3	68	-64

3 K 1

1	607	-603
2	385	-362
3	587	-592
5	200	214
6	187	201
8	197	-195
16	68	76
17	100	-99

3 k 2

1	232	-228
2	240	-241
3	113	-113
5	120	126
6	233	-247
10	209	210
13	78	-91
16	85	-89

3 k 3

0	417	-428
4	216	220
5	271	-301
7	287	-289
9	263	272
11	148	149
13	74	-93
15	79	-84
17	59	-71

3 k 4

1	76	-61
2	157	-136
3	119	115
4	185	-175
6	74	-71
7	93	90
8	110	114
9	61	51
10	66	84
11	79	-96

3 k 5

0	93	88
3	167	-144
4	115	-113
7	118	109
8	207	195
12	94	-95

3 k 6

4	76	-76
5	61	65
7	98	98
12	59	58

3 k 7

0	99	-90
3	64	-58
4	101	83
6	80	66

4 k 1

1	434	-420
3	83	-85
4	105	-110
5	435	423
6	141	-146
9	56	-72
11	71	90
13	121	-126

4 k 2

1	157	-161
2	156	-164
3	131	-143
4	153	-166
5	142	-159
6	177	190
7	63	-80
8	196	205
9	186	182
12	183	-181
13	77	-98
14	120	-122
16	68	69

4 k 3

3	88	-94
6	125	-131
7	211	215
9	108	108
10	78	88
11	117	-134
12	56	-80
13	89	-98

4 k 4

0	231	-234
1	87	-99
3	69	-62
4	134	141
6	117	122
8	74	86
10	71	-84

4 k 5

1	180	-154
2	104	-97
3	109	91
5	126	116
6	99	93
7	91	83
11	56	-54

4 k 6

0	69	-67
1	55	41
6	55	44

4 k 7

2	75	62

5 k 1

2	231	-218
5	62	-76
6	304	292
12	116	-116
14	58	-70

5 k 2

1	83	-68
2	322	-320
5	238	221
6	155	153
7	113	118
10	117	-135
12	61	-80
13	61	-69

5 k 3

0	88	-105
1	62	-78
4	74	91
5	92	112
6	110	111
14	59	-70

5 k 4

1	144	-139
2	144	138
3	99	112
4	91	88
5	90	112
6	84	-99

5 k 5

0	107	-118

5 k 6

6	67	49

6 k 1

1	81	-88
2	126	123
5	208	202
8	111	-111

6 k 2

0	124	-141
3	186	175
4	195	188
6	108	109
7	96	-94
8	69	-79
14	58	-72

6 k 3

4	91	95
7	73	92
13	81	-87

6 k 4

3	55	72
8	96	93

6 k 6

0	68	-70

7 k 1

0	151	139
1	157	160
3	167	175

7 k 2

2	114	110
4	75	82

7 k 3

5	102	103

7 k 4

4	79	88

7 k 5

3	75	80

8 k 1

6	93	83
10	87	-79

8 k 3

4	67	78
7	70	-72

-1 k 0

1	597	658
2	749	849
3	215	-215
5	294	287
6	650	-667
7	375	-395
8	218	-223
9	171	-184
10	137	149
11	310	330
19	112	-127

-1 k 1

0	823	728
1	133	123
2	332	308
3	810	797
4	263	244
6	90	-93
7	583	-567
8	479	-459
9	261	259
12	188	186
13	148	-150
14	94	107
15	118	121
18	156	-142

-1 k 2

1	626	647
2	376	-385
3	68	59
4	575	567
5	516	-516
6	181	175
9	127	133
10	100	-88
11	63	-60
12	221	-208
13	110	114
14	166	186
15	56	52
16	76	87
17	79	-79

-1 k 3

0	407	401
1	118	-124
2	357	359
3	91	78
4	451	-458
5	273	256
6	414	-404
7	77	71
8	322	325
9	77	-73
13	110	114
14	128	129

-1 k 4

1	59	-40
2	205	212
3	230	243
5	162	-165
6	70	70
7	211	-203
9	131	-128
12	114	110
13	253	235

