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

By F. R. Ahmed and D. R. Pollard†

Division of Biological Sciences, National Research Council of Canada, Ottawa K1A 0R6, Canada

The structure of the title compound has been determined by direct and Fourier methods and has been refined to $R=0\cdot057$ for 2495 reflexions. The unit cell is monoclinic, $P2_1/a$, $a=15\cdot602$, $b=15\cdot422$, $c=15\cdot477$ Å, $\beta=111\cdot38°$, $Z=8$. The molecules have approximate threefold symmetry with small perturbations at the outside atoms. The central P_3N_3 group forms a regular, non-planar ring with $P-N=1\cdot579$ (3) Å, $P-N-P=120\cdot3$ (3)°, $N-P-N=118\cdot1$ (2)°, and $\tau=\pm17\cdot5°$. Its atoms are displaced by about $\pm0\cdot070$ 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: $P-Cl=2\cdot057$ (2) Å, $P-NMe_2=1\cdot610$ (4) Å, $Cl-P-NMe_2=105\cdot0$ (2)°, $Cl-P-N(ring)=106\cdot8$ (1)°, $NMe_2-P-N(ring)=109\cdot6$ (1)°, $N-C=1\cdot470$ (5) Å, $P-N-C=118\cdot8$ (3)°, $C-N-C=112\cdot7$ (3)°. The P-Cl and P-NMe₂ 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 Cl₃[N(CH₃)₂]₃P₃N₃, which was reported as part I by Ahmed & Pollard (1972), the substituents on the three P atoms of the (PN)₃ phosphazene ring are Cl₂, (NMe₂)₂, and Cl(NMe₂). 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(NMe₂), with the three Cl atoms on one side of the ring and the three NMe₂ 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⁻¹.
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 $0\cdot2 \times 0\cdot2 \times 0\cdot3$ mm.
Unit cell: monoclinic, $P2_1/a$,
$a=15\cdot602$ (5), $b=15\cdot422$ (2), $c=15\cdot477$ (2) Å,
$\beta=111\cdot38$ (3)°, $V=3467\cdot7$ Å³, $Z=8$,
i.e. two molecules in asymmetric unit;
$D_x=1\cdot431$, $D_m=1\cdot437$ g.cm⁻³
(flotation in KI solution).

Radiation: Cu $K\alpha$ for cell measurements,
$\lambda(K\alpha_1)=1\cdot54050$, $\lambda(K\alpha_2)=1\cdot54434$ Å;
Mo $K\alpha$ and Nb filters for intensity measurements;
$\mu(Cu)=76\cdot3$, $\mu(Mo)=8\cdot3$ cm⁻¹.

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, $\sin\theta/\lambda \le 0\cdot538$; number of reflexions scanned $=5177$, observed $=2495$, unobserved $=2682$; number of observations per parameter $=5\cdot3$.

Corrections

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

Structure determination

Of 611 reflexions with $|E|>1\cdot500$, 479 were signed by the symbolic addition procedure. The E map gave the positions of 20 atoms, *i.e.* P₆, Cl₆, N₈. 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 $w=1/\{1+[(|F_o|-80)/60]^4\}$, $7\cdot0 \le |F_o| \le 476\cdot4$, 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 18×18 per pair of pseudo-related atoms to include the correla-

tion between their parameters. For these atoms, the mean and maximum Δ/σ in final cycle are 0·1 and 0·4.

