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# X-ray Crystallography of the Cl<sub>3</sub>[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>P<sub>3</sub>N<sub>3</sub> Compounds. II.\* Crystal Structure of the *cis* Nongeminal 2,4,6-Trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene

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The structure of the title compound has been determined by direct and Fourier methods and has been refined to R = 0.057 for 2495 reflexions. The unit cell is monoclinic,  $P_{2_1/a}$ , a = 15.602, b = 15.422, c = 15.477 Å,  $\beta = 111.38^{\circ}$ , Z = 8. The molecules have approximate threefold symmetry with small perturbations at the outside atoms. The central P<sub>3</sub>N<sub>3</sub> group forms a regular, non-planar ring with P-N = 1.579 (3) Å, P-N-P = 120.3 (3)°, N-P-N = 118.1 (2)°, and  $\tau = \pm 17.5^{\circ}$ . Its atoms are displaced by about  $\pm 0.070$  Å from its mean plane, in a slight chair form. The P atoms lie on the same side of the mean plane as the Cl substituents. The dimensions of the ligands are: P-Cl = 2.057 (2) Å, P-NMe<sub>2</sub> = 1.610 (4) Å, Cl-P-NMe<sub>2</sub> = 105.0 (2)°, Cl-P-N(ring) = 106.8 (1)°, NMe<sub>2</sub>-P-N(ring) = 109.6 (1)°, N-C = 1.470 (5) Å, P-N-C = 118.8 (3)°, C-N-C = 112.7 (3)°. The P-Cl and P-NMe<sub>2</sub> bond lengths are indicative of considerable transfer of charge, in a plane perpendicular to the ring, from each amino group to the Cl substituent on the same phosphorus.

#### Introduction

In the geminal  $Cl_3[N(CH_3)_2]_3P_3N_3$ , which was reported as part I by Ahmed & Pollard (1972), the substituents on the three P atoms of the (PN)<sub>3</sub> phosphazene ring are  $Cl_2$ ,  $(NMe_2)_2$ , and  $Cl(NMe_2)$ . In the *cis* nongeminal compound that is described in this paper, the three P atoms of the phosphazene ring are chemically equivalent. Each has substituents  $Cl(NMe_2)$ , with the three Cl atoms on one side of the ring and the three NMe<sub>2</sub> groups on the opposite side. The purpose of the X-ray studies is to determine how and to what degree the different substituents affect the stereochemistry of the phosphazene ring.

#### Crystal data

- *cis*-2,4,6-Trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene; F.W. 373.53 g.mole<sup>-1</sup>.
- Source: R. Shaw and R. Keat, recrystallized from petroleum spirit.
- Crystal habit: prismatic, colourless, becomes opaque after extended exposure to X-rays.
- Crystal dimensions: about  $0.2 \times 0.2 \times 0.3$  mm.
- Unit cell: monoclinic,  $P2_1/a$ ,

a = 15.602 (5), b = 15.422 (2), c = 15.477 (2) Å,

 $\beta = 111.38 (3)^{\circ}, V = 3467.7 \text{ Å}^3, Z = 8,$ 

*i.e.* two molecules in asymmetric unit;

 $D_x = 1.431, D_m = 1.437 \text{ g.cm}^{-3}$ 

(flotation in KI solution).

\* Part I: Acta Cryst. (1972). B28, 513.

Radiation: Cu  $K\alpha$  for cell measurements,  $\lambda(K\alpha_1) = 1.54050$ ,  $\lambda(K\alpha_2) = 1.54434$  Å; Mo  $K\alpha$  and Nb filters for intensity measurements;  $\mu(Cu) = 76.3$ ,  $\mu(Mo) = 8.3$  cm<sup>-1</sup>.

#### Experimental

# Intensities

# Measured on 4-circle automatic diffractometer, crystal mounted along **b**\*, $\theta$ -2 $\theta$ scan of 2.0 or 2.4° and two backgrounds per reflexion, sin $\theta/\lambda \le 0.538$ ; number of reflexions scanned = 5177, observed = 2495, unobserved = 2682; number of observations per parameter = 5.3.

### Corrections

(1) For small drifts in the detector circuit; (2) 1/Lp.

#### Structure determination

Of 611 reflexions with |E| > 1.500, 479 were signed by the symbolic addition procedure. The *E* map gave the positions of 20 atoms, *i.e.* P<sub>6</sub>, Cl<sub>6</sub>, N<sub>8</sub>. A Fourier map computed after two least-squares cycles produced all the other non-hydrogen atoms. All the H atoms were located unambiguously from a difference map computed after partial refinement.

#### Refinement

By block-diagonal least squares minimizing  $\sum w(\Delta F)^2$ , where  $w = 1/\{1 + [(|F_o| - 80)/60]^4\}$ ,  $7 \cdot 0 \le |F_o| \le 476 \cdot 4$ , and excluding all the unobserved reflexions. Since the two molecules of the asymmetric unit are approximately related by pseudo-symmetry, the final parameters of N, P, Cl, C are based on least-squares blocks of  $18 \times 18$ per pair of pseudo-related atoms to include the correla-

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tion between their parameters. For these atoms, the mean and maximum  $\Delta/\sigma$  in final cycle are 0.1 and 0.4.

#### Final agreement

R = 0.057 and  $R_w = 0.053$  for the 2495 observed reflexions;  $|F_c| \le |F_{th}|$  for 2577 unobserved reflexions and  $|F_{th}| < |F_c| \le 1.5 |F_{th}|$  for 105 unobserved.

#### f-curves

Hanson, Herman, Lea & Skillman (1964) for C, N, P, Cl; Stewart, Davidson & Simpson (1965) for H.



Fig. 1. A view of molecule I along the normal to its phosphazene ring.



Fig. 2. The (x, z) projection of one asymmetric unit showing the approximate pseudo-symmetry relation between molecules I and II.

Computer programs

The NRC Crystallographic Programs for the IBM/360 System by Ahmed, Hall, Pippy & Huber (1966).

#### Results

The molecular structure as viewed along the normal to the mean plane of the phosphazene ring is presented in Fig. 1. The two molecules of the asymmetric unit are approximately related by a pseudo-screw diad parallel to **b** at about  $(x = \frac{1}{4}, z = \frac{3}{4})$  for which the translation element is about **b**/4. The x, z projection of one of the asymmetric units is shown in Fig. 2. The atomic parameters, and their estimated standard deviations as obtained from the least-squares refinement, are listed in Table 1. The corresponding structure-factor data, for the observed reflexions only, are given in Table 2.

The bond lengths and valence angles, not corrected for thermal vibrations, are presented separately for molecules I and II on the schematic diagrams in Fig. 3. The C-H bond lengths are in the range 0.73 to 1.13 (9) Å, and their mean is 0.98 Å.

### Discussion

Analysis by the  $\chi^2$  test of the agreement among the chemically equivalent bonds and angles of molecules I and II is summarized in Table 3. This shows that the discrepancies are not significant for six of the eleven quantities listed in the Table, possibly significant for  $\dot{P}$ -NMe<sub>2</sub> and N-C (5% > P >  $\dot{0}$ ·1%), and significant for P-N, Cl-P-NMe<sub>2</sub> and P-N-C (P < 0.1%). However, these discrepancies do not seem to be correlated in any meaningful systematic manner, even when they are considered in terms of the torsion angles listed in Table 4, or the displacements of the atoms from the mean plane of the phosphazene ring, which are presented in Table 5. Despite the observed variations in the cyclic P-N bond lengths, the means of the two bonds in the different P-N-P islands are 1.579, 1.580, 1.578, 1.579, 1.581, 1.574 (6) Å, and the discrepancies among them are not significant. All the observed discrepancies in the bond lengths and angles become insignificant if the estimated standard deviations obtained from the least-squares refinement are increased by only 25%. Such an increase can be justified in this case in view of the relatively low ratio of observed reflexions to unknown parameters, which is 5.3 compared with 10.6 for the geminal structure. The reason for this is that the approximate pseudo-symmetry relation between molecules I and II introduces near systematic absences, in addition to the space-group absences.

On this basis, the estimated standard deviations in Tables 1 and 3, and Fig. 3, should be increased by 25%, and the chemically equivalent bond lengths and angles should be averaged. This factor has been applied to the e.s.d.'s quoted in Table 5 and in the remainder of the discussion.

The phosphazene ring in the *cis* nongeminal molecule can be described as a regular, non-planar ring of dimensions: P-N = 1.579 (3) Å, P-N-P = 120.3 (3), and N-P-N = 118.1 (2)°. Its atoms are displaced by about  $\pm$  0.070 Å from the mean plane of the ring in the form of a slight chair, and with the P atoms on the same side of the plane as the Cl substituents. This slight deviation from planarity does not seem to be caused by

Table 1. Fractional coordinates and vibration tensor compo	ments and their e.s.d.'s
as derived from the least-squares refinem	ient

The temperature-factor expression is  $T = \exp\left[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl + \ldots)\right]$ .

