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X-ray Crystallography of the Cl₃[N(CH₃)₂]₃P₃N₃ Compounds. I. Crystal Structure of the Geminal 2,2,4-Trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene

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The crystal structure of the geminal 2,2,4-trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene, $Cl_3[N(CH_3)_2]_3P_3N_3$, has been determined by the symbolic addition procedure, and has been refined by least-squares to R = 0.05 for the 2495 observed reflexions. The unit cell is monoclinic, $P_{2_1/n}$, with a = 15.867, b = 11.869, c = 8.861 Å, $\beta = 93^{\circ}44'$, Z = 4. The P_3N_3 ring has a distorted boat conformation. The two bonds of each P–N–P segment are of different lengths, 1.546 ± 0.001 and 1.607 ± 0.001 Å for two of the segments, and 1.563 and 1.592 Å for the third, but the average of the two bonds in each segment is 1.577 Å. The endocyclic N–P(NMe₂)₂–N angle is only 113.1° , while the N–PCl₂–N and N–PCl (NMe₂)–N angles are 120.7 and 119.0° . The P–N ligands are of nearly equal lengths 1.628, 1.639, and 1.642 ($\sigma = 0.004$) Å, but the P–Cl ligands are of significantly different lengths 1.992, 2.014 and 2.051($\sigma = 0.002$) Å.

Introduction

The X-ray crystal structure analysis of small phosphonitrilic systems is intended to enhance the understanding of the P–N bonding mechanism, since the theoretical concepts of valency in these compounds are usually complicated due to the wide variety of *d*-orbitals and the different symmetries of the *p*- and *d*-orbitals, Paddock (1964). Beside the academic interest in the valency problem, there has been an increasing industrial interest in the phosphonitriles because of their use as fire proofing reagents (Shaw, 1968).

In all the trimeric phosphonitriles examined so far by X-rays, the molecular formulae were of the types

 $R_6P_3N_3$ and $R_4R'_2P_3N_3$, with two like substituents $(R_2 \text{ or } R'_2)$ at each P atom. A study of the crystal structure of Cl₅FP₃N₃ by Olthof (1969) did not quite achieve the objectives of the analysis since the F atom was found to be equally distributed over the six halogen positions. The present series on the $Cl_3[N(CH_3)_2]_3P_3N_3$ compounds has been undertaken in order to examine the stereochemistry of the P_3N_3 ring as the positions of the substituents on the ring are altered. These compounds were characterized by Keat & Shaw (1965) who also supplied suitable crystals for the X-ray analvsis. The three compounds of this series are: (I) geminal 2,2,4-trichloro-4,6,6-trisdimethylamino-, (II) cis non-geminal 2,4,6-trichloro-2,4,6-trisdimethylaminoand (III) trans non-geminal 2,4,6-trichloro-2,4,6-trisdimethylamino-cyclotriphosphazatriene. The crystal

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а

b с

structure of the geminal compound (I) is presented in this paper, and that of the cis non-geminal compound (II) is now under study.



Experimental

Crystals of the geminal compound (I) which were used for the data collection were cut from larger crystals into approximate cubes of 0.2-0.3 mm length. The quality of the crystals deteriorated on exposure to X-rays, and four crystals in total had to be used. On exposure, the crystals became opaque, the profile of the diffracted intensities broadened, and the integrated intensities dropped steadily. Similar changes were also noted for crystals of the *cis* non-geminal compound (II).

The space group assignment was based on precession photographs. The unit-cell dimensions and the intensity data were measured on a Picker automatic diffractometer with Mo radiation and Nb filters, placed before the crystal, and with **b** along the φ axis of the instrument. The cell constants were derived from the 2θ and φ values of a few axial reflexions measured with a narrow slit at a take off angle of 1°. The integrated intensities were measured at a 2θ scan rate of 2°/min over a scan range of 2.0 or 2.4° in 2θ , and the background was measured for 20 sec at the start and at the end of each scan. The 004 and 130 reflexions were monitored every 20-40 reflexions. The crystal density was obtained by flotation in a solution of carbon tetrachloride and toluene at 20°C. The crystal data are presented in Table 1.