Final agreement

$R=0·057$ and $R_w=0·053$ for the 2495 observed reflexions; $|F_c| \leq |F_{th}|$ for 2577 unobserved reflexions and $|F_{th}| < |F_c| \leq 1·5\ |F_{th}|$ for 105 unobserved.

f-curves

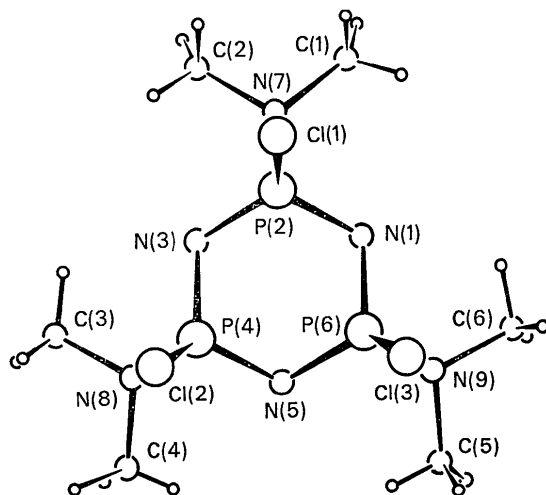Hanson, Herman, Lea & Skillman (1964) for C, N, P, Cl; Stewart, Davidson & Simpson (1965) for H.

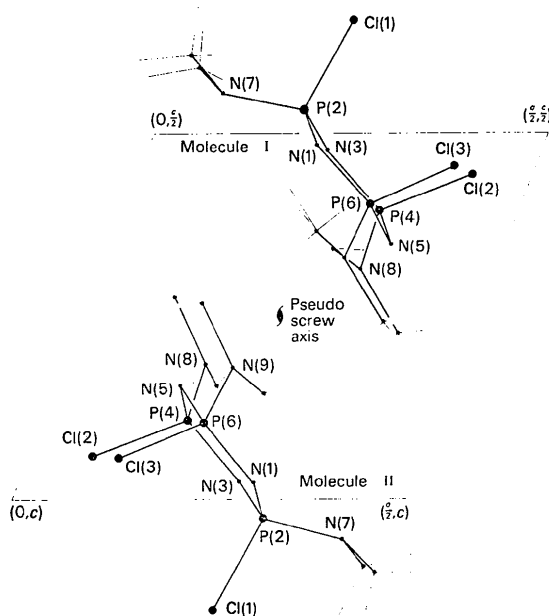Fig. 1. A view of molecule I along the normal to its phosphazene ring.

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 χ^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 P–NMe$_2$ and N–C $(5\% > P > 0·1\%)$, and significant for P–N, Cl–P–NMe$_2$ 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 ± 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 components and their e.s.d.'s as derived from the least-squares refinement*