All quantities  $\times 10^4$ . The isotropic *B* and its e.s.d. are in Å<sup>2</sup>.

Mol. I	x	У	Z	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{23}$	$2U_{13}$	$2U_{12}$
N(1) P(2)	2096 (5) 1782 (2)	8 (4) 913 (2)	5152 (5) 4691 (2)	642 (50) 476 (15)	510 (48) 531 (16)	475 (44) 401 (14)	68 (72) 20 (24)	-60(75) - 142(23) -	106 (78) - 20 (25)
N(3) P(4)	2275 (5) 3234 (2)	1751 (5) 1686 (1)	5231 (5) 6065 (2)	584 (50) 503 (15)	612 (52) 424 (14)	533 (49) 487 (15)	263 (78)	191 (85)	79 (81)
N(5)	3541 (5)	772 (4)	6515 (5)	578 (47)	501 (47)	451 (44)	42 (70)	-101(72) -	- 30 (23) 317 (75)
P(6) N(7)	3073 (2) 673 (5)	-82(1) 1004(5)	5974 (2) 4411 (5)	516 (15) 636 (53)	457 (14) 687 (55)	451 (14) 691 (56)	9(25) - 142(89)	154(23) - 246(88) -	-31(25)
N(8)	3268 (5)	2376 (5)	6854 (5)	587 (50)	507 (48)	622 (51)	-16(80)	15 (80)	40 (78)
Cl(1)	3009 (S) 1969 (2)	-800(4) 898(2)	6702 (5) 3444 (2)	694 (50) 870 (20)	381 (42) 966 (22)	575 (46) 579 (17)	-153(73) -23(30)	413 (80) -	-96 (76) 54 (34)
Cl(2)	4229 (2)	2070 (2)	5572 (2)	672 (18)	1010 (23)	880 (21)	461 (36)	664 (33) -	100 (34)
C(3) C(1)	91 (7)	- 394 (2) 275 (8)	3403 (2) 3917 (7)	740 (18) 576 (67)	818 (19) 1001 (89)	663 (16) 801 (76)	- 267 (29) - 395 (134)	596(29) - 17(113) -	- 83 (31) 396 (126)
C(2)	255 (6)	1856 (7)	4087 (8)	510 (63)	888 (86)	1008 (86)	-176 (134)	172 (121)	85 (115)
C(4)	4072 (7)	2388 (7)	7732 (7)	777 (73)	502 (71) 771 (76)	1065 (95) 679 (69)	-203(133) -271(119)	-285(165) -24(115) -	3 (144) 138 (123)
C(5) C(6)	3822 (7) 2530 (8)	-925(7) -1623(6)	7586 (7) 6336 (7)	647 (66) 1163 (89)	847 (77) 507 (63)	721 (68)	627 (122)	251 (110)	180 (119)
Mol. II		(-)			507 (05)	155 (11)	107 (107)	010 (155) -	177 (123)
N(1)	2964 (5)	2373 (5)	- 220 (5)	808 (58)	642 (54)	619 (52)	126 (84)	258 (89)	629 (92)
P(2) N(3)	3274 (2) 2770 (5)	3286 (2) 4123 (5)	-273(2) -230(5)	632 (17) 751 (57)	613 (17) 480 (48)	387 (14) 561 (54)	111(26) - 59(78)	187 (25) :	352 (28)
P(4)	1814 (2)	4044 (1)	-1085(2)	529 (16)	490 (14)	464 (15)	-20(26)	35 (24)	205 (26)
P(6)	2027 (2)	2279 (2)	-1564(5) -1058(2)	703 (53) 747 (18)	498 (49) 434 (14)	547 (48) 506 (15)	- 128 (77) 35 (26)	-67(83) 366(28)	126 (81) 229 (27)
N(7) N(8)	4376 (5)	3415 (6) 4766 (5)	562(5)	633 (53)	894 (63)	602 (53)	231 (93)	353 (87)	448 (95)
N(9)	2137 (5)	1615 (5)	-1796(5)	871 (60)	554 (51)	685 (53)	-118(86)	607 (94)	48 (84) 48 (92)
Cl(1) Cl(2)	3087 (2) 802 (2)	3222 (2) 4382 (2)	1525(2) - 593(2)	1006 (24)	1227 (27)	579 (17) 857 (21)	96 (34) 	663 (34) 576 (33)	358 (40)
Cl(3)	1117 (2)	1690 (2)	-561(2)	939 (21)	913 (22)	837 (20)	463 (35)	876 (35)	330 (36)
C(1) C(2)	4961 (7) 4780 (9)	4245 (8)	1009 (8) 940 (9)	650 (71) 1051 (97)	972 (89) 986 (100)	972 (86) 1030 (100)	774 (145) 	314(127) ( 549(164) - 2	536 (132) 238 (157)
C(3)	2009 (8)	5686 (7)	-1549 (7)	1179 (96)	552 (70)	825 (77)	- 127 (118)	196 (139) - 3	301 (132)
C(5)	1422 (8)	1507 (8)	-2675(8)	936 (88)	996 (89)	647 (67) 980 (88)	– 709 (129)	94 (105) – 684 (145) – 3	- 34 (121) 362 (148)
C(6)	2669 (10)	806 (8)	-1439 (10)	1426 (117)	754 (87)	1310 (109)	25 (158)	1224 (190) 5	537 (166)
Mol. I	x	у	Z	В	Mol. II	x	у	Z	В
H(1,1)	362 (53)	-318(53)	3909 (55)	9.2(2.2)	H(1,1)	4792 (52)	2058 (50)	597 (53)	4.5 (2.0)
H(1,2) H(1,3)	- 569 (51)	213 (50)	3978 (51)	$5 \cdot 7 (2 \cdot 2)$ $5 \cdot 2 (2 \cdot 0)$	H(1,2) H(1,3)	5619 (51)	2455 (54) 2797 (49)	1566 (56)	$8 \cdot 1 (2 \cdot 1)$ 5 \cdot 8 (2 \cdot 0)
H(2,1) H(2,2)	611 (52) 84 (54)	2295 (53) 1857 (51)	4262 (55)	6.0(2.1) 9.2(2.1)	H(2,1)	4676 (58)	4694 (57)	790 (59)	8.1 (2.4)
H(2,3)	-347 (54)	2048 (51)	4209 (55)	6.3 (2.1)	H(2,2) H(2,3)	5354 (58)	4294 (36) 4278 (55)	765 (59)	6.7(2.3)
H(3,1) H(3.2)	2200 (56) 3259 (55)	3169 (53) 3547 (56)	5025 (58) 5609 (57)	7.0(2.2) 6.0(2.3)	H(3,1) H(3,2)	2504 (58)	5683 (56)	-977(60)	$6 \cdot 2 (2 \cdot 3)$
H(3,3)	2823 (56)	3627 (55)	7177 (57)	9·3 (2·3)	H(3,3)	2249 (58)	5890 (56)	-2043(59)	7·3 (2·3)
H(4,1) H(4,2)	4214 (55) 4549 (56)	1883 (54) 2911 (55)	7937 (57) 7687 (57)	9·7 (2·3) 6·6 (2·2)	H(4,1) H(4,2)	867 (57) 491 (54)	4173 (56) 4865 (53)	-2968(60) -2799(55)	9.2(2.4) 6.2(2.1)
H(4,3)	3833 (56)	2648 (56)	8275 (57)	6.1 (2.2)	H(4,3)	1322 (55)	4882 (55)	- 3286 (56)	8.7 (2.3)
H(5,2)	4373 (62)	-427(30) -1150(60)	7529 (63)	10.8 (2.3)	H(5,1) H(5,2)	990 (54) 899 (58)	2006 (52) 1314 (57)	- 2933 (55) - 2622 (59)	6·4 (2·1) 7·9 (2·4)
H(5,3) H(6,1)	3606 (58)	-1182(58) -1477(57)	8145 (60)	5.9 (2.4)	H(5,3)	1615 (63)	1123 (60)	-3143 (64)	12.0 (2.6)
H(6,2)	2786 (61)	-1963(58)	6008 (63)	14.0 (2.3)	H(6,1) H(6,2)	2309 (59) 2309 (55)	929 (57) 487 (55)	- 9/1 (61) - 1445 (57)	9·8 (2·5) 7·2 (2·2)
H(6,3)	2228 (57)	- 1749 (56)	6799 (59)	7.8 (2.4)	H(6,3)	3078 (55)	539 (55)	- 1849 (57)	7.5(2.2)

T 11 0	<b>G</b> ( ),	<i>c</i> ,	1	1.0	c d	1 1	<i>a</i> ·	
Table 2.	Structure	jactor c	iata (	× 10) j	for the	observea	reflexions	

