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X-Ray Crystallography of the Phenyltriphosphonitriles.

II. The Crystal Structure of 2,2-Dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene

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The crystal structure of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene, $\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$, has been determined by three-dimensional Patterson, Fourier, and difference syntheses. It has been refined to an R index of 0.091 by differential-synthesis and least-squares methods. The crystals are monoclinic, with $a = 25.117$, $b = 23.610$, $c = 18.931$ Å, $\beta = 117^\circ 50'$, $Z = 16$, space group $C2/c$. In the asymmetric unit there are two molecules which are related by translations of almost $\frac{1}{2}$, $\frac{1}{2}$, 0 along the directions of the three principal axes. The cyclotriphosphazene ring, P_3N_3 , has a slight boat form in contrast to the slight chair form in the diphenyltetrachloro compound. As in the latter there are three sets of P-N bonds of different lengths, 1.556, 1.578, 1.609 Å averaged over the two molecules in the asymmetric unit in the present case. Taking the means for these two molecules, the exocyclic Cl-P-Cl angle is 98.5° , the C-P-C angle is 104.4° , the two types of N-P-N angle are 120.7° and 115.5° , and the two types of P-N-P angle are 121.0° and 124.9° . A few average bond lengths are 1.792 Å for P-C, 2.017 Å for P-Cl, and only 1.376 Å for C-C. The last is virtually identical with the average length of the C-C bond in diphenyltetrachlorocyclotriphosphazene.

Introduction

The crystal structure of 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene, $(\text{C}_6\text{H}_5)_2\text{Cl}_4\text{P}_3\text{N}_3$, was recently determined in this laboratory (Mani, Ahmed & Barnes, 1965). The present paper is concerned with the structure of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene, $\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$, the schematic formula of which is shown in Fig. 1 of Mani, Ahmed & Barnes (1965). Whereas crystals of diphenyltetrachlorocyclotriphosphazene showed no extraneous diffraction effects, those of the dichlorotetraphenyl compound presented some difficulties arising from a propensity for reflection twinning across (001), disorder (shown by streaked rows parallel to c^* and confined almost exclusively to the odd-numbered a^*c^* and b^*c^* nets) which appears to be dependent upon the temperature at which the crystals are grown from light petroleum,

and (in one case) the appearance of satellite spots on the streaked rows which vitiates the mirror symmetry across c^* in the odd-numbered b^*c^* nets and the diad axis in the corresponding a^*c^* nets. Of nine crystals examined, the one selected for the structure investigation showed no evidence of twinning, no satellite spots, and only relatively light streaking of reciprocal lattice rows parallel to c^* on precession photographs even after exposure times of 100 to 200 hours with copper radiation (Ni filter). For all practical purposes, therefore, the selected crystal was virtually ordered. A description and discussion of the interesting diffraction effects observed with the other crystals may be given later in a separate communication.

Crystal data

The crystal employed for the determination of the unit-cell constants and for the collection of intensity data was grown from a light-petroleum solution at 0°C . It

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was prismatic with $\{110\}$ and $\{\bar{1}10\}$ as the predominant forms, and it had dimensions of $0.12 \times 0.15 \times 0.33$ mm.

Dichlorotetraphenylcyclotriposphazene is monoclinic with $a = 25.117$ ($\sigma = 0.006$), $b = 23.610$ ($\sigma = 0.008$), $c = 18.931$ ($\sigma = 0.008$) Å, $\beta = 117^\circ 50'$ ($\sigma = 5'$), $U = 9927.54$ Å³, F.W. 514.28, D_m (floatation in aqueous potassium iodide solution) = 1.37_3 g.cm⁻³ at 22°C, $Z = 16$, $D_c = 1.376$ g.cm⁻³, $\mu(\text{Cu}) = 82.7$ cm⁻¹, $\mu(\text{Mo}) = 4.8$ cm⁻¹, $F(000) = 4224$.

Possible space groups are Cc (no. 9) and $C2/c$ (no. 15) with hkl absent when $h+k=2n+1$ and $h0l$ absent when $l=2n+1$ ($h=2n+1$). It will be shown that $C2/c$ is the probable space group with two molecules in the asymmetric unit, and that these molecules are related by translations of almost $\frac{1}{2}, \frac{1}{2}, 0$ along the directions of the three principal axes. It may be noted that if this relationship were exact a systematic non-space-group set of extinctions would occur, namely, hkl absent when h and k are both even and $h+k = \pm(4n+2)$.