-1 k 5

0	80	-90
1	93	101
3	57	-57
4	98	106
6	156	-156
7	176	164
8	281	-275
9	113	-104
12	223	219
14	79	65

-1 k 6

1	151	167
3	105	-115
5	104	-111
7	96	-101
11	105	108

-1 k 7

0	168	195
1	60	46
3	58	63
4	78	-95
6	55	-39
7	100	-95

-1 k 8

7	62	-62

-2 k 0

0	114	150
1	60	-87
2	320	-310
3	386	370
4	195	192
5	302	297
6	204	218
7	317	-326
8	332	-352
9	290	-304
10	113	119
11	191	-204
15	104	126

-2 k 1

1	261	-248
2	714	-688
3	505	502
4	428	422
5	442	413
6	72	82
7	406	-386
8	134	-119
9	226	-214
10	220	-214
11	207	195
12	312	-313
13	84	93
14	201	187
16	116	133
17	83	-83

-2 k 2

0	258	257
1	92	-80
2	478	488
3	391	407
5	205	203
6	360	-369
7	230	-227
8	69	77
11	220	-207
14	55	61
16	71	-90

-2 k 3

1	211	208
2	783	849
4	320	334
5	337	-340
6	288	-297
7	79	84
8	131	-136
9	78	86
11	150	-150
13	129	129
18	88	80

-2 k 4

0	66	-62
1	263	274
2	107	111
3	158	164
6	64	-67
7	124	119
9	123	-121
10	95	-105
12	86	91
14	86	88
17	96	94

-2 k 5

1	169	183
2	66	-78
3	91	-95
5	136	-147
6	297	321
7	86	-85
10	218	-221
11	80	92

-2 k 6

0	216	230
3	76	92
4	135	-133
5	86	102
6	55	-66
8	61	-67
9	103	-121
10	66	69

-2 k 7

2	79	100
4	59	78
6	63	-65
7	86	-91
8	67	-58
9	64	-61

-3 k 0

1	111	-136
2	393	380
3	294	-292
4	452	449
5	296	301
6	266	-268
8	243	-255
9	119	-134
12	165	-176
16	102	113

-3 k 1

0	277	266
1	507	-477
2	72	-74
3	91	95
4	301	-303
5	472	447
7	185	-182
8	298	290
9	240	-231
10	67	60
11	358	-329
12	189	-172
15	223	213

-3 k 2

1	175	151
2	59	-71
3	89	95
4	361	352
5	309	-301
7	183	186
8	238	-235
9	233	238
10	205	-198
11	178	-172
12	80	-85
15	143	138

-3 k 3

0	468	-468
1	235	233
2	226	229
3	278	276
4	342	363
6	64	-65
9	154	-158
10	140	-137
11	109	-112
12	89	82
16	130	-121
17	78	71

-3 k 4

1	127	-131
2	217	235
3	218	234
5	93	99
6	206	207
7	64	-63
9	88	-90
10	234	-236
13	55	71
15	91	-86
16	98	93

-3 k 5

0	230	230
1	189	199
3	154	169
4	138	-157
5	74	76
9	139	-151
14	55	-64

-3 k 6

1	75	81
2	199	217
3	117	-132
4	107	123
8	81	-92

-3 k 7

5	74	80
8	63	-75

-4 k 0

0	475	-487
1	259	-261
2	284	-272
4	294	294
5	177	186
6	135	143
8	207	-212
11	173	-177
15	152	162

-4 k 1

1	162	-143
2	213	204
3	100	-97
4	366	346
6	281	-265
7	156	140
8	155	-156
9	131	127
11	104	-97
12	178	-157
14	73	69
16	57	60

-4 k 2

0	314	-313
1	287	288
3	490	482
5	137	-134
6	133	129
7	384	-379
8	344	320
10	161	-150
12	163	-157

-4 k 3

1	174	-172
2	62	46
3	156	156
6	84	76
7	190	177
8	56	-55
10	205	-197
11	141	-137
15	62	-60