* FO FC	* F0 FC * 1+7 35	× +0 +C	* *0 *C	0 100 -84	F0 FC	< F0 FC 9 135 120	· · · · · · · · · · · · · · · · · · ·	x F0 FC	* 231 2+2	8 FO FC	1 414 352	8 FO FC	5 191 -191	* FO FC	1 102 1-0
4 547 -510 6 210 -255 8 1390 -1338	1 111 123 135 134 12 20 -172	8 241 -232 9 251 253	+ 215 210 + 215 210 + 200 -235 + 1031	6 147 148 10 165 178 11 570 -580	2 3-6 203 9 186 -1+9		0 320 -356 10 791 825 12 107 -107 13 215 -189	2 1010 -096 3 395 405 4 213 215 5 698 -496	5 140 130 H= 6, (= 11 6 259 -277	11 310 300 Me -7, 10 8 1 1237 -1285	3 172 186 5 230 -228 9 264 -220	8 233 220 9 157 154 #9, [- 7	6 287 -207 9 17L 196 10 203 215	4 142 97	2 245 -236 3 170 140
10 410 409 12 1322 1369 10 152 -167 18 194 173	15 375 -367 Me -1. (* 2 1 1210 1196	1 353 -308 213 -101 7 365 -336	10 157 151 12 100 -1'3 40 2. (* 7	12 034 056 15 206 158 16 251 219	He -3, (* 13 2 175 186 3 312 -316 4 301 -316	3 665 658 4 208 237 5 193 -189 6 1510 1951	1 221 493	6 177 -139 8 161 -165 9 225 -2C6 12 368 -299	0 365 -417	2 161 156 3 271 267 4 645 -652 6 196 181	0 628 -649 1 1294 1328	1 456 -468 2 643 676 3 195 -195 5 120 -116	He-13, Le 7 3 204 -100 4 315 313 4 155 -112	2 456 -434 5 248 -214	3 217 -218
N= C, L= 1 1 1123 1036 2 1025 -1513	2 92 94 3 737 730 4 1529 -1465 6 124 121	11 346 -321	6 157 -1*7 1 1075 10#1 7 115 -132	1 100 -200	5 521 603 0 160 -102 7 152 114	4 112 -318 0 123 -73 10 207 -701	6 082 975 5 395 -507 6 129 135	13 3+9 33+ H0, L- 1	2 201 172 0 1+3 -144	7 887 182 8 160 153 11 391 -372	3 523 530 276 -266 5 253 -267	7 160 -136 8 259 746 10 245 -278	6 545 545 7 289 256 9 195 180	1 101 143 1 101 143	1 325 -298 2 219 -198 3 221 205
3 1301 -1155 4 373 -341 6 373 -310	7 521 552 8 327 -316 10 205 221	3 100 155 4 165 143 7 184 189	6 1270 1275 9 528 -526 11 169 -197	6 121 -113 5 329 366 6 830 -796	** 3, c* 1* * 23* -190 7 1** -121	13 275 284	1 32 -33	1 744 -753 2 509 -550 3 302 -392	0 216 202 3 231 112 3 174 144	13 105 -142	8 192 239 9 659 -670 11 240 -228	1 239 -258	3" 13, 1°, 3		4 354 -103 10 195 294
8 234 -263 9 362 324 10 514 -388	12 235 25-	1. (* 1) 2. 155 -126 5. 221 - 224	15 18 BI	13 264 -254	Her -3, La 1a 1 273 -209	1 149 -130 3 283 257 4 705 732	1 1540 1531 2 84 156 3 221 226	0 324 332 7 220 -224 9 294 368	7 219 -246	3 330 -329 5 266 295 7 158 193	13 317 200 3 207 -324	a 279 261	7 176 -157 8 194 155 H4-10, 14 8	5 511 -526 4 151 -109 5 344 -342 7 180 153	1 189 201 2 199 -201 3 160 176
1+ 171 -100 1+ 0, c+ 2 0 2537 2-07	1 742 751 2 1.78 -1114 3 866 -835	* 231 191 7 221 204 10 234 185	1 132 133 2 336 341 3 264 177 4 177 -162	2 1361 1339	2 184 145 1 273 -273 4 524 -534 6 184 223	5 101 284 5 141 134 7 607 -629 8 275 301	6 415 437 7 154 -207	10 246 273 12 142 -152 13 190 -203	2 191 120 3 551 551 5 326 305 7 152 -89	1 213 200	7 164 267	1 6C2 502 3 134 -90 4 783 -799	0 254 207 1 111 -147 2 220 -214	* 221 -188	5 107 -211 7 145 117 10 208 180
1 +24 +72 2 84 -53 3 1942 1833 5 1142 1156	5 2165 2157 6 180 -173 7 86C 5-9 8 371 371	1 198 -177 • 140 130 5 455 -473	5 119 118 5 1572 -1663 7 329 -370 8 229 219	6 605 -728 7 193 165 8 153 127	100 10 100 100 100 100 100 100 100 100		9 224 -217 10 724 -313 11 534 634	0 1215 1206 1 133 122 1 133 122	a 224 - 202	+ 174 -146 + 129 115 7 196 -170	1 372 401 2 305 325 6 244 -244	e 173 -162 8 230 240 11 406 463	5 212 212 6 209 -196 10 237 198	1 173 105 2 206 259 3 272 256	* 130 - 94 5 172 113
0 108 133 7 701 - 704 8 589 - 599 9 115 - 134	9 441 -443 12 108 -179 17 208 259	5 3: 533	* 132 -117 10 356 -375 12 228 -257		** - 3, L* 15 * 237 - 200	2 187 -180 3 263 -296 6 663 -670	14 145 -100 	5 323 298 7 141 -178 8 346 341	2 144 -157	1 25 25	15 336 -221	2 267 230 6 158 162	5 17; -202	2 374 393	7 137 - 11
10 145 147	1 105 -197 1 105 -197 2 1902 -1899	3 220 199 5 319 561	1 227 213		1. 2), 1. 18 3. 2), 1. 18	· · · · · · ·	3 374 - 375 5 439 -462 7 237 -236	10 +03 3+2 11 +66 3+6 12 +76 +97	1 249 -252 3 277 -256	· 230 -210	1 234 240 6 354 350 6 156 -102	7 3: "	1+-10, L+ 9 0 334 333	** 12, L* 2	***-13, t* 10 1 242 232
15 304 280	7 1010 -1073 7 126 -136 8 347 372	2 32 - 320	eli elo e eso -eso 10 151 -13e	3 545 -547	2 5+1 - 527 2 143 - 100	2 133 -44 3 240 302 4 240 -232	12 134 156	5 2433 -2445	0 218 -228	5 200 -194	10 256 -236	* 267 -279 7 151 -99	3 432 -443	2 140 149 3 181 196	5 193 -227
1 +0C 353 2 1+3 -130 3 +41 -435	13 341 -416 T 11 15.15	2 214 227	#* -2, L* *	11 226 -233	5 529 533 7 1066 -1010 8 766 371	* 182 -108 * 279 -297	1 235 -247	* 163 -181 * 152 154 * 214 275	1 241 -213 3 292 361 4 175 136	6 156 111 7 158 198 8 248 261 9 156 136	1 000 007 1 000 007 2 020 055 0 200 255	19 215 -121	* 256 260 10 154 -138	* 259 -256 * 219 -206 10 173 152 12 235 228	* 275 268 5 158 1+1
5 181 -183 7 196 -191 9 +65 -+55	2 83 87 3 860 -840 4 851 -899	· 300 32-	3 813 -8-6 + 569 812 5 1+3 101	3 1129 1134 • ••• •••	10 186 195 11 716 707 15 630 636	0 430 414 1 617 -617 2 377 -364	5 746 -875 6 363 358 8 218 -216	1 257 246 1 135 -118 1 486 847	2 100 157	11 147 102 H= 7, (= 11 2 295 -201	5 310 -324 6 449 484 7 216 223 9 237 -226	1 172 155	H+ 10, L- 10 + 786 303	H+-12, L+ 2 0 418 -398 1 166 -146	2 342 347 14 13. La 14
10 322 -246 11 126 -111 12 319 318 17 209 -197	5 251 -253 6 145 156 7 235 257 6 195 -163	C 3114 -3328 1 201 -244 2 114 110 3 2037 -2728	6 200 199 7 115 -173 8 821 860 9 260 235	6 1-0 -1-7 7 1196 -1231 8 407 -4-7 9 237 255	He e, te 1 6 140 -133 1 1466 -1314	4 171 126 6 986 981 8 273 -214 9 321 3*3	9 448 -471 15 294 244 11 135 119 12 148 157	16 167 -156 15 153 180	6 298 -260	3 276 -204 5 258 291 7 185 126	13 191 187 	1 437 465	40-10, L= 10 0 237 223 5 193 205 6 239 224	3 433 438 4 224 -225 6 172 -148	1 350 -306
H- 0, L- 4 0 1+53 -1-89 1 +53 +15	11 200 202 15 178 -196	+ 732 72E 5 993 -976 6 244 -246 7 307 304	11 332 333 12 191 -213	10 233 233 11 1251 -1222 13 156 -129	2 1079 1067 3 391 - 372 5 379 - 336	10 275 -246	13 232 -217	2 407 -373 3 453 -452 4 242 237	- 22- 200	1 174 -103 2 1-1 -117	7 176 236	8 241 -226 10 179 148 12 283 257	10 232 163 11 161 -172	4- 12, 1- 3 2 320 -310	1 165 196