Data collection

Final unit-cell and intensity data were collected on an XRD-5 scintillation-counter diffractometer as described previously (Mani, Ahmed & Barnes, 1965) except that Nb filters were employed for the Mo radiation.

So few reflections were observed outside the sphere corresponding to $\sin \theta/\lambda = 0.542$ that the intensity measurements were confined to this volume of reciprocal space, which contains 13,670 non-equivalent hkl and $\bar{h}\bar{k}l$ reciprocal lattice sites. Reflections corresponding to 7043 of these are prohibited by the space-group symmetry; 4599 possible reflections were not observed, and only 2028 were observed. The net intensity counts of the observed reflections were placed on the same relative scale, appropriate $1/L_p$ corrections were applied, but no absorption corrections were considered necessary.

Structure analysis

The positions of the P, Cl, and N atoms were established from a three-dimensional sharpened Patterson synthesis. The presence of a strong vector concentration at the mesh point $\frac{1}{2}, \frac{1}{2}, 0$ in Patterson space with a value of more than 50% of that at the origin was particularly suggestive and later served to confirm the translational relationship between the two molecules in the asymmetric unit of the structure. The C atoms were located from a Fourier synthesis based on 88% of the observed data and the contributions of the P, Cl, and N atoms. The R index for this initial structure was 0.26.

Two cycles of differential syntheses, assuming the two molecules in the asymmetric unit to be independent and applying isotropic temperature factors to all atoms, reduced the R index to 0.16. A difference synthesis showed that the structure must be basically correct and also indicated the sites of most of the hydrogen atoms. After four cycles of least squares with the coordinates

of all atoms except hydrogen, anisotropic thermal parameters for P, Cl, and N, but isotropic for C, the R index was 0.10, and it was clear that corresponding atoms of the two molecules in the asymmetric unit were separated by translations of almost, if not exactly, $\frac{1}{2}, \frac{1}{2}, 0$ along the directions of the three principal axes. This accounted for the exceptionally high vector concentration in the Patterson synthesis, and the fact that only 63 reflections, all relatively weak, out of 1634 possible ones with h and k both even and $h+k = \pm(4n+2)$ were above threshold values.

The positions of the hydrogen atoms were refined on the basis of a second difference synthesis, but the variations in length (1.27 to 1.45 Å) among some of the C-C bonds were not satisfactory. Three more cycles of least squares and two of differential syntheses (including the contributions of the hydrogen atoms in the structure-factor calculation), therefore, were carried out, after which the indicated shifts did not contribute significant changes to the bond lengths or angles. A final difference synthesis (omitting the hydrogen atoms) showed residual electron densities within ± 0.5 e.Å⁻³ near some of the atomic positions and a general background within ± 0.3 e.Å⁻³. The final R index (hydrogen atoms included) for all the observed data was 0.091.

The atomic scattering-factor curves employed in the structure-factor calculations were taken from *International Tables for X-ray Crystallography* (1962).

Results

A perspective view of a molecule derived from the coordinates of the two molecules in the asymmetric unit is illustrated in Fig. 1. The final coordinates of the N, P, Cl, and C atoms and their e.s.d.'s (calculated with the expressions of Cruickshank (1949, 1950) and increased by a factor of 1.50 to allow for the large proportion of unobserved reflections) are listed in Table 1 separately for the two molecules in the asymmetric unit. The observed and calculated electron densities and mean curvatures for all atoms except H, together with

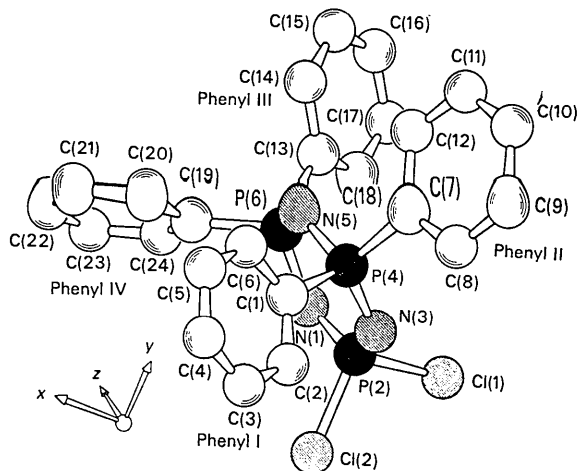


Fig. 1. Perspective view of a molecule derived from the coordinates of the two molecules in the asymmetric unit.