-4 k 4

0	80	77
3	84	-85
4	60	-53
5	174	180
7	185	188
8	105	118
9	280	-279
11	129	-128
13	90	90
14	99	-103

-4 k 5

2	205	211
3	69	-67
4	92	104
5	71	87
7	67	78
8	110	-117
10	68	-81
12	55	54
13	89	-88

-4 k 6

0	115	-126
1	90	99
2	84	-83
3	131	141
4	115	135
6	104	120
8	82	-88

-4 k 7

4	74	76

-4 K 8

3	55	65

-5 k 0

2	356	-365
3	263	-256
6	138	142
8	132	151
7	204	211
9	181	182
13	192	-194

-5 k 1

0	270	-259
1	154	-149
2	99	-102
5	76	74
7	115	-110
8	184	174
12	120	-119

-5 k 2

1	509	-480
2	93	82
3	276	258
5	203	190
6	95	-96
11	72	-77
12	63	-66

-5 k 3

0	389	-382
1	73	64
3	58	-49
4	143	143
6	112	109
7	82	75
8	104	97
9	85	-86
10	64	-63
11	90	-95

-5 k 4

2	158	154
3	135	-126
7	216	216
8	86	-85
9	81	85
11	82	-96
12	70	71
13	118	-113

-5 k 5

1	109	115
2	80	-78
3	93	96
6	155	169
7	61	-65
12	70	-67

-5 k 6

1	74	-83
5	128	137
6	63	66

-5 k 7

5	64	75

-6 k 0

2	98	-98
3	99	110
6	141	143
7	96	-96
8	108	109
9	178	174
11	86	96
12	102	-110

-6 k 1

1	179	-172
6	188	-168
7	214	193
10	211	194
11	171	-149

-6 k 2

0	264	-251
1	134	-133
3	182	-173
7	107	94
8	122	116

-6 k 3

1	85	-85
2	137	-136
4	102	-97
6	140	127
7	104	93
9	87	84
10	127	-115
13	70	-63

-6 k 4

0	130	-136
1	90	88
2	87	-89
5	83	-91
6	139	137
11	54	49

-6 k 5

1	126	-133
4	76	-75
5	197	191
9	58	-66

-6 k 6

6	55	59

-6 k 7

7	56	66

-7 k 0

2	87	-102
10	86	95

-7 k 1

0	224	-259
4	177	176
9	153	156

-7 k 2

1	93	-99
2	70	-74
4	132	-109
7	70	58
8	119	111
10	69	70

-7 k 3

4	129	-117
5	90	-86
8	117	111
11	103	93
12	59	-54

-7 k 4

1	58	-56
4	84	-83
5	57	52

-7 k 5

0	70	-72
1	80	-73
3	126	-121
4	67	57

-7 k 6

2	84	-76

-8 k 0

9	73	80

-8 k 1

2	132	-145

-8 k 2

3	94	-87
7	89	82

-8 k 3

4	100	-84
8	69	60
10	91	74

-8 k 4

3	81	-68
5	68	-68
8	59	-55
9	63	64

-8 k 5

2	73	-67

-9 k 2

1	74	85
5	65	-60

-9 k 4

2	68	-66

TABLE 3

Final parameters and standard errors for $(CH_3NPCl_3)_2$. (The thermal parameters and errors are $\times 10^4$, and the standard errors are given in parentheses below the parameter)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	0·0363	0·1864	0·1468	364	35	366	20	67	−27
	(0·0003)	(0·0001)	(0·0003)	(7)	(1)	(7)	(2)	(6)	(2)
Cl(2)	0·3769	0·1265	0·1823	242	71	356	−53	−13	−14
	(0·0003)	(0·0002)	(0·0003)	(6)	(2)	(7)	(2)	(5)	(3)
Cl(3)	0·1726	0·1177	−0·2869	287	67	262	−32	79	28
	(0·0003)	(0·0002)	(0·0003)	(6)	(1)	(6)	(2)	(5)	(2)
P	0·0996	0·0783	0·0127	176	29	200	−8	28	0
	(0·0003)	(0·0001)	(0·0003)	(4)	(1)	(5)	(2)	(4)	(2)
N	0·1246	−0·0283	0·1186	144	32	258	2	−4	4
	(0·0007)	(0·0004)	(0·0009)	(13)	(3)	(17)	(5)	(11)	(6)
C	0·2781	−0·0772	0·2761	180	74	316	40	−35	57
	(0·0010)	(0·0006)	(0·0012)	(20)	(6)	(25)	(8)	(18)	(10)

computed using the function and error programme of Busing, Martin, and Levy.[17] These are given in Table 4