In total, 3809 permissible non-equivalent reflexions within $2\theta = 55^{\circ}$ (sin $\theta/\lambda = 0.65$ Å⁻¹) were scanned, but only 2495 reflexions (65.4%) were observed above threshold. The very strong reflexions were remeasured at the end with a lower current setting. The Lorentzpolarization corrections were applied, but the absorption corrections for Mo radiation were considered to be negligible.

Table 1. Crystal data

а	15·867 (5) Å	C6H18N6P3Cl3	
Ь	11.869 (5)	M.W.	373.53 g/mole
с	8.861 (6)	Space group	$P2_1/n$
ß	93·73 (6)°	Ż	4
U	1665·21 Å ³	F(000)	768 electrons
D_x	1.490 g.cm ⁻³	$\mu(Cu)$	76·3 cm ⁻¹
D_m	1.493 g.cm ⁻³	μ(Mo)	8·3 cm ⁻¹
	Systematic absences:	h0l when $h+l=0k0$ when $k=2n$	2n+1;+1.

Structure determination

The structure was determined by the direct method of symbolic addition, as described by Karle & Karle (1963) and Karle & Karle (1966). In attempting to phase the 170 reflexions with |E| > 2.0, the computer program selected 3,11,3, 12,3,1, and 465 as the origindefining reflexions, and assigned symbols A, B, C to three others at different stages when they were needed. The value of each symbol and symbol-product was determined independently from the multiple sign indications accumulated for each reflexion during the phasing process, as described by Ahmed (1970). This procedure gave self consistent signs, *i.e.* satisfying identities such as s(A). s(B) = s(AB), and the phases of the 170 reflexions were determined unambiguously. Using these phases and the \sum_2 relationships, phases were derived for 323 of the 327 reflexions with $2 \cdot 0 \ge |E| \ge 1 \cdot 5$. The 493 accepted signs were later found to be all correct.



Fig. 1. A view of the molecule down the normal to the phosphazene ring, with the short intramolecular distances (Å) indicated.

The positions of the P, N, and Cl atoms were taken from the E map, and those of the C atoms were accepted from the first Fourier map. The R index for this trial structure was 0.22, and it was reduced to 0.08 after six anisotropic cycles of block-diagonal leastsquares. A difference map calculated at this stage showed all the H atoms with peak heights 0.3-0.5e.Å⁻³. The refinement was continued until *R* for the observed reflexions was reduced to 0.050, and the shifts in the atomic parameters were $< 0.3\sigma$ for P, N,

Table 2. Fractional coordinates,	vibration	tensor	components	· (Ų) for	the expression
$T = exp \left[-2\pi^2 (U_{11}a^{*2}h^2)\right]$	++2l	$J_{23}b^{*}c^{*}$	kl +]], a	and their	e.s.d.'s

All quantities $\times 10^4$.