the anisotropic thermal parameters for the N, P, and Cl atoms, are given for both molecules in Table 2; similar data for the C atoms but with the isotropic temperature factor B are shown in Table 3. The coordinates of the hydrogen atoms, and the electron-density maxima of those derived from the final difference synthesis are collected in Table 4, where each H has been assigned the same number as the C to which it is attached.

Table 1. *Fractional atomic coordinates (e.s.d.'s $\times 10^4$ Å in parentheses)*

Molecule I			
Atom	x	y	z
N(1)	0.1933 (72)	-0.0874 (69)	-0.0619 (75)
P(2)	0.1759 (30)	-0.0863 (33)	0.0068 (32)
N(3)	0.1969 (84)	-0.0374 (83)	0.0688 (80)
P(4)	0.2428 (30)	0.0104 (32)	0.0700 (30)
N(5)	0.2546 (72)	0.0104 (77)	-0.0050 (59)
P(6)	0.2300 (30)	-0.0356 (30)	-0.0735 (29)
Cl(1)	0.0863 (39)	-0.0945 (48)	-0.0392 (50)
Cl(2)	0.2002 (47)	-0.1619 (39)	0.0642 (42)
C(1)	0.3123 (102)	0.0011 (128)	0.1608 (111)
C(2)	0.3174 (146)	-0.0367 (141)	0.2204 (147)
C(3)	0.3733 (194)	-0.0425 (152)	0.2890 (179)
C(4)	0.4211 (192)	-0.0097 (221)	0.2957 (287)
C(5)	0.4156 (164)	0.0288 (189)	0.2397 (213)
C(6)	0.3621 (122)	0.0330 (161)	0.1726 (129)
C(7)	0.2169 (110)	0.0795 (117)	0.0792 (87)
C(8)	0.1984 (113)	0.0879 (141)	0.1372 (101)
C(9)	0.1776 (147)	0.1433 (125)	0.1445 (123)
C(10)	0.1739 (158)	0.1854 (173)	0.0951 (176)
C(11)	0.1914 (137)	0.1756 (192)	0.0343 (165)
C(12)	0.2131 (159)	0.1222 (126)	0.0304 (189)
C(13)	0.1810 (111)	-0.0036 (107)	-0.1675 (116)
C(14)	0.2007 (138)	0.0435 (140)	-0.1951 (149)
C(15)	0.1627 (228)	0.0682 (156)	-0.2680 (153)
C(16)	0.1080 (407)	0.0460 (279)	-0.3148 (198)
C(17)	0.0899 (170)	-0.0005 (276)	-0.2880 (185)
C(18)	0.1277 (198)	-0.0254 (156)	-0.2149 (143)
C(19)	0.2906 (111)	-0.0625 (122)	-0.0867 (93)
C(20)	0.3476 (117)	-0.0432 (123)	-0.0441 (129)

Table 1 (cont.)