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

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

Mol. I	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
N(1)	2096 (5)	8 (4)	5152 (5)	642 (50)	510 (48)	475 (44)	68 (72)	− 60 (75)	−106 (78)
P(2)	1782 (2)	913 (2)	4691 (2)	476 (15)	531 (16)	401 (14)	20 (24)	142 (23)	− 20 (25)
N(3)	2275 (5)	1751 (5)	5231 (5)	584 (50)	612 (52)	533 (49)	263 (78)	191 (85)	79 (81)
P(4)	3234 (2)	1686 (1)	6065 (2)	503 (15)	424 (14)	487 (15)	114 (25)	160 (24)	− 50 (25)
N(5)	3541 (5)	772 (4)	6515 (5)	578 (47)	501 (47)	451 (44)	42 (70)	− 101 (72)	−317 (75)
P(6)	3073 (2)	−82 (1)	5974 (2)	516 (15)	457 (14)	451 (14)	9 (25)	154 (23)	− 31 (25)
N(7)	673 (5)	1004 (5)	4411 (5)	636 (53)	687 (55)	691 (56)	− 142 (89)	246 (88)	−283 (89)
N(8)	3268 (5)	2376 (5)	6854 (5)	587 (50)	507 (48)	622 (51)	− 16 (80)	15 (80)	40 (78)
N(9)	3009 (5)	−800 (4)	6702 (5)	694 (50)	381 (42)	575 (46)	− 153 (73)	413 (80)	− 96 (76)
Cl(1)	1969 (2)	898 (2)	3444 (2)	870 (20)	966 (22)	579 (17)	− 23 (30)	616 (31)	54 (34)
Cl(2)	4229 (2)	2070 (2)	5572 (2)	672 (18)	1010 (23)	880 (21)	461 (36)	664 (33)	−100 (34)
Cl(3)	3968 (2)	− 594 (2)	5403 (2)	740 (18)	818 (19)	663 (16)	− 267 (29)	596 (29)	− 83 (31)
C(1)	91 (7)	275 (8)	3917 (7)	576 (67)	1001 (89)	801 (76)	− 395 (134)	− 17 (113)	−396 (126)
C(2)	255 (6)	1856 (7)	4087 (8)	510 (63)	888 (86)	1008 (86)	− 176 (134)	172 (121)	85 (115)
C(3)	2825 (9)	3211 (7)	6596 (9)	1377 (110)	502 (71)	1065 (95)	− 203 (133)	285 (165)	3 (144)
C(4)	4072 (7)	2388 (7)	7732 (7)	777 (73)	771 (76)	679 (69)	− 271 (119)	−24 (115)	−138 (123)
C(5)	3822 (7)	− 925 (7)	7586 (7)	647 (66)	847 (77)	721 (68)	627 (122)	251 (110)	180 (119)
C(6)	2530 (8)	−1623 (6)	6336 (7)	1163 (89)	507 (63)	759 (71)	− 167 (109)	818 (133)	−177 (123)
Mol. II									
N(1)	2964 (5)	2373 (5)	− 220 (5)	808 (58)	642 (54)	619 (52)	126 (84)	258 (89)	629 (92)
P(2)	3274 (2)	3286 (2)	273 (2)	632 (17)	613 (17)	387 (14)	111 (26)	187 (25)	352 (28)
N(3)	2770 (5)	4123 (5)	− 230 (5)	751 (57)	480 (48)	561 (54)	− 59 (78)	− 75 (92)	161 (85)
P(4)	1814 (2)	4044 (1)	−1085 (2)	529 (16)	490 (14)	464 (15)	− 20 (26)	35 (24)	205 (26)
N(5)	1548 (5)	3119 (5)	−1564 (5)	703 (53)	498 (49)	547 (48)	− 128 (77)	− 67 (83)	126 (81)
P(6)	2027 (2)	2279 (2)	−1058 (2)	747 (18)	434 (14)	506 (15)	35 (26)	366 (28)	229 (27)
N(7)	4376 (5)	3415 (6)	562 (5)	633 (53)	894 (63)	602 (53)	231 (93)	353 (87)	448 (95)
N(8)	1775 (5)	4766 (5)	−1846 (5)	714 (55)	586 (52)	483 (46)	− 88 (79)	113 (81)	48 (84)
N(9)	2137 (5)	1615 (5)	−1796 (5)	871 (60)	554 (51)	685 (53)	− 118 (86)	607 (94)	48 (92)
Cl(1)	3087 (2)	3222 (2)	1525 (2)	1006 (24)	1227 (27)	579 (17)	96 (34)	663 (34)	358 (40)
Cl(2)	802 (2)	4382 (2)	− 593 (2)	703 (18)	930 (22)	857 (21)	− 74 (35)	576 (33)	244 (33)
Cl(3)	1117 (2)	1690 (2)	− 561 (2)	939 (21)	913 (22)	837 (20)	463 (35)	876 (35)	330 (36)
C(1)	4961 (7)	2667 (8)	1009 (8)	650 (71)	972 (89)	972 (86)	774 (145)	314 (127)	636 (132)
C(2)	4780 (9)	4245 (8)	940 (9)	1051 (97)	986 (100)	1030 (100)	− 160 (155)	549 (164)	−238 (157)
C(3)	2009 (8)	5686 (7)	−1549 (7)	1179 (96)	552 (70)	825 (77)	− 127 (118)	196 (139)	−301 (132)
C(4)	1054 (6)	4729 (7)	−2771 (7)	513 (62)	1112 (90)	647 (67)	218 (129)	94 (105)	− 34 (121)
C(5)	1422 (8)	1507 (8)	−2675 (8)	936 (88)	996 (89)	980 (88)	− 709 (149)	684 (145)	−362 (148)
C(6)	2669 (10)	806 (8)	−1439 (10)	1426 (117)	754 (87)	1310 (109)	25 (158)	1224 (190)	537 (166)