				7 m quan	they with .				
	x	Y	Z	U11	U22	U33	2023	2013	2012
N(1)	4036(2)	2441(3)	6804(4)	434(19)	783(27)	419(19)	-39(37)	-140(30)	-436(37)
P(2)	3755(1)	2584(1)	5251(1)	377(5)	502(6)	406(6)	25(10)	15(8)	-257(10)
N(3)	3015(2)	2550(3)	4248(4)	467(19)	664(24)	395(18)	245(34)	-171(30)	-359(35)
P(4)	2515(1)	1481(1)	48C8(1)	324(5)	475(6)	368(5)	10(10)	-64(8)	-157(10)
N(5)	2708(2)	1048(3)	6441(4)	479(20)	704(25)	392(18)	26(35)	-138(30)	-429(36)
P(6)	3478(1)	1488(1)	7553(1)	393(5)	509(6)	323(5)	54(10)	-70(8)	-43(10)
	4810(1)	2968(1)	4000(1)	546(8)	1239(13)	644(7)	-67(17)	388(12)	-546(16)
	3657(1)	4641(1)	5500(2)	1148(13)	480(7)	1007(11)	-48(16)	-212(19)	-133(16)
(13)	2775(1)	199(1)	3359(1)	887(10)	663(9)	631(7)	-318(14)	236(13)	165(14)
N(7)	1507(2)	1710(3)	4492(4)	392(18)	588(24)	622(22)	114(37)	-85(32)	-74(33)
N(8)	3076(2)	1922(3)	9110(4)	587(22)	632(24)	389(18)	-95(35)	84(31)	-20(38)
N(9)	4144(2)	498(3)	8139(4)	529(22)	637(25)	538(22)	-20(39)	-150(35)	225(38)
(III)	1215(3)	2217(5)	3061(6)	474(27)	1008(44)	781(36)	265(66)	-367(49)	125(58)
(12)	928(3)	870(6)	5055(7)	444(28)	962(45)	1220(50)	311(77)	124(59)	-314(58)
(13)	2261(4)	2485(6)	9023(7)	760(37)	1031(49)	834(40)	-484(72)	180(61)	452(68)
C(4)	3654(4)	2335(5)	10324(5)	889(38)	850(40)	402(24)	-337(53)	-169(48)	-33(64)
((5)	3824(4)	-401(5)	9072(7)	863(40)	643(34)	874(39)	427(62)	-255(62)	74(61)
6(6)	4735(4)	104(6)	7072(6)	772(37)	1057(49)	686(34)	-270(68)	-78(57)	739(70)
	1610(28)	2830(49)	2718(58)	481 (314)	1552(555)	1117(433)	1020(830)	-1064(595)	-1087(705)
H(2)	1203(32)	1674(50)	2229(57)	766(392)	1550(586)	957(426)	-779(817)	114(639)	1242(800)
H(3)	681(30)	2517(42)	3063(50)	818(374)	1009(443)	606(320)	448(630)	-447(557)	-692(651)
H(4)	654(35)	321(56)	4380(65)	846(441)	1544(614)	1171(499)	-422(917)	331744)	-114(844)
8(5)	476(34)	1216(57)	5293(83)	520(379)	1558(671)	2637(830)	2303(1234)	403(918)	54(795)
H(6)	1109(34)	548(53)	6134(61)	1024(468)	1691(627)	956(433)	1412(882)	-1088(719)	-1199(897)
H(7)	1956(35)	2077(54)	8216(63)	980(455)	1229(532)	1204(496)	384 (854)	-566(749)	-127(820)
H(8)	1984(40)	2368(63)	10035(72)	1319(603)	1943(781)	1377(593)	96(1114)	692(951)	1079(1113)
н(9)	2235(38)	3270(62)	8871(68)	987(486)	2106(788)	1153(509)	-920(1065)	432(811)	-131(1010)
HIION	36(8(35)	2344(57)	11323(53)	1133(486)	1974(709)	520(349)	441(814)	160(658)	-558(958)
нсіті	4212(32)	2070(49)	10346(55)	965(417)	1345(524)	722(361)	-946(740)	-1043(623)	318(785)
H(12)	3751(32)	3187(46)	10165(54)	981(417)	1076(465)	713(355)	133(678)	-903(613)	-687(737)
H(13)	3548(48)	-960(53)	8445(69)	2514(816)	1028(515)	1073(486)	-331(839)	-2363(1052)	142(1101)
H(14)	3434(39)	-120(41)	9947(61)	1752(602)	384(335)	1192(476)	244(654)	1010(878)	156(733)
H(15)	4240(31)	-692(42)	9556(51)	927 (40C)	820(396)	818(375)	1269(654)	-18(624)	391(654)
H(16)	5225(35)	-202(53)	7625(55)	1018(445)	1649(617)	686(375)	63(799)	-667(658)	713(866)
H(17)	50(2(35)	661(52)	6636(57)	1069 (463)	1623(594)	751(388)	-1645(806)	396(684)	236(867)
H(18)	4408(36)	-389(54)	6273(62)	1222(507)	1584(612)	1008(454)	-1617(883)	-6(757)	1226(920)
114 101		201011	02.01021						



Fig. 2. Bond lengths (Å) and angles (°), and their e.s.d.'s in parentheses. E.s.d.'s of bond lengths are $\times 10^3$.