Molecule II			
Atom	x	y	z
C(21)	0.3956 (138)	-0.0648 (159)	-0.0540 (171)
C(22)	0.3845 (167)	-0.1056 (152)	-0.1062 (152)
C(23)	0.3278 (189)	-0.1275 (170)	-0.1541 (167)
C(24)	0.2812 (126)	-0.1034 (152)	-0.1435 (119)
N(1)	0.4426 (84)	0.1613 (75)	-0.0596 (75)
P(2)	0.4259 (32)	0.1623 (32)	0.0091 (32)
N(3)	0.4470 (86)	0.2127 (83)	0.0706 (89)
P(4)	0.4937 (30)	0.2590 (33)	0.0726 (30)
N(5)	0.5050 (72)	0.2592 (77)	-0.0029 (57)
P(6)	0.4801 (33)	0.2136 (32)	-0.0714 (30)
Cl(1)	0.3365 (41)	0.1543 (50)	-0.0355 (57)
Cl(2)	0.4510 (41)	0.0874 (39)	0.0675 (42)
C(1)	0.5627 (96)	0.2490 (116)	0.1638 (116)
C(2)	0.5672 (188)	0.2128 (153)	0.2209 (138)
C(3)	0.6231 (189)	0.2092 (275)	0.2925 (177)
C(4)	0.6694 (204)	0.2372 (212)	0.3054 (216)
C(5)	0.6652 (182)	0.2736 (294)	0.2457 (239)
C(6)	0.6113 (152)	0.2798 (185)	0.1727 (158)
C(7)	0.4669 (113)	0.3285 (141)	0.0830 (90)
C(8)	0.4499 (129)	0.3375 (131)	0.1408 (108)
C(9)	0.4315 (128)	0.3907 (128)	0.1508 (140)
C(10)	0.4293 (218)	0.4332 (177)	0.1020 (212)
C(11)	0.4446 (176)	0.4256 (147)	0.0436 (216)
C(12)	0.4658 (135)	0.3722 (143)	0.0344 (186)
C(13)	0.4319 (113)	0.2448 (107)	-0.1671 (101)
C(14)	0.4515 (149)	0.2918 (135)	-0.1952 (156)
C(15)	0.4135 (246)	0.3158 (176)	-0.2700 (143)
C(16)	0.3577 (713)	0.2942 (308)	-0.3148 (267)
C(17)	0.3382 (185)	0.2482 (269)	-0.2870 (191)
C(18)	0.3761 (221)	0.2242 (176)	-0.2127 (179)
C(19)	0.5400 (125)	0.1851 (113)	-0.0830 (95)
C(20)	0.5971 (113)	0.2055 (137)	-0.0398 (126)
C(21)	0.6458 (153)	0.1823 (174)	-0.0503 (179)
C(22)	0.6349 (173)	0.1413 (153)	-0.1042 (149)
C(23)	0.5807 (192)	0.1200 (152)	-0.1450 (147)
C(24)	0.5324 (165)	0.1426 (147)	-0.1372 (134)

The complete structure-factor table based on the final parameters has been deposited in the National Science Library of Canada at the National Research Council, Ottawa. An agreement summary (Ahmed &

Table 2. *Electron densities (e.Å⁻³), mean curvatures (e.Å⁻⁵) and anisotropic thermal parameters ($\times 10^5$) for the N, P, and Cl atoms from the expression $T = \exp - (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)$*

Molecule I										
Atom	q_0	q_c	$-q_0''$	$-q_c''$	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
N(1)	7.78	7.86	47.1	48.6	324	189	387	-176	614	-252
P(2)	17.96	18.24	107.7	108.9	187	214	336	-62	248	-123
N(3)	7.00	7.07	41.4	41.8	273	236	543	-300	474	-280
P(4)	18.37	18.74	110.7	112.2	203	201	329	-122	308	-99
N(5)	7.91	7.91	50.2	51.2	323	256	288	-196	565	-189
P(6)	18.86	19.00	114.8	115.0	200	194	265	-106	302	-31
Cl(1)	14.61	14.61	75.0	74.3	203	392	713	-214	315	-128
Cl(2)	14.84	15.08	80.2	80.6	431	225	643	182	512	47

Molecule II										
Atom	q_0	q_c	$-q_0''$	$-q_c''$	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
N(1)	7.46	7.58	44.0	45.6	333	226	290	-145	540	-211
P(2)	18.10	18.40	109.4	110.5	208	191	375	-38	297	-128
N(3)	6.97	7.05	39.8	40.7	293	222	490	-125	458	-167
P(4)	18.18	18.53	109.0	110.6	205	199	306	-56	291	-57
N(5)	7.96	7.89	50.8	51.6	335	317	262	-193	519	-100
P(6)	18.34	18.06	107.1	106.8	330	155	257	-43	347	15
Cl(1)	13.83	14.00	70.2	70.7	195	406	874	-200	341	-141
Cl(2)	15.27	15.37	83.4	83.0	372	230	702	231	544	51