| Mol. I	x	y	z	B	Mol. II	x	y	z	B
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)	− 50 (53)	290 (52)	3261 (54)	5·7 (2·2)	H(1,2)	5033 (54)	2455 (54)	1566 (56)	8·1 (2·1)
H(1,3)	− 569 (51)	213 (50)	3978 (51)	5·2 (2·0)	H(1,3)	5619 (51)	2797 (49)	1015 (52)	5·8 (2·0)
H(2,1)	611 (52)	2295 (53)	4262 (55)	6·0 (2·1)	H(2,1)	4676 (58)	4694 (57)	790 (59)	8·1 (2·4)
H(2,2)	84 (54)	1857 (51)	3432 (56)	9·2 (2·1)	H(2,2)	4700 (58)	4294 (56)	1624 (60)	7·0 (2·3)
H(2,3)	− 347 (54)	2048 (51)	4209 (55)	6·3 (2·1)	H(2,3)	5354 (58)	4278 (55)	765 (59)	6·7 (2·3)
H(3,1)	2200 (56)	3169 (53)	6025 (58)	7·0 (2·2)	H(3,1)	2504 (58)	5683 (56)	− 977 (60)	6·2 (2·3)
H(3,2)	3259 (55)	3547 (56)	6609 (57)	6·0 (2·3)	H(3,2)	1381 (61)	6041 (58)	−1642 (63)	8·4 (2·5)
H(3,3)	2823 (56)	3627 (55)	7177 (55)	9·3 (2·3)	H(3,3)	2249 (58)	5890 (56)	−2043 (59)	7·3 (2·3)
H(4,1)	4214 (55)	1883 (54)	7937 (57)	9·7 (2·3)	H(4,1)	867 (57)	4173 (56)	−2968 (60)	9·2 (2·4)
H(4,2)	4549 (56)	2911 (55)	7687 (57)	6·6 (2·2)	H(4,2)	491 (54)	4865 (53)	−2799 (55)	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(5,1)	4098 (57)	− 427 (56)	7814 (60)	6·1 (2·3)	H(5,1)	990 (54)	2006 (52)	−2933 (55)	6·4 (2·1)
H(5,2)	4373 (62)	−1150 (60)	7529 (63)	10·8 (2·6)	H(5,2)	899 (58)	1314 (57)	−2622 (59)	7·9 (2·4)
H(5,3)	3606 (58)	−1182 (58)	8145 (60)	5·9 (2·4)	H(5,3)	1615 (63)	1123 (60)	−3143 (64)	12·0 (2·6)
H(6,1)	1979 (57)	−1477 (57)	5738 (60)	5·8 (2·3)	H(6,1)	3200 (59)	929 (57)	− 971 (61)	9·8 (2·5)
H(6,2)	2786 (61)	−1963 (58)	6008 (63)	14·0 (2·6)	H(6,2)	2309 (55)	487 (55)	−1445 (57)	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)