3 1160 1100 3 1160 1100 5 405 865	1 306 103 20-3 - 2100 257 - 257	4 281 250 10 452 -445 11 104 -220	0 100 -111 1 310 200 2 400 -46-		7 481 4471 3 363 351 12 147 155	1 194 192	5 248 -225 7 669 703 8 873 -615	6 297 -303 7 218 -217 8 185 -1=*	5 101 -795 5 101 101 6 116 -99		1 227 -205	2 219 210	H+-10, L+ 11 5 237 142 6 306 -263	2 20 22	0 147 121 233
6 127 108 10 213 -219 11 146 -146	9 178 -176 10 184 182 11 512 533	15 207 -186	+ 332 309 + 1280 1286 7 290 318	3 602 -567 5 1155 1146 6 73 -461	15 176 -111	· · · · · · · · · · · · · · · · · · ·	He -5, Le &	10 306 -405	4 365 371 12 297 290 13 210 140	2 124 -167 3 247 256 4 161 -163	7 306 279 8 178 -137 12 3-0 -301	· 104 -159	H10, L- 12	· 233 237 • 237 -204	0 238 -201 3 160 -181 5 184 -144
	1 245 273	0 70 -20 1 900 -801 2 765 804	1 - 2 - 1 - 4 1 - 29 - 506 2 - 375 - 349	5 28 28	0 105 117 1 111 -207 2 724 -711	1 184 -181 1 187 -154 3 437 -412	3 053 -018 • 030 055 5 107 00	0 345 344	7, (* 1 2 1446 1459 3 193 191	7 153 186 No 7, Lo 13	0 205 100 1 367 -331	2 133 -106 4 136 -99 7 321 -338	5 194 159 6 276 255 7 153 -179	10 254 -227	7 103 155 H14, 1- 2 - 275 742
2 144 -185 3 493 -461 4 192 232 8 1401 1471	3 96 -102 - 139 -143 - 335 214	* 365 -364 * 184 152 * 1340 1243	5 215 -700 7 310 -322 9 321 -375	2 535 -562 3 1264 1357 4 244 242	3 433 435 4 438 432 5 43 46 4 1022 -1010	* 288 -278 M* 4. L* 11 0 151 -135	7 111 326 8 352 346 9 336 -335 10 349 -345	3 700 744 4 177 145 6 579 540 7 256 -268	6 262 -253 7 209 218 9 317 -325 10 687 -665	2 262 -319 He -7, L- 13 J 317 306	3 145 -124 4 173 193 0 147 160 11 174 145	10 161 131 n= -9, t= 13 2 139 142	He-13. Le 11 6 101 152 8 194 -142	3 317 333 3 244 276 5 150 176 7 259 -257	* 105 170 H= 14, L= 3 2 302 325
12 169 147 13 177 -104	6 213 197 7 123 66 8 176 144 9 261 -237	7 263 -211 7 266 -226 10 197 -146 12 197 146	11 220 -194 13 235 231 He 2. Le 13	5 335 346 6 286 325 7 470 434 8 136 -155	0 4°0 -437 12 409 -353 40 4, (4 2	2 796 -323 6 145 177 8 186 -177	11 1006 1632 15 170 -134	9 216 -238 12 253 249	12 157 254	4 272 201 5 472 -469 7 279 -241 9 100 172	AL 8. L- 12 0 2-8 23- 4 190 -206	5 374 374 7 321 201	He-13, Le 14 3 161 167 4 215 -206	He-12, Le 4 0 202 -231 1 229 -229	0 190 -188 He-14, Lo 3 3 191 -138
3 8ut 745 6 640 -501 5 333 316	10 100 101 13 271 -289 14 107 154	17 149 144 	0	10 386 368 12 193 -171	0 2232 -2117 1 113 -54 3 389 -383	6 165 163 1 152 -152	1 143 -171 2 341 -404 3 474 -456 5 512 537	0 1341 -1368 1 462 455 2 148 -125 3 268 -262	2 1396 -1447 3 364 280 4 160 172 5 1088 -1137	HF -7, LF 14 1 100 -108 2 199 -185		1 235 144 3 143 -152 7 282 -287	2 111 171 8 246 246 7 336 - 331	2 143 -179 3 -56 -471 6 213 -211	* 156 -186 5 363 363 6 364 -368
8 473 -476 9 182 -190 11 391 -364 1- 148 -117	1 2e1 -2e7 3 510 511 4 222 256	2 165- 975 3 075 -049 4 119 -101 1 300 -331	6 1+0 -106 7 +07 399 6 351 -355 11 226 -239		3 103 -94 8 246 -247 7 362 -361 8 432 421	2 163 -137 6 167 -145 5 162 163	6 416 -412 7 731 204 9 144 -165 13 157 -119	5 -46 -424 7 670 -661 8 333 3-1 11 207 245	7 310 -244 8 204 -237 9 129 -158 10 448 416	3 200 244	6 186 -192 7 256 272 8 210 185	40 - 9, 10 15 2 176 - 155 1 156 - 125 5 212 - 218	40-10, L0 15 0 212 238 1 251 -257	H+ 12, L+ 5 2 201 -218 6 300 243	0 186 -145
- 0, L+ 7	5 750 -762 6 356 -343 7 256 -232	6 373 -400 7 250 278 8 305 287	H2, L- 13 0 149 -141	• 239 247 • 171 195 11 459 -472	10 251 -228 11 136 312 12 618 -603	10 103 -135	······································	8 13 15	11 207 10	3 100 100	10 - 24 - 250 1 - 257 - 117	M# -9. L* 16 1 312 201	HF-10, L= 16 0 291 -284	He-12, (* 8 0 263 275 1 365 -356	- 14. 1- 5 7 103 105
1 184 -715 5 146 341 5 135 129	1. 13 - 13	10 135 127 12 497 501 13 179 -210	141 -215 7 275 245 4 136 164	1 12 14	13 13 141	7 205 165	3 533 -614 7 202 196 6 140 -131	0 757 -743 1 367 -373 2 106 -122	3 305 -302 4 327 -298 7 616 -647		· · · · · · · · · · · · · · · · · · ·	H- 10, L- 3 0 1220 1276 1 546 -535	1 552 -370 4 276 247 5 186 -193	5 172 209 9 290 272 10 194 -178	1 740 230
7 +29 +0a 9 3a8 3c+ 17 198 213	1 517 473			3 719 761 5 137 -139 5 136 -125	9 2375 240e 1 772 315 2 152 -179	0 1101 1114 1 124 141 1 121 -122	10 482 4497 11 111 -106 13 100 -114	5 736 -739 7 315 -100	• 2L3 -205 10 2e3 -253 11 277 -245	3 454 440 5 155 131 6 137 148	7 107 105 	3 901 915 5 603 396 5 637 652	100 -107 10 11, Le 1 2 834 -846	11 106 13 11 106 13 11 106 13	• 330 -355 • 155 -1•3
1. 100 -101	1 403 405 4 154 -142 11 647 -13	6 156 -128 3 1034 -992 6 279 -713	2 459 -448 7 462 -449 10 417 101	7 635 -656 6 498 314 9 135 -130	* 245 277 7 171 100 * 598 605	7.5.13		10 349 -385 11 2-1 252	He -7, 1 - 7 1 241 311	4 166 153 10 474 -458 11 477 -478	2 140 -107	* 181 -174 11 201 209	• 223 222 • 244 • 265 242	5 165 150 5 364 338 5 187 173	0 287 -248 3 100 -170 4 142 -181
0 217 -211 3 936 928 5 410 385	12 195 204	5 1514 -1502 8 124 -118 7 1224 1162 8 1098 -1058	11 193 176 	11 726 -733 12 335 -374 13 141 -44 15 202 271	* 128 185 10 620 633 11 605 190 12 815 844	He -4. Le 13 0 200 -183 1 553 500	6 215 -162 6 250 -250 9 203 162	1 221 -218 2 419 434 4 205 150	* 105* 1027 5 2** 3*1 * 1** 171 7 1*7 115	12 +30 -435	* 366 -361 5 *51 *55 8 *15 -*12 15 231 213	12 221 191 == 10, L= 1 7 713 -756	7 224 204	7 330 -347 8 265 248 10 149 104	6 191 202 Ma-14, La 7 1 361 344
7 311 -312 8 255 296 9 236 -236 10 207 196	2 97 -81 3 562 517 4 923 995 5 147 127	9 217 215 12 314 309 15 351 -245	1 217 -208 2 139 149 4 134 145 2 185 -145		16 196 -153 4- 4, (* 3 1 1-08 -1416	2 134 -115	11 250 -250 ma -4, Lo 8 L 425 405	6 746 800 7 444 -463 8 250 -244 16 228 -226	10 255 -246 11 241 263	2 239 227 5 277 -307 7 189 190 8 285 249	12 167 -147 10 9, 10 1 1 300 380	3 208 -291 5 173 163 13 174 -178	3 3-8 -3-7 5 6-8 63- 6 275 216 7 301 202	40 12. L0 7 6 346 356 H0-12. L0 7	3 275 271