Table 3. *Electron densities ($e \cdot \text{\AA}^{-3}$), mean curvatures ($e \cdot \text{\AA}^{-5}$) and isotropic temperature factors (\AA^2) for the C atoms*

Molecule I					
Atom	ρ_o	ρ_c	$-\rho_o''$	$-\rho_c''$	B
C(1)	5.60	5.56	30.3	30.4	4.57
C(2)	4.68	4.69	23.6	23.7	6.33
C(3)	4.22	4.18	19.6	19.2	7.56
C(4)	4.11	3.84	14.9	15.3	8.39
C(5)	4.08	3.99	18.2	17.8	7.38
C(6)	5.06	5.03	25.3	25.6	5.78
C(7)	5.86	5.86	33.1	33.0	4.25
C(8)	5.04	4.96	29.5	28.6	5.44
C(9)	4.88	4.74	26.1	24.7	5.77
C(10)	4.40	4.45	20.3	20.8	6.50
C(11)	4.37	4.46	21.1	22.4	6.55
C(12)	4.80	4.88	22.0	23.1	5.55
C(13)	5.56	5.48	30.8	30.0	5.04
C(14)	4.47	4.57	24.0	23.9	6.82
C(15)	4.18	4.06	19.7	17.9	6.74
C(16)	3.44	3.50	12.7	13.8	8.97
C(17)	3.91	3.94	17.0	18.7	8.45
C(18)	4.42	4.47	21.0	21.7	6.42
C(19)	6.04	6.02	32.0	32.6	4.14
C(20)	5.10	5.17	27.7	27.7	4.87
C(21)	4.58	4.66	21.9	23.1	6.41
C(22)	4.74	4.70	21.9	21.8	6.61
C(23)	4.15	4.01	19.5	18.8	7.62
C(24)	4.99	4.93	26.1	25.7	6.32

Molecule II					
Atom	ρ_o	ρ_c	$-\rho_o''$	$-\rho_c''$	B
C(1)	5.60	5.60	31.4	31.5	4.61
C(2)	4.50	4.49	21.7	21.7	6.36
C(3)	3.81	3.89	16.6	17.5	8.28
C(4)	4.00	3.94	16.2	17.0	8.94
C(5)	3.67	3.83	14.9	16.2	8.65
C(6)	4.22	4.44	20.8	22.1	6.51
C(7)	5.71	5.68	31.1	31.6	4.31
C(8)	5.16	5.24	28.2	28.4	5.81
C(9)	4.84	4.76	25.9	25.0	6.05
C(10)	4.17	4.25	17.0	17.7	6.59
C(11)	4.20	4.25	19.3	20.3	6.31
C(12)	4.86	4.96	22.5	23.7	5.59
C(13)	5.65	5.57	32.1	31.3	5.00
C(14)	4.35	4.43	23.3	22.9	6.57
C(15)	3.91	3.93	19.1	18.8	7.80
C(16)	3.26	3.12	9.7	9.1	8.59
C(17)	3.96	3.80	16.4	17.4	8.60
C(18)	4.07	4.14	18.0	19.0	6.67
C(19)	5.89	5.95	31.4	31.7	4.03
C(20)	5.03	5.18	27.5	28.0	4.97
C(21)	4.42	4.43	20.3	20.8	6.08
C(22)	4.44	4.37	21.7	21.1	6.43
C(23)	4.33	4.13	21.2	20.1	7.26
C(24)	4.64	4.58	23.2	22.5	6.26

Table 4. *Fractional coordinates of the hydrogen atoms and their electron-density maxima ($e \cdot \text{\AA}^{-3}$)*

The theoretical positions for the unobserved atoms are indicated with an asterisk

Molecule I				
Atom	x	y	z	ρ_o
H(2)	0.280	-0.062	0.218	0.40
H(3)	0.374	-0.072	0.337	0.40
H(4)	0.454	-0.017	0.357	*
H(5)	0.448	0.055	0.239	0.36
H(6)	0.355	0.058	0.130	0.42
H(8)	0.203	0.057	0.181	0.35
H(9)	0.163	0.148	0.192	0.40
H(10)	0.160	0.227	0.105	0.40

Table 4 (cont.)