Table 2. *Structure factor data* ($\times$ 10) *for the observed reflexions*

steric interference between the *cis* $N(CH_3)_2$ groups of the molecule. The shortest intramolecular H···H distances between different amino groups are 3·2–3·5 Å, which are considerably longer than the H···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 (I)	Mean (II)	Mean (I+II)	χ^2 (I+II)	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	0·10–0·05
P–NMe₂	6	1·590–1·630 (8)	1·615 (5)	1·606 (5)	1·610 (3)	13·5	0·05–0·01
N–C	12	1·420–1·501 (14)	1·474 (6)	1·466 (6)	1·470 (4)	29·4	0·01–0·001
Angle							
P–N–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	0·10–0·05
N–P–Cl	12	106·0–107·3 (4)	106·9 (2)	106·8 (2)	106·8 (1)	17·1	0·20–0·10
N–P–NMe₂	12	109·1–110·3 (4)	109·5 (2)	109·7 (2)	109·6 (1)	12·8	0·50–0·30
Cl–P–NMe₂	6	104·2–105·8 (3)	105·2 (2)	104·8 (2)	105·0 (1)	21·2	<0·001
P–N–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	0·10–0·05
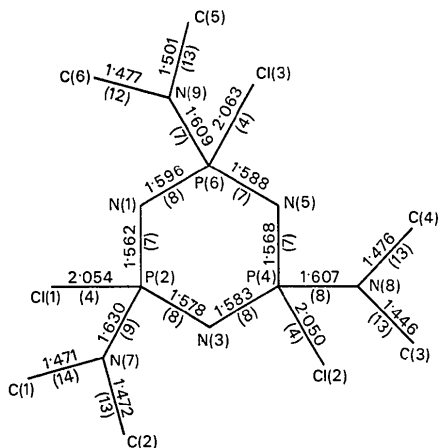
Molecule I
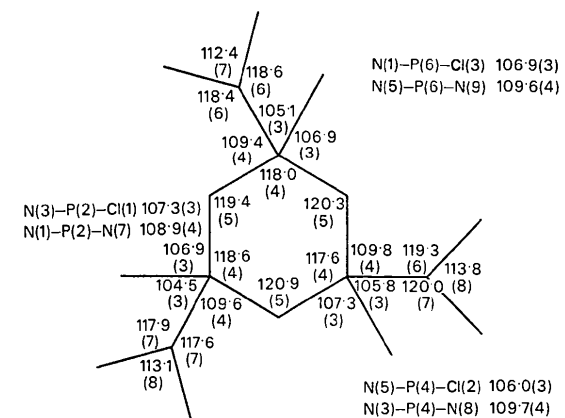
Molecule II

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	−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 *e.s.d.*) × 10^3 *in parentheses*

	Molecule I	Molecule II
N(1)	−0·081 (10)	0·059 (11)
N(3)	−0·060 (10)	0·060 (10)
N(5)	−0·078 (10)	0·079 (10)
Mean, |Max–Min|	−0·073, 0·021	0·066, 0·020
P(2)	0·069 (4)	−0·053 (4)
P(4)	0·065 (4)	−0·072 (4)
P(6)	0·086 (4)	−0·072 (4)
Mean, |Max–Min|	0·073, 0·021	−0·066, 0·019
Cl(1)	1·930 (4)	−1·907 (4)
Cl(2)	1·938 (4)	−1·948 (4)
Cl(3)	1·989 (4)	−1·949 (4)
Mean, |Max–Min|	1·952, 0·059	−1·935, 0·042
N(7)	−0·969 (10)	0·995 (10)
N(8)	−0·961 (10)	0·951 (10)
N(9)	−0·900 (10)	0·925 (11)
Mean, |Max–Min|	−0·943, 0·069	0·957, 0·070
C(1)	−1·018 (14)	1·067 (15)
C(2)	−1·124 (14)	1·138 (17)
C(3)	−1·232 (17)	0·992 (15)
C(4)	−1·090 (14)	1·214 (12)
C(5)	−1·018 (14)	1·037 (16)
C(6)	−0·979 (15)	1·126 (19)
Mean, |Max–Min|	−1·077, 0·253	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 ≡PClNMe$_2$ 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 ≡PCl$_2$ of the geminal molecule, and the mean value 1·985 (2) Å in Cl$_6$P$_3$N$_3$ 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 ^{35}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 ≡PClNMe$_2$ 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$_2$ bond of about 1·610 (4) Å, compared with 1·640 (3) Å in the unit ≡P(NMe$_2$)$_2$ of the geminal molecule, and a norm of 1·678 (7) Å in (NMe$_2$)$_8$P$_4$N$_4$ as determined by Bullen (1962). Similarly, a somewhat shortened exocyclic P–N bond of length 1·628 (4) Å was observed in the unit ≡PClNMe$_2$ of the geminal molecule, but by itself was not considered as sufficient evidence that the exocyclic P–N bond in the unit ≡PClNMe$_2$ was shorter than those in the unit ≡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$_2$, is very nearly perpendicular (89·0–90·5°) 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$_2$, while the Cl–P–NMe$_2$ angle is 105·0 (2)°. These are very nearly equal to the corresponding mean angles 106·7 (1), 109·5 (1), and 104·6 (1)° in the unit ≡PCl(NMe$_2$) 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$_2$ bonds. This is to be expected since P–NMe$_2$ 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$_2$ 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°. 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$_2$ 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···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_2 plane is in the range 84·4–89·1°.