11 215 -210 12 196 151	6 526 -134 7 115 -140 8 741 -816 9 223 217	C 4241543 1 537 -565 2 125 116	• • • • • • • • • • • • • • • • • • •	1 192 101 1 113 -115 2 30 219 6 777 237	4 984 1202 4 441 427 4 113 -135 5 245 241	0 354 -334	2 143 151 3 561 -567 4 1784 1833 5 279 116	······································	**************************************	16 405 482 17 159 126	3 420 462 4 156 -168 5 1261 -1292	a-10, L- 1 - 155 - 155 1 193 - 229 2 127 - 167	4 254 -218 12 155 -155 He 11, 14 - 2	0 166 191 1 256 -263 3 267 -272	0 222 -191 3 247 -224 5 166 -176
1 993 -575 2 225 -268 3 373 -365 6 1517 -1568	10 181 146 11 257 -379 12 330 361 15 211 191	3 150 141 - 169 167 - 154 -151 - 154 -151	2 150 150 2 150 150	7 166 -1.0 9 112 224 19 311 307	• 140 112 • 305 -347 • 136 148	1 224 174	6 284 - 304 7 310 344 8 399 -405	2 227 -208 3 200 277 4 215 233	10 215 -235 13 159 147 14 264 -165	0 124 142 1 323 -360 3 642 -619	* 151 135	3 296 -313 6 196 -180 5 352 -335 5 352 -335	2 101 -130 3 436 -460 7 168 -162	5 556 511 6 555 -525 7 171 -125	0 108 126 2 109 -120
8 159 137 • 140 136 16 316 30•	······································	* 31.9 321 10 449 -443 11 350 -341	0 348 - 177 1 104 - 172 2 101 - 103 1 265 - 193	······································	13 372 - 344	2 207 -174 8 286 -244	··· · · · · · ·	6 1428 1492 7 211 205 8 206 -229	1 247 288	4 201 225 174 192 9 201 -201 17 101	1 178 144 2 1142 1188 4 221 -204	7 135 -46 9 253 253	He-11, (* 2 1 290 -316 3 375 389	** 12, L* # * 217 -195	5 148 -127 6 280 262
13 137 -107	3 301 -294 5 165 -163 7 134 -113	13 104 -147 13 363 -340 16 168 127	5 457 -150 5 457 -502 6 156 -120	5 443 -442 5 499 511 6 466 -470	1 566 612 2 765 .756 3 719 -756	3 166 -179 3 262 -225 3 260 -225	5 362 315 5 165 176	10 256 -286 12 163 117 13 197 -205	+ 142 -175 + 124 -73 -7 112 -76	12 206 173	1 162 -245 1 162 -185 9 217 272	0 554 -540 2 147 45 3 730 749	5 217 -225 7 262 306 8 15C 172	3 335 -138 3 139 -149	0 186 -192 3 227 -180 5 157 -150
6 442 -438 4 880 842 1 491 321	9 491 -489 10 316 -367 12 195 178	1 251 -247 2 256 -212	* 187 -158 ** 3313		5 309 305 6 896 -898 7 146 -157	0 103 -235	1 229 245 2 251 -193 3 363 -453	0 161 -175 3 586 -596	10 176 -129	1 30% 297 3 5%7 -559 5 773 -775	12 227 197 	5 623 635 7 573 -596 10 198 -187	44 11, 14 3 1 751 216 2 528 -547	**************************************	0 145 172 1 226 180
7 621 -617 8 691 692	······································	4 204 -191 5 126 -140 6 253 192	244 254	1 419 4424 3 207 -273 4 1310 -1374	15 512 578 12 516 -525 13 168 199	1 1320 1200	5 497 592 6 156 -169 8 171 1-7	• 231 -244 • 175 -163 11 180 175	3 289 -289 4 631 -625 7 610 -642	7 1680 1098	2 118 60 9 455 468 9 154 -114	0 1200 1234	10 207 207	44-12, 14 0 1 139 125 3 170 137	5 202 -251
1 230 251	3 546 611 5 308 330 5 326 - 369 6 101	8 164 -91 10 196 -179	3 363 315	7 165 165 8 310 330 12 150 -119	0 707 726 1 514 -467	1 107 -100	He 5. (* 10 1 676 -653 11 358 -374	0 1503 1670 2 253 -235	10 213 -211 11 322 -302 12 142 -115		7 145 200 10 216 168 11 220 167	7 167 157 7 355 363 6 155 -143	1 141 -227 1 141 - 143 1 141 - 143	5-14: 1.18	······································
7 216 -316	• 249 323 12 215 -259 13 1+5 1++	0 103 134 1 1562 -1437 2 1234 1148	0 350 305	1 753 750 3 104 -115	3 102* -1031 525 -416 5 178 -183	• 121 • 97 • 173 • 1• 9 17 270 • 267	** -5, (* 10 1 572 -573 2 163 157	+ 158 2Co 5 587 -601 • 205 -212	He -7, Le 4 1 573 -550 2 304 294	* 2*2 250 5 666 -694 7 356 374	HE -9, LA 2 1 471 -536 2 149 144	12 232 215 T 12: 1- 3	11. Le		5 25 235
5 192 3e1 7 2e4 -276 6 179 202	7.81.18	3 433 -444 9 732 733 9 194 409	3 185 -382 4 159 82 5 498 -503	5 167 -175 6 369 363 7 170 -136	6 266 -364 12 1-5 -167	1 11 12	5 176 164 7 216 162	9 166 -162 H- 6, L- 7	+ 1375 1+23 5 247 278 • 150 -133	12 254 -237	• 178 173 • 200 207	10 171 152 13 187 -210	1 111 1 111	2 244 214 6 273 247	·
5 19 -157	• 112 1.5 5 150 159 • •71 -•11	11 272 255 13 274 - 109	······································	9 164 -218 10 256 -271 11 312 144	C 3633 -3741 1 324 -331 2 63 122	2 976 -995 3 181 187 3 458 452		2 134 123 3 194 181 4 156 175	12 (46 (43 77 (14 (4)	2 219 221	2 401 624 3 246 236 4 103 -186	2 342 -359 1 410 421 2 313 359	\$ 207 -214 7 314 303	0 036 -014 1 295 -263 2 169 -109	ma-15. La 3 2 161 -108
0, L- 1- 0 0-0 -567 5 172 10-	11 307 303 17 208 257	0 2065 2254 1 264 -241 4 377 -335	· · · · · · · · · · · · · · · · · · ·		6 1C0 - 76 5 576 601 6 662 676	7 205 230 2 120 135 10 527 523	2 216 -212 3 171 159 5 187 -166	+ 1017 1042 + 267 256 10 232 -259	1 24 101 1 553 553	13 235 216 TT TI IT	6 154 -141 7 454 -462 9 189 -152	5 314 -327 6 234 -253 7 231 -160		**-12. 1• 13 • • • • • • • • • • • • • • • • • • •	5 275 227
1 281 -244	1 462 -490	6 142 106 6 518 - 67 12 331 286	- 204 - 117	2 307 330 7 32- 93 8 200 - 180	6 712 755 9 170 174 15 365 351	12 313 -316 34 376 -394	· 226 159	13 210 -208 0 -55 - 13	9 274 269 9 274 269 10 203 269 12 152 -131	1 005 -080 2 240 -230 5 310 -339	1 201 203	19 212 218 5° 189 1-712	7 153 -182	3 155 122	3 145 141 • 230 -218 • 167 149
	5 205 218 7 731 -758 4 306 -321	C 1001 -1010 1 283 -309	· · · · · ·	7 300 -283 14 208 176	11 114 114 T	1 533 -191 2 529 -153 3 89 -77	3 217 -213 • 313 -30• 5 • 72 • 46	2 655 -670 3 617 -623 6 250 -279		· 245 246	• 177 -163 • 177 -163 • 227 -210	4 192 142 7 246 216 10 228 -208	5 200 230 8 289 280	3 334 -260 4 206 189 5 184 -182	5 204 -222
5 122 - 133	11 7vo -011	3 1717 1840 4 137 -124 5 654 -660	2 232 224 3 1636 1187 • 1414 1664	1 400 -416 2 747 754 3 358 -357	2 531 510 3 196 154 6 18; -168	3 416 407 7 363 364 9 156 -167		6 369 -346 9 782 814 10 166 -101	5 575 -531 5 692 722 9 751 757	0 332 333 • 382 -•10 5 •52 -•51 • 24• 235	10 280 -296 13 150 105 14 156 134	0 315 331	1 152 -159 6 272 -257	· · · · · · · · · · · · · · · · · · ·	1 169 134