TABLE 4

Interatomic distances and angles (Å) (errors in parentheses) for $(CH_3NPCl_3)_2$. (The atoms are labelled as shown in the Figure)

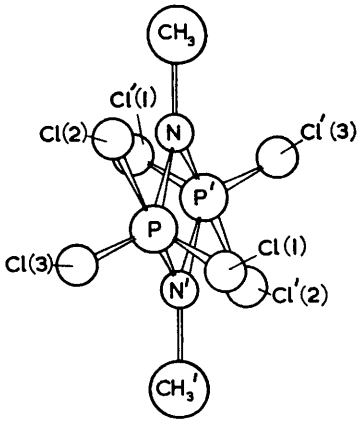
Bond distances

P–Cl(1)	2·029 (0·005)	N–Cl′(1)	2·758 (0·008)
P–Cl(2)	2·133 (0·003)	N–Cl′(2)	3·898 (0·011)
P–Cl(3)	2·023 (0·003)	N–Cl′(3)	2·740 (0·009)
P–N	1·635 (0·007)	Cl(1)–Cl(2)	2·954 (0·009)
P–N′	1·769 (0·007)	Cl(1)–Cl(3)	3·320 (0·009)
P–P′	2·600 (0·004)	Cl(1)–C	4·324 (0·012)
P–C	2·870 (0·010)	Cl(1)–C′	3·204 (0·012)
P–C′	2·893 (0·011)	Cl(2)–Cl(3)	2·944 (0·009)
N–C	1·475 (0·010)	Cl(2)–C	3·036 (0·012)
N–N′	2·202 (0·013)	Cl(2)–C′	4·955 (0·015)
N–Cl(1)	3·249 (0·009)	Cl(3)–C	4·332 (0·013)
N–Cl(2)	2·788 (0·008)	Cl(3)–C′	3·179 (0·013)
N–Cl(3)	3·250 (0·010)	C–C′	5·143 (0·019)

Bond angles

Cl(1)–P–Cl(2)	90·4° (0·2)	Cl(3)–P–N	125·0° (0·3)
Cl(1)–P–Cl(3)	110·0$_5$ (0·2)	Cl(3)–P–N′	92·3 (0·3)
Cl(1)–P–N	124·6 (0·3)	P–N–P′	99·5 (0·4)
Cl(1)–P–N′	92·9 (0·3)	N–P–N′	80·5 (0·4)
Cl(2)–P–Cl(3)	90·2 (0·2)	C–N–P	134·6 (0·6)
Cl(2)–P–N	94·5 (0·3)	C–N–P′	125·9 (0·6)
Cl(2)–P–N′	175·0 (0·3)		

with the labelling of the atoms corresponding to that in the Figure.



Molecule of $(CH_3NPCl_3)_2$

DISCUSSION

Structure.—Visualisation of the structure of *N*-methyltrichlorophosphinimine dimer is simplified by first examining a molecule of gaseous phosphorus pentachloride.[18] The five chlorine atoms are arranged at the vertices of a trigonal bipyramid centred on the phosphorus atom. The P–Cl bond distances for equatorial and apical chlorine atoms are $2·026 \pm 0·006$ and $2·133 \pm 0·006$ Å, respectively.

The co-ordination of each phosphorus atom in $(CH_3NPCl_3)_2$ is similar to that in PCl_5 if two nitrogen atoms are substituted for chlorine atoms, one in an apical, and the other in an equatorial position. In this way a planar, four-membered ring of alternating phosphorus and nitrogen atoms is formed as the molecular framework.