Table 3. Structure factor data ($\times 10$)

* Indicates unobserved reflexions and $|F_{th}|$ in place of $|F_o|$.

| x +C +C
+ +C +C
+ +L(3) +C
+C +C +C
+C +C +C
+C +C + | x +3 +C
L5 +0.4 +2
H+ -1, L+ L
J 175 157
L L+31 -1+2+
2 142 -11+
3 794 -727
4 LUU LUCO
5 59 -22
0 LGB 154
7 423 -511 | x Fr) Fu
12 Ju -50
14 -12, La 7
0 341 Jau
1 40 -136
2 12 -54
3 37 34
4 235 -237
5 578 -10
6 232 280
1 Law -124 | x +0 +C
+ 176 -176
1J 97 93
11 275 -233
12 80* 38
13 66 91
14 38* 11
16 38* 11
16 -2, L* 3
1 730 -160
2 72 -60
3 82 -876 | <pre>k F0 Fc m+ 2, 1+ 10 u 210 214 1 108 -98 2 014 -23 3 92 -01 4 105 103 3 104 105 6 62* 16 7 06* -20 ma -2, 1* 10</pre> | a by fc
11 92 92
12 62* 14
13 65* -4
13 65* -4
10 56* -568
1 678 66*
2 416 619
3 4.0* 412
4 225 245
5 281 -500 | x 51 50
5 100 -3
6 273 280
7 307 -326
9 131 -309
9 274 -326
9 131 122
10 6 -58
11 156 170
12 77 70
13 556 16
14 55 16 | 4 43 40
9 95 - 99
10 350 - 29
11 95 - 29
11 122
2 57 - 62
3 85 - 62
4 80 89
3 55 - 30 | A FL FL 1 373 -3733 2 -555 54 3 -515 14 4 -115 14 5 -13 -553 6 -116 42 7 -564 27 8 -118 17 9 -5195 52 10 -507 52 | k ku ku k ku ku k ku ku k ku<th>6 1 1 FL
12 89 -13
14 11 63
2 150 -161
3 76 70
6 113 100
5 61 -81
6 113 -70
7 100 122
8 62 55</th><th>i 17 i 3 106 124 4 322 124 5 444 124 6 130 314 7 177 167 8 542 124 9 444 127 9 546 -317 9 547 -307 10 445 -317 11 55 -31 12 450 -164</th><th>k F7 F4 5 272 -276 6 281 281 7 68 59 8 598 -28 9 598 -28 10 524 -75 11 74 -86 12 127 -117 13 574 -36 14 604 -44</th><th>x + + - + + + + + + + + + + + + + + + +</th><th>108</th><th>f0 fc 17e 17e 17e 103 7 9; 103 9; -20 0 03 -70 10 04 12 34 -29 11 104 11 12 34 -20 13 627 -61 14 14 15 627 -61 15</th> | 6 1 1 FL
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He G, Le 2 G 1075 1506 1 858 017 2 766 -007 3 229 -036 4 116 121 5 83 -76 6 47 52 7 106 172 8 276 -272 9 136 32	5 v05 922 6 510 511 7 111 104 8 v2 -17 10 157 175 11 127 105 12 157 175 12 17 12 13 61 -12 14 57 -7 15 6.4 -7 16 -12 16 57 -7 17 12 18 57 -7 19 6.4 -7 10 -12 10 -12	+ -1, (+ -2) + -1, (+ -2) + -1, (+ -3) +
11 514 - 18 12 124 - 117 13 144 15 14 57 - 29 15 60 38 14 606 41 2 535 - 590 3 617 - 64 5 512 560 5 512 560		
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4 20 -15
5 538 -527
4 575 -681
5 249 -272
6 463 -464
7 158 -157
4 268 -284
9 538 29
14 538 -18
14 538 -18
14 538 -18 | v 36* 38
lu 23* -25
li 60* 33
p= 1, L= v
- 6 **
1 170 -186
2 110 -103
3 57* 15
* 35* -10
5 64* 2
E 60* -17
7 78 -8* | 1 46 - 4
1 542 - 563
1 300 - 510
2 30 - 510
3 420 - 510
3 420 - 510
5 320 - 512
6 446 - 512
6 446 - 512
7 560 - 24
4 205 - 213
7 560 - 24
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7 560 - 26
 | 2 213 200
2 222 501
9 548 34
10 189 179
11 558 -29
12 111 105
13 135 124
14 578 -4
15 605 27
He 3. [4 1
0 772 163
1 1241 1246 | 4 254 253
5 107 -305
6 124 128
7 101 102
4 368 -50
9 168 16
10 368 -16
11 368 17
13 608 33
14 3, Le 7
C 273 256 | 7 132 146
8 134 150
9 106 94
10 344 -329
11 117 123
12 124 113
13 55* 21
14 123 113
He b. L- 3
1 38* 15
2 510 548
3 669 696
 | 0 192 -178 HI -57 -22 2 96 -163 3 196 185 4 100 171 5 73 196 6 141 162 7 84 -55 8 80 -89 9 63= 59 | 7 (1 | 14 55 e es
14 6, 1e 2
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2 14 2 - 245
2 20 - 257
4 12 - 257
4 12 - 257
4 12 - 257
5 12 - 157
5 14 - 428
7 35 - 58
8 - 27 | 1 | Lu 28 - 29
L1 274 - 30
L2 255* 14
L3 85 - 86
H* 7, L* 5
U 64* L0
L 816 - 85
H* 618
2 63* 30
3 95 29
5 241 244
5 65* 4
 | 11 52 8
12 00 - 05
13 89 - 40
14 02 - 13
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14 02 - 13
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1 /46 - 229
2 39 - 14
3 45 - 59
4 1/5 136
5 207 277
6 312 378 | <pre>+ 1ut -100 > 53* -54 + 65* -54 ? 56* -55 * 58* 3 9 *** 2u H** a. 1* 4 1 *2 -87 2 82 -70 1 11 105 * 73* 61 5 *3* -14</pre> | • 1(3) -114
5 42 -143
6 61 81
7 114 -116
8 56 -18
10 558 -16
10 558 -16
10 558 -21
11 83 -67
14 004 -21
44 0, (* 6)
1 544 0
2 121 -126
 | 12 50* 8
++-10, 1* 3
1 60 47
2 197 207
3 36* -805
5 56* 30
6 231 -263
7 102 100
8 71 76
9 74 -56
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Table 3 (cont.)