2 238 201	5 252 276 6 236 -210 8 257 231	7 #6n 912 8 236 255 9 151 -156	1 147 -121 9 139 262 12 172 -11	6 140 126 8 243 -237 13 271 -225	7 174 140 6 740 247		··· -1, (* 12 1 100 -220 2 121 105		13 152 -123	10 240 236 12 282 252	A- 0, [- 0 3 /02 256 5 105 217	3 159 120	1 550 57 3 255 -275 5 171 140	1 200 204 1 215 - 124	5 199 -149
3 1529 -1487 4 526 549 5 160 180	10 246 -309	11 120 - 101 15 143 - 151 10 2. 10 5	13 13 14	12 100 177 1 013 549	5.11.11	Tulk Sof	5 333 -287 5 331 -522 5 162 -144 7 152 136	1 133 -134	5 344 - 394 5 526 - 456 6 251 272	0 1113 1130 1 352 342 2 165 192	• 105 -104 • -V, L. • 1202	6 130 -128 7 355 365 8 318 -325	6 726 -736 8 788 -753 16 105 138 11 164 180	2 243 261 - 144 -130 5 226 -173	1 144 207 2 246 209 3 256 -228 4 156 137
7 795 744 8 845 820 11 147 187	2 1/6 -147 3 560 540 4 198 206 5 461 -499	1 1600 1071 4 310 -313 6 336 -171 7 126 93	1 452 445 1 452 445 1 452 445 1 452 445	3 2(1 - 199 • 693 -643 5 163 145 1 147 143	1 12 52 1073 2 222 246 3 929 944 4 159 -164	1 240 247 4 934 910 5 165 -177 7 935 -573	7 A 'A	2 148 -116 4 522 -551 5 135 -110 7 166 -148	# 220 189 12 197 -157 He -7, Le 6	3 104 -103 4 401 397 5 202 -199 8 108 -157	3 164 170 4 507 -531 5 267 -227 7 247 242	10, L. 3 3 105 -100 177 177	12 195 185 He-11, Le 7 1 169 -173	2 277 -257	
12 507 404 14 233 -255 15 216 -222 16 199 179	8 2C2 -225 9 436 470 20 484 516	16 126 -96 11 185 -176 13 174 182	6 363 340 7 666 -663 8 395 -393 9 613 610	11 349 341	6 142 -154 7 497 -518 9 727 -764 11 351 -316	11 1*2 140 12 364 -378	2 280 -282 9 172 -130		3 130 101 4 731 730 6 147 -127	11 167 -110 m 0, 1 5	9 160 170 11 217 -193 12 230 -220	10 180 201 H+-10, L+ 5	5 246 218 5 259 -235 5 168 131	* 232 235	1 170 -217
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3 2382 -2289 6 108 -111 5 2089 2099 6 870 -662	3 3+7 303 4 418 8+3 6 241 -235 7 59+ -586	2 467 -341 3 680 -717 4 423 436 5 151 154	n= -3, (= 1 1 10= -155 2 326 321 3 631 910	7 252 244 4 204 159 10 147 -133 11 319 320	1 543 -547 3 379 365 5 335 -237 5 335 -314	• 125 -150 • 225 -225 7 •96 -716 • 115 -63	2 355 -144 4 148 175	8 103 -135 	11 543 -546 12 107 -100 44 7, 14 7	He -8. Le 5 0 278 -294 1 277 273	4 224 -228 10 344 -358 44 -9, L4 5	4 145 104 5 268 -288 6 266 291 7 140 102	He-11, Le 8 1 167 169 2 132 -131	H+-13, L+ 2 1 134 84 4 140 147 6 162 -114	2 198 -164 He-16, L= 3 1 200 215
r 350 352 8 172 -217 9 815 -626 10 606 -661	8 291 -273 9 200 1-5 11 227 -241 12 331 290	6 1257 -1326 7 206 205 8 159 175 9 324 350	+ 1+5 15+ 5 078 -08+ 6 567 -435 7 201 -207	No. 3. (* 11 2. 322 - 344 3. 137 - 153	9 732 -240 9 143 -123 12 237 176	* 182 -188 11 195 -208 12 463 -451 25 172 193	5 350 -347 7 255 -164 He -5, (+ 16	2 275 252 3 164 -157 5 218 188 9 254 247	1 179 -184 2 142 146 3 165 -157 6 194 237	2 331 350 3 370 -362 4 452 -507 6 739 -772	1 160 151 2 475 501 3 204 198 6 189 197	* +255 -397 10 208 -234 11 171 -146 13 244 236	6 210 262 7 249 -278 8 603 -594 13 273 296	11-13. (- 3 3-156 -128 3-193 -219	3 162 154 Mar. 16, 14 6 0 152 -135
11 187 -219 12 373 393 13 565 569 17 269 279	100 -1. L. 13 3 172 156 4 10 4431	16 555 17/ 11 5/7 197 12 361 -386 13 186 -151	8 202 193 9 379 384 10 679 -696 12 505 492	5 112 - 318 7 146 -116 9 166 -202 10 197 -200	N* L* 6 0 1211 - 1220 1 120 101 2 191 174	He 3, [* 3 ] 256 - 266 3 + 09 390	· >>> >>>	0 130 183 1 200 201	10 100 100 10 100 100	9 313 297 11 293 279	1 195 -150 1 104 104	4- 10, 14 6 9 401 -403 1 154 157	11 320 -260 Maril, La 4 1 109 222	• 229 -217 7 145 148 • 179 -149	* 224 -225 #*-16, (* 5 2 198 -219
H= -1, t= 1 1 228 -259 2 2599 -2574	6 265 244 7 142 -160 8 257 276 9 143 -152	0 1311 -1264 1 526 551	10 101 -139 He 3, 10 2 1 005 -569	······································	3 1404 -1445 4 444 -444 5 176 173 7 714 -245	* 1+0 -123 5 952 -927 5 513 512 7 212 -123	1 410 304 2 00 -07 3 311 -272 4 241 -247	2 149 151 6 449 -463 5 162 140 6 879 -905	1 663 706 2 214 -170 3 178 144 4 119 -155	3 185 -171 4 245 242 8 268 308 10 392 107	1 173 -141 1 290 326 11 203 -215	* 219 -226 7 151 153	2 13894 7 253 252 10 246 226	H==13, 1= 3 6 200 -230 9 320 326	3 160 111 4 207 198 H16, L- 7
3 155 146 6 214 -183 7 157 -178 8 502 498	11 179 -156 12 191 -203	2 181 171 3 226 222 4 108 85 5 327 320	2 137 -111 3 326 316 4 240 254 5 91 -34	5 238 258 6 329 -149 13 326 -263	10 150 -110 11 325 355	140 -142 4 330 313 13 376 757 12 170 -152	5 520 -401 8 213 234 7 754 785 8 308 271	8 141 153 *** 8, 1* 10 0 308 376	5 383 387 6 245 228 9 128 126 10 360 367	1 313 248 2 263 215	+++ -9, 1- + 3 273 247 4 1016 -1038 5 220 -183	0 345 392 1 163 166 3 200 197 4 227 -226	He-11, Le 10 0 176 126 7 215 -147 8 186 -157	100 13, 14 4 3 233 -140 4 154 -147	2 100 -244 Harla, La 8 0 173 154
9 127 -129 10 773 806 12 631 -635 13 107 -206	2 191 -147 5 101 108 5 386 389 6 162 131	0 144 129 7 215 -201 10 102 -199 11 135 -136	6 605 379 7 1084 1104 8 345 334 12 225 188		16 181 -107 17 183 -118	13 199 -200 7 102 -1100	10 366 367 11 203 -223 12 313 311 14 229 -219	1 318 -367 3 297 306 7 386 -385	13 216 230 1" 54 1" 57	3 240 -255 5 263 234 6 122 110 8 245 -226	7 354 389 8 443 461 9 183 152 10 268 -205	5 159 -118 6 315 -322 7 270 276 8 241 -239	9 182 -138 10 160 113 M11, L+ 11		3 188 -136
14 176 -214 14 1, 14 2 1 465 -435	1 129 -140 1 129 -140 1 161 174	12 212 -247 0 2352 -2494	14 236 -224 14 -3, 14 -2 1 -44 -437	1 100 -160 529 505 7 145 100	• 331 -325 • 1•79 -1505 7 209 202 • 155 145	5 055 -658 7 175 155	15 267 -223 16 175 -167 H* 64 .* 1	0 1000 1008 1 390 370 2 211 209	3 224 -200 4 160 121 5 188 -139 7 172 197	12 204 -176 14 190 137 + 8,14 7	11 277 252 10 9, (* 7 2 218 219	11 234 -258 1 217 -228	2 194 -340 7 211 174 9 220 -194 10 334 274	v 174 -131 13 218 224 H+-13, L= 5	Na-16, La 10 0 219 252 1 230 196
3 4301 -1446	3 861 -704	1 236 -224	· /us -ese/												