The only intermolecular distances which are somewhat shorter than acceptable van der Waals contacts are two of the type Cl···H, involving atoms Cl(1) and Cl(2) of molecule I. Their Cl···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^{-3} occur at the positions of the P atoms, and about −0·20 e.Å^{-3} at the Cl atoms. In addition, positive peaks 0·20 to 0·40 e.Å^{-3} are present across the middle of the P–Cl bonds, as well as smaller peaks 0·15 to 0·30 e.Å^{-3} away from these bonds at 1·25 Å from the Cl atoms. Elsewhere in the map $|\Delta\varrho| \leq 0\cdot2$ e.Å^{-3}. The estimated standard deviation, $\sigma(\varrho)$, is 0·11 e.Å^{-3}.

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. $Cl_8P_4N_4$, 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:

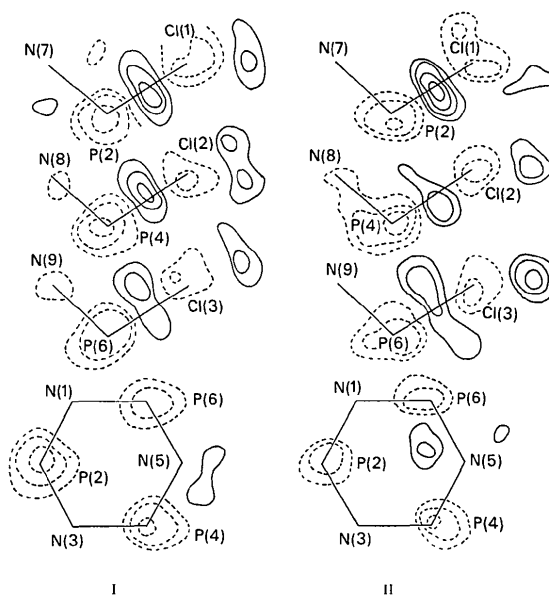(1) Both D and E indicate that a considerable transfer of charge in the units $\equiv PClNMe_2$ takes place be-

Fig. 4. Sections of the residual electron-density distribution. Contour lines are drawn starting at ±0·1 e.Å^{-3}, then at intervals of ±0·1 e.Å^{-3}, $\sigma(\varrho)=0\cdot11$ e.Å^{-3}.

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_2 bond is 0·05–0·07 Å shorter than in C.

(2) In E, the two P–NMe_2 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 $\equiv PCl_2$, (b) in $\equiv P(NMe_2)_2$, (c) in $\equiv PClNMe_2$.