The Cl–P–Cl bond angle for equatorial chlorine atoms in $(CH_3NPCl_3)_2$ is the only phosphorus–chlorine parameter which is not identical, within experimental error, with its equivalent in PCl_5. This is due to packing effects between adjacent non-bonded equatorial chlorine atoms. This distance reaches a minimum value of $3·486 \pm 0·007$ Å compared with the van der Waals 3·60 Å as given by Pauling.[19] This is the only intermolecular distance less than the sum of van der Waals radii.

The carbon atoms lie in the plane of the $(P–N)_2$ ring and are equidistant from the two phosphorus atoms. The carbon temperature factors suggest no pronounced anisotropic character, and thus it appears that these are the correct positions for the carbon atoms rather than a statistical averageing of non-planar positions. Also, no significant electron density was found in the difference electron-density map in the non-planar regions. This planar co-ordination of the nitrogen atoms is unusual, since three-co-ordinate nitrogen is tetrahedral in

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virtually all other compounds except trisilylamine,[20] $N(SiH_3)_3$, where the nitrogen atom is trigonal.

The optimum values of the angles around the phosphorus and nitrogen atoms would be approximately 90 and 120°, respectively. Non-bonded interactions and orbital-overlap considerations determine the compromise values of $N-P-N' = 80{\cdot}48° \pm 0{\cdot}36°$ and $P-N-P' = 99{\cdot}52° \pm 0{\cdot}36°$.

Bonding.—On first glance it might seem that a bonding scheme similar to Rundle's proposal [21] for PCl_5 could explain the structure of $(CH_3NPCl_3)_2$. The phosphorus atom uses an sp^2-hybrid orbital to form σ-bonds to the equatorial chlorine and nitrogen atoms. The apical chlorine and nitrogen atoms form a three-centre four-electron bond with the remaining phosphorus *p*-orbital. No *d*-orbitals are used in bonding. An sp^2-hybrid orbital on the nitrogen atom forms σ-bonds to the carbon and two phosphorus atoms. Using the fractional bond order formula as given by Pauling,[19] and considering the equatorial P–N bond to be a whole σ, the apical P–N bond is calculated to be $\frac{1}{2}\sigma$.

However, this first approximation does not explain the planar co-ordination of the nitrogen atoms, or the equality of the apical P–N bond length to the " pure " P–N σ-bond length [22] found in $NaHPO_3NH_2$, or the relatively high average P–N bond energy as determined by Fowell and Mortimer.[23] They found $E[P-N] = 74{\cdot}3$ kcal./mole, a higher value than the $E[P-N] = 66{\cdot}8$ kcal./mole in the tervalent phosphorus compound, $P(NEt_2)_3$.

A calculation of the $d\pi-p\pi$ overlap integral was made using the programme of Silver.[24] The maximum overlap was found at a P–N bond distance of 1·635 Å, the value for the equatorial P–N bond. The overlap in the case of the longer P–N bond distance was not as favourable for $d\pi-p\pi$ bonding but of a value sufficient to suggest at least a partial π-bond. Thus, it seems likely that both the apical and equatorial P–N bonds have some $d\pi-p\pi$ character.

The minimum intramolecular C–Cl distances are $3{\cdot}04 \pm 0{\cdot}01$ Å [C–Cl(2)] and $3{\cdot}19 \pm 0{\cdot}01$ Å [C–Cl(*eq*)]. These distances indicate steric repulsion between the carbon and adjacent chlorine atoms which is minimised by the carbon atom assuming coplanarity with the $(P-N)_2$ ring. The resultant destruction of the usual sp^3-hydridisation of the nitrogen orbitals could effectively raise the energy of the nitrogen *p*-orbital perpendicular to the ring, making it more compatible with the relatively higher energy of the phosphorus *d*-orbitals. The lone pair of electrons on the nitrogen atom could now be used to form $d\pi-p\pi$ bonds with the phosphorus atoms. This multiple bonding would explain the P–N bond lengths and bond strengths.

More detailed considerations of the bonding in this compound cannot be made until further structural information on other related compounds is available.

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