steric interference between the *cis*  $N(CH_3)_2$  groups of the molecule. The shortest intramolecular  $H \cdots H$  distances between different amino groups are 3·2-3·5 Å, which are considerably longer than the  $H \cdots H$  van

der Waals contact of 2·4 Å. In the geminal molecule atom P(4), which has substituents  $Cl(NMe_2)$ , is also displaced from the mean plane of the ring by 0·073 Å on the same side of the plane as its Cl substituent.

# Table 3. Agreement analysis for the chemically equivalent bonds (Å) and angles (°)

The e.s.d.'s, in parentheses, are those derived from the least-squares refinement and refer to the least significant digits. I and II are the molecule numbers.

Bond	Number	Range (I+II)	Mean (l)	Mean (II)	Mean (l+Il)	$\chi^{2}$ (1+11)	P limits
P-N	12	1.557-1.598 (8)	1.579 (3)	1.578 (3)	1.579 (2)	37.7	< 0.001
P-Cl	6	2.050 - 2.065(4)	2.056 (2)	2.059 (2)	2.057 (2)	10.1	0.10-0.02
P-NMe <sub>2</sub>	6	1.590-1.630 (8)	1.615 (5)	1.606 (5)	1.610 (3)	13.5	0.02-0.01
N-C	12	1.420-1.501 (14)	1.474 (6)	1.466 (6)	1.470 (4)	29.4	0.01-0.001
Angle							
PN-P	6	119.4-121.0 (5)	120.2 (3)	120.4 (3)	120.3 (2)	7.8	0.20-0.10
N-P-N	6	117.4-118.8 (4)	118.1(2)	118.1 (2)	118.1 (2)	9.3	0.10-0.02
N-P-Cl	12	106.0-107.3 (4)	106.9 (2)	106.8 (2)	106.8 (1)	17.1	0.50-0.10
N-P-NMe <sub>2</sub>	12	109.1-110.3 (4)	109.5 (2)	109.7 (2)	109.6 (1)	12.8	0.20-0.30
Cl-P-NMe <sub>2</sub>	6	104.2-105.8 (3)	105.2 (2)	104.8 (2)	105.0 (1)	21.2	< 0.001
PN-C	12	116.5-120.8 (7)	118.6 (3)	118.9 (3)	118.8 (2)	33.6	< 0.001
C-N-C	6	110.6-113.8 (8)	113.1 (5)	112.4 (5)	112.7 (3)	9.7	0.10-0.02





Molecule I



Molecule II

Fig. 3. Bond lengths (Å), angles (°), and their e.s.d.'s as derived from the least-squares refinement.

## Table 4. Torsion angles (°)

	Molecule I	Molecule II
P(6) - N(1) - P(2) - N(3)	-18.6	-15.1
N(1) - P(2) - N(3) - P(4)	17.2	14.9
P(2) - N(3) - P(4) - N(5)	-16.7	-16.3
N(3) - P(4) - N(5) - P(6)	18.1	18.2
P(4) - N(5) - P(6) - N(1)	- 19.8	- 18·4
N(5) - P(6) - N(1) - P(2)	19.9	16.6
Mean $ \tau $	18.4	16.6
C(1)-N(7)-P(2)-N(1)	- 47.5	-45.0
C(2)-N(7)-P(2)-N(3)	40.3	41.7
C(3) - N(8) - P(4) - N(3)	- 35.5	<i>−</i> 49·0
C(4) - N(8) - P(4) - N(5)	44.8	37.9
C(5) - N(9) - P(6) - N(5)	-42.6	-40.2
C(6)-N(9)-P(6)-N(1)	44.5	42.4
Mean $ \tau $	42.5	42.7

Table 5. Distances (Å) from the mean plane of the phosphazene ring, and  $(1.25 \text{ e.s.d.}) \times 10^3$  in parentheses

N(1) N(3) N(5) Mean,  Max-Min	Molecule I - 0.081 (10) - 0.060 (10) - 0.078 (10) - 0.073, 0.021	Molecule II 0.059 (11) 0.060 (10) 0.079 (10) 0.066, 0.020
P(2) P(4) P(6) Mean,  Max-Min	0·069 (4) 0·065 (4) 0·086 (4) 0·073, 0·021	$\begin{array}{c} -0.053 & (4) \\ -0.072 & (4) \\ -0.072 & (4) \\ -0.066, & 0.019 \end{array}$
Cl(1) Cl(2) Cl(3) Mean,  Max-Min	1·930 (4) 1·938 (4) 1·989 (4) 1·952, 0·059	- 1.907 (4) - 1.948 (4) - 1.949 (4) - 1.935, 0.042
N(7) N(8) N(9) Mean,  Max-Min	- 0.969 (10) - 0.961 (10) - 0.900 (10) - 0.943, 0.069	0·995 (10) 0·951 (10) 0·925 (11) 0·957, 0·070
C(1) C(2) C(3) C(4) C(5) C(6) Mean,  Max-Min	$\begin{array}{c} -1.018 \ (14) \\ -1.124 \ (14) \\ -1.232 \ (17) \\ -1.090 \ (14) \\ -1.018 \ (14) \\ -0.979 \ (15) \\ -1.077, \ 0.253 \end{array}$	1.067 (15) 1.138 (17) 0.992 (15) 1.214 (12) 1.037 (16) 1.126 (19) 1.096, 0.222

The mean P-Cl bond length is 2.057 (2) Å, which is comparable with the value 2.051(2) Å in the corresponding unit  $\equiv$ PClNMe<sub>2</sub> of the geminal molecule. These are considerably longer than the P-Cl bond lengths 1.992 (2) and 2.014 (2) Å in the unit  $\equiv PCl_2$  of the geminal molecule, and the mean value 1.985 (2) Å in Cl<sub>6</sub>P<sub>3</sub>N<sub>3</sub> as determined by Bullen (1971); all before correction for thermal vibration. As described by Keat, Porte, Shaw & Tong (1972), the P-Cl bond lengths which have been determined from the X-ray analyses of these and other chlorocyclophosphazenes show a definite straight line correlation with their observed <sup>35</sup>Cl n.m.r. frequencies. This evidence further confirms the observed variations in the P-Cl bond lengths in the different structures. The elongation of the P-Cl bond of the unit  $\equiv$ PCINMe<sub>2</sub> has been described by Bruniquel, Faucher, Hasan, Krishnamurthy, Labarre, Shaw & Woods (1972) as indicative of a considerable transfer of charge from the amino group to the chlorine atom on the same phosphorus, and represents delocalization in the bisecting plane perpendicular to the ring. In the cis nongeminal molecule, each elongated P-Cl bond is accompanied by a rather short P-NMe<sub>2</sub> bond of about 1.610 (4) Å, compared with 1.640 (3) Å in the unit  $\equiv P(NMe_2)_2$  of the geminal molecule, and a norm of 1.678 (7) Å in  $(NMe_2)_8P_4N_4$  as determined by Bullen (1962). Similarly, a somewhat shortened exocyclic P-N bond of length 1.628 (4) Å was observed in the unit  $\equiv$ PCINMe<sub>2</sub> of the geminal molecule, but by itself was not considered as sufficient evidence that the exocyclic P-N bond in the unit  $\equiv$  PClNMe<sub>2</sub> was shorter than those in the unit  $\equiv P(NMe_2)_2$ . However, in view of the present results, this hypothesis should now be accepted as valid.

The plane formed by each pair of nongeminal ligands, P-Cl and P-NMe<sub>2</sub>, is very nearly perpendicular  $(89.0-90.5^{\circ})$  to the mean plane of the ring. The valence angles between each ligand and the two adjacent sides of the ring are 106.8 (1) for P–Cl, and 109.6 (1)° for P-NMe<sub>2</sub>, while the Cl-P-NMe<sub>2</sub> angle is  $105 \cdot 0$  (2)°. These are very nearly equal to the corresponding mean angles 106.7 (1), 109.5 (1), and 104.6 (1)° in the unit  $\equiv$ PCl(NMe<sub>2</sub>) of the geminal molecule. The first and second angles in each case indicate that there is less repulsion between the P-N(ring) and the elongated P-Cl bonds, than between the P-N(ring) and P-NMe<sub>2</sub> bonds. This is to be expected since P-NMe<sub>2</sub> has partial double-bond character, hence more concentration of electrons on the bond near the P atom and more repulsion with the adjacent P-N(ring) bonds.

The average dimensions of the NMe<sub>2</sub> groups are: N-C=1.470 (5) Å, P-N-C=118.8 (3), C-N-C=112.7 (3)°, and the sum of the three valence angles at these N atoms is  $350.2^{\circ}$ . As shown in Table 5, the C atoms are not all equally spaced away from the mean plane of the phosphazene ring. They are located at distances -0.979 to -1.232 Å in molecule I, and 0.992 to 1.214 Å in II [e.s.d. (r.m.s.) = 0.015 Å]. Such variations in the solid state can be attributed to the different packing environments of the crystallographically independent dimethylamino groups, but would probably not occur in solution. Similar but smaller variations are also observed among the distances of the chlorine and amino nitrogen atoms from the mean plane of the ring. It is conceivable that these perturbations, which must exist in the solid state, could result in the observed discrepancies among some of the chemically equivalent bonds and angles. However, there appears to be no consistent correlation between them to justify such a conclusion.