Cl, C and $<0.5\sigma$ for H. The weights assigned to the reflexions were calculated by the expression

$$w = 1/\{1 + [(|F_o| - 40)/40]^4\}$$

where $|F_o| = 3.7$ to 185.9. The scattering factor curves employed in the analysis were those by Hanson, Herman, Lea & Skillman (1964) for P, N, C, Cl, and by Stewart, Davidson & Simpson (1965) for H.

Results

The atomic parameters and estimated standard deviations resulting from the least-squares refinement are listed in Table 2, and the corresponding structure factor data are given in Table 3. The observed data show no outstanding discrepancies, and of the 1314 unobserved reflexions only 59 are calculated above threshold but not more than 1.3 times the threshold amplitudes. The final $[\sum wd^2/(m-n)]^{1/2}$ is 1.14.

A view of the molecule along the normal to the mean plane of the P_3N_3 ring is shown in Fig. 1. The bond lengths and angles, not corrected for thermal vibration, are presented in Fig. 2. The C-H bond lengths are in the range 0.84 to 1.05 Å, and their mean is 0.96 Å.

Discussion

The P_3N_3 ring segments of $Cl_2P(2)-N(1)-P(6)$ (NMe₂)₂ and (NMe₂)ClP(4)-N(5)-P(6) (NMe₂)₂ are very similar,