	$Cl_6P_3N_3$	$Cl_8P_4N_4$	$(NMe_2)_8P_4N_4$	Cis nongeminal $Cl_3(NMe_2)_3P_3N_3$	Geminal $Cl_3(NMe_2)_3P_3N_3$	
P——N (cyclic)	1·575 (2)	1·570 (6)	1·578 (7)	1·579 (3)	{ 1·546, 1·607 (3) ×2	
					{ 1·563, 1·592 (4) ×1	
P——Cl (a)	1·985 (2)	1·989 (3)			{ 1·992, 2·014 (2)	
(c)				2·057 (2)	{ 2·051 (2)	
P——NMe_2 (b)			1·678 (7)		{ 1·640 (3) ×2	
(c)				1·610 (4)	{ 1·628 (4) ×1	
N——C			1·45 (1)	1·470 (5)	1·455 (3)	
N——P–N (cyclic)	118·4 (2)	121·2 (5)	120·1 (5)	118·1 (2)	113·1, 119·0 120·7 (2)	
P——N–P	121·3 (3)	131·3 (6)	133·0 (6)	120·3 (3)	118·5, 123·4, 124·2 (2)	
Cl——P–Cl	101·4 (7)	102·8 (2)			99·6 (1)	
NMe_2–P–NMe_2			103·8 (5)		103·7 (2)	
Cl——P–NMe_2				105·0 (2)	104·6 (1)	
Cl——P–N (ring)	108·9 (1)	{ 105·2 (3)		106·8 (1)	105·7–109·6 (1)	
		{ 110·5 (3)				
NMe_2–P–N (ring)			{ 103·3 (4)	109·6 (1)	105·9–114·2 (2)	
			{ 112·7 (4)			
P——N–C (mean)			118·8 (4)	118·8 (3)	117·9 (1)	
C——N–C			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 π-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_π 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 ≡P(NMe₂)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.

The authors wish to thank Professor R. A. Shaw for commenting on the discussion, Professor Shaw and Dr R. Keat for supplying the crystals and preprints of their recent publications on the phosphazenes, and Mrs M. E. Pippy for assistance with the computations.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *World List of Crystallographic Computer Programs*. 2nd Ed. Appendix, p. 52. Utrecht: Oosthoek.
AHMED, F. R. & POLLARD, D. R. (1972). *Acta Cryst.* B28, 513.
AHMED, F. R., SINGH, P. & BARNES, W. H. (1969). *Acta Cryst.* B25, 316.
BRUNIQUEL, M. F., FAUCHER, J. P., HASAN, M., KRISHNAMURTHY, S. S., LABARRE, J. F., SHAW, R. A. & WOODS, M. (1972). Private communication.
BULLEN, G. J. (1962). *J. Chem. Soc.* p. 3193.
BULLEN, G. J. (1971). *J. Chem. Soc.* (*A*), p. 1450.
DEWAR, M. J. S., LUCKEN, E. A. C. & WHITEHEAD, M. A. (1960). *J. Chem. Soc.* p. 2423.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040.
HAZEKAMP, R., MIGCHELSEN, T. & VOS, A. (1962). *Acta Cryst.* 15, 539.
KEAT, R., PORTE, A. L., SHAW, R. A. & TONG, D. A. (1972). *J. Chem. Soc.* In the press.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 9, 3175

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

BY J. COETZER, A. JORDAAN, G. J. LOURENS AND M. J. NOLTE

National Physical and Chemical Research Laboratories, Council for Scientific & Industrial Research, P.O. Box 395, Pretoria, South Africa

The crystal structure of 5-brosyl-3-deoxy-3-C-(ethoxycarbonylformamido)methyl-1,2-O-isopropylidene-α-D-ribofuranose has been determined by three-dimensional Patterson and Fourier techniques. The crystals are monoclinic with space group $P2_1$. The unit cell of dimensions $a=10·381$, $b=9·142$, $c=11·850$ Å and $\beta=99·92°$ 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 α-(formylamino)acrylic esters can be prepared from α-metalated isocyanoacetic esters and carbonyl compounds (Schöllkopf, Gerhard