In every case, the plane formed by the NC<sub>2</sub> atoms bends away from the adjoining P–N bond towards the Cl atom on the same phosphorus, as shown in Fig. 2. In this preferred orientation, somewhat short intramolecular  $H \cdots N(ring)$  distances of 2.49, 2.53, 2.60, 2.61, 2.62 ... (9) Å are observed, whereas the sum of the van der Waals radii is 2.7 Å. The dihedral angle between the plane of the ligands and the NC<sub>2</sub> plane is in the range  $84.4-89.1^{\circ}$ .

The only intermolecular distances which are somewhat shorter than acceptable van der Waals contacts are two of the type  $Cl \cdots H$ , involving atoms Cl(1) and Cl(2) of molecule I. Their  $Cl \cdots H$  distances are 2.85 and 2.79 (9) Å, and the corresponding van der Waals contact should be 3.0 Å.

Sections of the residual electron-density distribution in the mean planes of the phosphazene rings and in the planes of the ligands are presented in Fig. 4. Residual troughs of -0.25 to -0.35 e.Å<sup>-3</sup> occur at the positions of the P atoms, and about -0.20 e.Å<sup>-3</sup> at the Cl atoms. In addition, positive peaks 0.20 to 0.40 e.Å<sup>-3</sup> are present across the middle of the P-Cl bonds, as well as smaller peaks 0.15 to 0.30 e.Å<sup>-3</sup> away from these bonds at 1.25 Å from the Cl atoms. Elsewhere in the map  $|\Delta \varrho| \le 0.2$  e.Å<sup>-3</sup>. The estimated standard deviation,  $\sigma(\varrho)$ , is 0.11 e.Å<sup>-3</sup>.

## Conclusions

A compilation of the X-ray results of the following related phosphonitrilic compounds is presented in Table 6:

A.  $Cl_6P_3N_3$ , Bullen (1971);

B. Cl<sub>8</sub>P<sub>4</sub>N<sub>4</sub>, Hazekamp, Migchelsen & Vos (1962);

C.  $(NMe_2)_8P_4N_4$ , Bullen (1962);

D. cis nongeminal  $Cl_3(NMe_2)_3P_3N_3$ , present paper; and E. geminal  $Cl_3(NMe_2)_3P_3N_3$ , Ahmed & Pollard (1972). Based on these results, the following conclusions can be drawn:

(1) Both D and E indicate that a considerable transfer of charge in the units  $\equiv$ PClNMe<sub>2</sub> takes place be-



Fig.4. Sections of the residual electron-density distribution. Contour lines are drawn starting at  $\pm 0.1$  e.Å<sup>-3</sup>, then at intervals of  $\pm 0.1$  e.Å<sup>-3</sup>,  $\sigma(\varrho) = 0.11$  e.Å<sup>-3</sup>.

tween the amino nitrogen and the Cl atom of the same unit, in a plane perpendicular to the central phosphazene ring. In these units, the P-Cl bond is about 0.07 Å longer than in A and B, and the P-NMe<sub>2</sub> bond is 0.05-0.07 Å shorter than in C.

(2) In *E*, the two P-NMe<sub>2</sub> bond lengths of the unit  $\equiv P(NMe_2)_2$  are about 0.04 Å shorter than in *C*, and one of the P-Cl bonds of the unit  $\equiv PCl_2$  is longer by about 0.03 Å than in *A* and *B*. This is indicative of some charge transfer between the substituents on the different P atoms, but to a lesser degree than in the case discussed under (1). A similar observation has

Table 6. Bond lengths (Å) and angles (°) for some related phosphonitrilic compounds

E.s.d.'s in parentheses refer to least significant digits.

(a) In  $\equiv$  PCl<sub>2</sub>, (b) in  $\equiv$  P(NMe<sub>2</sub>)<sub>2</sub>, (c) in  $\equiv$  PClNMe<sub>2</sub>.

		<i></i>		Cis nongeminal	Geminal
	$Cl_6P_3N_3$	$Cl_8P_4N_4$	$(NMe_2)_8P_4N_4$	$Cl_3(NMe_2)_3P_3N_3$	$Cl_3(NMe_2)_3P_3N_3$
PN (cyclic)	1.575 (2)	1.570 (6)	1.578 (7)	1.579 (3)	$\int 1.546, 1.607 (3) \times 2$
					$1.563, 1.592(4) \times 1$
$\mathbf{P}$ Cl (a)	1.985 (2)	1.989 (3)			↓ 1.992, 2.014 (2)
(c)				2.057 (2)	2.051 (2)
$P N Me_2(b)$			1.678 (7)	• •	$1.640(3) \times 2$
(c)				1.610 (4)	1.628(4) ×1
NC			1.45 (1)	1.470 (5)	1.455 (3)
NP-N (cyclic)	118.4 (2)	$121 \cdot 2(5)$	120.1(5)	118.1 (2)	113.1, 119.0 120.7 (2)
PN-P	121.3(3)	131.3 (6)	133.0 (6)	120.3(3)	118.5, 123.4, 124.2 (2)
ClP-Cl	101.4(7)	102.8 (2)			99.6 (1)
$NMe_2 - P - NMe_2$			103.8 (5)		103.7(2)
ClP-NMe <sub>2</sub>				105.0 (2)	104.6 (1)
Cl - P - N (ring)	108.9 (1)	(105.2 (3)		106·8 (Ì)	105.7-109.6 (1)
		110.5 (3)			
NMe <sub>2</sub> -P-N (ring)			( 103·3 (4)	109.6 (1)	105.9-114.2 (2)
			112.7(4)		
PN-C (mean)			118.8 (4)	118.8 (3)	117.9 (1)
CNC			115.8 (7)	112.7 (3)	113.8 (2)

been reported by Ahmed, Singh & Barnes (1969), where the lengths of the P-R ligands have been found to be influenced by the electronegativity of all the substituents on the phosphazene ring.

(3) In each P-N-P island in *E*, the P-N bond nearest the P atom with an excess of chlorine substituents is 0.03-0.06 Å shorter than the other P-N bond of the same island. This indicates that the electron density in the P-N-P islands is unequally shared between the two P-N bonds, is drawn nearer to the P atom which carries more Cl atoms, and thus pulls the N atom with it closer to that phosphorus.

(4) Despite the observed effects discussed under (1), (2), and (3), the net bonding-electron-density in each P-N-P  $\pi$ -bond centre remains unchanged. No significant change is observed in the mean of the two P-N bonds of each P-N-P island in the five compounds under consideration.

(5) Comparison of the cyclic angles of the trimeric compounds A and D to those of the tetrameric compounds B and C shows that the main difference is in the P-N-P angles, but that the N-P-N angles are maintained close to 120°. This supports the directional nature of the  $d_{\pi}$  orbitals of the P atoms, as described by Dewar, Lucken & Whitehead (1960). However, a substantial reduction of the cyclic N-P-N angles to about 113° appears to be possible as observed in the unit  $\equiv P(NMe_2)_2$  of E. The two P-N bonds forming the sides of this angle are the longest (1.606 and 1.608 Å) of any in the rings under consideration. Therefore, this small angle is consistent with an expected lower

repulsion between the two elongated bonds which would have lower electron-density distribution.

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# The Crystal and Molecular Structure of 5-Brosyl-3-deoxy-3-C-(R)-(ethoxycarbonylformamido)methyl-1,2-O-isopropylidene- $\alpha$ -D-ribofuranose

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The crystal structure of 5-brosyl-3-deoxy-3-C-(ethoxycarbonylformamido)methyl-1,2-O-isopropylidene-  $\alpha$ -D-ribofuranose has been determined by three-dimensional Patterson and Fourier techniques. The crystals are monoclinic with space group P2<sub>1</sub>. The unit cell of dimensions a=10.381, b=9.142, c=11.850 Å and  $\beta=99.92^{\circ}$  contains two formula units. The final R index for 1474 independent non-zero reflexions was 0.055. The carbon atom on C3 was shown to have R-stereochemistry. As a result of intermolecular hydrogen bonding between the N and O atoms of the NHCO-functional group, a continuous chain of these arrangements is observed about a twofold screw axis.

#### Introduction

Several investigators have shown interest in the synthesis of various branched-chain carbohydrates (Overend, 1963). There is also a general interest in the amino sugars, partly because they occur as basic constituents of many antibiotics (Fox, Watanabe & Bloch, 1966).

The method by which  $\alpha$ -(formylamino)acrylic esters can be prepared from  $\alpha$ -metalated isocyanoacetic esters and carbonyl compounds (Schöllkopf, Gerhard