with $P(2)-N(1) \simeq P(4)-N(5) = 1.546 \pm 0.001$ Å, P(6)- $N(1) \simeq P(6) - N(5) = 1.607 \pm 0.001$ Å, and the angles at N(1) and N(5) = $123.8 \pm 0.4^{\circ}$. The two remaining cyclic P-N bonds in the $Cl_2P(2)-N(3)-P(4)Cl(NMe_2)$ segment are 1.563 and 1.592 Å, and the angle between them is 118.5° . The four bond lengths quoted here are significantly different from each other since $\sigma(P-N) =$ 0.004 Å. Despite these variations in the cyclic P-N bond lengths, the mean of the two bonds in a P-N-Psegment is $1.577 \pm 0.000_5$ Å in each case. This mean value is nearly identical with the mean P-N bond length of 1.578 Å found for the Cl₂P-N-PCl₂ segment in (C₆H₅)₂Cl₄P₃N₃ by Mani, Ahmed & Barnes (1965), and for the cyclic P-N bonds in (Me₂N)₈P₄N₄ by Bullen (1962). Also since the Cl and N substituents have the same electronegativity of 3.0, the results of this analysis are therefore in agreement with the conclusion of Ahmed, Singh & Barnes (1969), that the mean P-N bond length of a P-N-P segment is dependent primarily on the mean electronegativity of the two pairs of substituents on the bordering P atoms of the segment. However, it is obvious from the present results that consideration of the electronegativity of the ligands is not sufficient by itself to explain the observed variations in the cyclic P-N bond lengths. A possible cause for these variations is the difference in the orientations of the dimethylamino groups and its effect on the degree of efficient overlapping between the orbitals, and the degree of electron exchange between the substituents and the ring. In this structure, the NC₂ group substituted at P(4) is rotated by only 1° around the P(4)–N(7) bond, while those at P(6) are rotated by angles of 50 and 53° round the P(6)–N(8) and P(6)–N(9) bonds respectively.

The equations of the mean plane of the phosphazene ring, the planes of the ligands and the planes of the dimethylamino groups, referred to the orthogonal axes $X' = ax + cz \cos \beta$, Y' = by, $Z' = cz \sin \beta$, are listed in Table 4. The phosphazene ring has a distorted boat form and its atoms are within -0.056 and 0.073 Å from the mean plane as shown in detail in Fig. 3. The planes of the ligands at P(2), P(4), and P(6) make dihedral angles of 88.2, 89.1, and 87.1° respectively, with the mean plane of the phosphazene ring. The C(1)-N(7)-C(2) plane makes a dihedral angle of 89.2° with the plane of the ligands at P(4), while the C(3)-N(8)-C(4) and C(5)-N(9)-C(6) planes make dihedral angles of 48.0 and 45.3° , respectively, with the plane of the ligands at P(6), as can be seen from the projections given in Figs. 1 and 3. The three bonds joined at each of N(7), N(8), and N(9) are not coplanar; the mean interbond angle at each of these atoms is within $116.5 + 0.5^{\circ}$.

Table 4. Parameters of the mean planes for the normal equation lX' + mY' + nZ' - p = 0

	1	m	п	р
Phosphazene ring	0.6298	-0.6666	- 0.3988	0.6020
Cl(1), P(2), Cl(2)	-0.5485	0.0288	-0.8357	- 6.9146
Cl(3), P(4), N(7)	0.2393	0.6700	-0.7027	-0.9208
N(8), P(6), N(9)	-0.7203	-0.6823	-0.1246	- 5.6984
C(1), N(7), C(2)	0.4998	-0.7141	- 0.4902	-2.3302
C(3), N(8), C(4)	0.3907	0.6814	-0.6189	- 1.7299
C(5), N(9), C(6)	-0.7149	-0.1519	-0.6826	- 9·3667

The exocyclic P(6)–N(8) and P(6)–N(9) bonds are nearly equal in length, 1.640 ± 0.002 Å, while P(4)–N(7) is only 1.628 Å, and the difference of 0.012 Å between them is possibly significant; $\sigma = 0.004$ Å and P = 0.02. These three ligands are considerably shorter than the single P–N bond length of 1.77 Å, and the P–N ligands of 1.68 Å in (NMe₂)₈P₄N₄. The C–N bonds of the dimethylamino groups are between 1.452 and 1.461 Å, and their mean is 1.455 Å as in (NMe₂)₈P₄N₄.

The three P-Cl ligands have significantly different lengths of 2.014, 1.992, and 2.051 ($\sigma = 0.002$) Å. The longest of these is P(4)-Cl(3) which shares atom P(4) with the shortest P-N ligand, and the shortest is P(2)-Cl(2) which is *trans* to the longest P-Cl bond.

Bond angles

In small phosphonitrilic rings, the endocyclic N–P–N angles are usually expected to be close to the trigonal value of 120°. The widest deviations from this value are observed in the N–P(C_6H_5)₂–N angles of

 $Cl_2(C_6H_5)_4P_3N_3$ and $(C_6H_5)_2Cl_4P_3N_3$ by Mani, Ahmed & Barnes (1965, 1966), and of $(C_6H_5)_2F_4P_3N_3$ by Allen, Moeller & Paul (1969), where they occur in the range

115·2–115·9°. In the present structure, the N(1)–P(2)–N(3) and N(3)–P(4)–N(5) angles are 120·7 and 119·0° respectively, but the N(1)–P(6)–N(5) angle is only 113·1°. This is indicative of a more tetrahedral coordination of the bonds at P(6) than of those at P(2) and P(4). The six bond angles at P(6) vary from 103·7 to 114·2° (mean = 109·4°), while those at P(2) vary from 99·6 to 120·7° (mean = 109·1°), and the angles at P(4) vary from 104·6 to 119·0° (mean = 109·3°).

The exocyclic Cl(1)–P(2)–Cl(2) angle of 99.6° is intermediate between the corresponding values of 98.5° and 100.3° found in $Cl_2(C_6H_5)_4P_3N_3$ and

 $(C_6H_5)_2Cl_4P_3N_3$ respectively, but is considerably smaller than the values of $102 \cdot 1^\circ$ for $Cl_6P_3N_3$ by Wilson



Fig. 3. Deviations (Å) of the atoms from the mean plane of the phosphazene ring.



Fig.4. Residual electron density distribution in the planes of the ring and the ligands. Contour lines start at ± 0.1 and are at intervals of ± 0.1 e.Å ⁻³.

& Carroll (1960), and $102 \cdot 8^{\circ}$ for $Cl_8P_4N_4$ by Hazekamp, Migchelsen & Vos (1962). The exocyclic N(8)–P(6)–N(9) angle of $103 \cdot 7^{\circ}$ in this structure is comparable to the corresponding value of $103 \cdot 8^{\circ}$ in (NMe₂)₈P₄N₄.

Intramolecular contacts

Although there are no intermolecular contacts shorter than expected, there are four short intramolecular contacts between some of the H atoms of the methyl groups and the N atoms of the ring. These are $H(7) \cdots N(5)$, 2.46; $H(1) \cdots N(3)$, 2.55; $H(6) \cdots N(5)$, 2.60; and $H(17) \cdots N(1)$, 2.62 ($\sigma = 0.05 - 0.06$) Å, as identified in Fig. 1. The corresponding van der Waals contact based on the radii given by Pauling (1960) is 2.7 Å, and according to the statistics only the shortest of these contacts can be considered statistically different from the expected value. The C-H...N angles for these short contacts are 109, 106, 102, and 106° respectively.

Residual electron density

The residual electron density distribution in the mean plane of the phosphazene ring, and in the planes of the ligands is shown in Fig. 4. The positions of the P atoms have negative residual electron densities around them with troughs as low as -0.15, -0.20, and -0.28 e.Å^{-3} at P(2), P(4), and P(6), respectively. The positions of the N atoms of the ring have positive residual electron densities of about $0.1-0.2 \text{ e.Å}^{-3}$ around them. The estimated standard deviations of the electron density is 0.08 e.Å^{-3} .

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Barium Aluminate Hydrates. IV. The Crystal Structure of α-Ba₂[Al₄ (OH)₁₆]

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The barium aluminate hydrate α -BaO. Al₂O₃.4H₂O has been shown by X-ray structural analysis to contain anions of formula [Al₄(OH)₁₆]⁴⁻ consisting of a cluster of four Al(OH)₆ octahedra sharing edges. The anions are linked by the barium ions and by hydrogen bonding. The compound is thus a complex hydroxide whose formula should be written Ba₂[Al₄(OH)₁₆].

Introduction

The existence of a compound of empirical formula $BaO.Al_2O_3.4H_2O$ was first reported by Sainte-Claire-

Deville (1862). Subsequent preparations have been reported and its stability relationships have been investigated (Carlson & Wells, 1948; Carlson, Chaconas & Wells, 1950). Thilo & Gessner (1965) also prepared it; they added the prefix α to distinguish it from a different polymorph (β) which they prepared by dehydration of a higher hydrate.

The single crystals used in the present study were

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