Atom	x	y	z	ρ_o
H(11)	0.189	0.209	-0.003	*
H(12)	0.228	0.112	-0.009	0.50
H(14)	0.242	0.058	-0.155	0.39
H(15)	0.178	0.100	-0.300	0.36
H(16)	0.077	0.067	-0.372	*
H(17)	0.038	-0.017	-0.323	0.29
H(18)	0.114	-0.067	-0.198	0.35
H(20)	0.357	-0.005	-0.006	0.36
H(21)	0.442	-0.052	-0.008	0.40
H(22)	0.420	-0.123	-0.117	0.40
H(23)	0.318	-0.153	-0.193	0.50
H(24)	0.238	-0.122	-0.176	0.47

Molecule II				
Atom	x	y	z	ρ_o
H(2)	0.529	0.187	0.205	0.50
H(3)	0.617	0.178	0.325	0.50
H(4)	0.704	0.233	0.357	*
H(5)	0.705	0.298	0.253	0.30
H(6)	0.602	0.310	0.122	0.40
H(8)	0.455	0.305	0.177	0.40
H(9)	0.417	0.383	0.189	0.50
H(10)	0.412	0.480	0.102	0.37
H(11)	0.439	0.459	-0.003	*
H(12)	0.480	0.365	-0.012	0.70
H(14)	0.489	0.303	-0.155	0.30
H(15)	0.433	0.350	-0.293	0.35
H(16)	0.327	0.317	-0.372	0.32
H(17)	0.295	0.233	-0.317	*
H(18)	0.362	0.188	-0.198	0.45
H(20)	0.607	0.245	-0.006	*
H(21)	0.690	0.193	-0.020	0.45
H(22)	0.672	0.127	-0.110	0.42
H(23)	0.580	0.090	-0.190	0.33
H(24)	0.490	0.122	-0.168	0.45

Table 5. *Agreement summary*

2028 observed reflections ($21.2 \leq |F_o| \leq 1075.6$)

$$R = 0.091$$

Category	Limits	Number
1	$ \Delta F \leq 1.0 F_{th} $, or $ \Delta F / F_o \leq 0.18$	2018
2	$1.0 F_{th} < \Delta F \leq 2.0 F_{th} $, or $0.18 < \Delta F / F_o \leq 0.27$	10

4599 unobserved reflections ($|F_c|_{max} = 66.8$)

Category	Limits	Number
1	$ F_c \leq 1.0 F_{th} $	4376
2	$1.0 F_{th} < F_c \leq 1.5 F_{th} $	218
3	$1.5 F_{th} < F_c \leq 2.0 F_{th} $	5

$|F_{th}| = \text{threshold amplitude} = 15.6 \text{ to } 51.2$

Barnes, 1963) is presented in Table 5. The bond lengths and bond angles, not corrected for thermal vibrations, and their e.s.d.'s (*International Tables for X-ray Crystallography*, 1959, p. 331) are recorded in Fig. 2. The C-H bonds have a mean value of 1.068 \AA ($\sigma = 0.071 \text{ \AA}$) which is directly comparable with that in diphenyl-tetrachlorocyclophosphazene.

Discussion

Because of the relatively small proportion of observed reflections, resulting in part from the special relationship between the two molecules in the asymmetric unit,

very high accuracy was not to be expected in the present structure investigation, and the e.s.d.'s of the bond lengths and angles are higher than those in the structure determination of diphenyltetrachlorocyclophosphazene. The χ^2 and t tests carried out on the discrepancies among chemically equivalent bonds and equivalent angles in the two molecules of the asymmetric unit of the tetraphenyl compound showed that the errors are not significant except in the case of the P-Cl bonds. For the four P-Cl bonds, $\chi^2=17.7$ and for $\nu=3$, $P < 0.1\%$; in each of the two molecules, one bond has a length of about 2.01 Å while the second has a length of about 2.03 Å with $\sigma=0.005$ Å (Fig. 2). Differences among the lengths of the C-C bonds cannot be considered as significant because of the disappointingly high e.s.d.'s of the final results. It is of interest, however, that the mean C-C bond length is 1.376 ($\sigma=0.033$) Å which is virtually identical with the mean value of 1.377 ($\sigma=0.014$) Å in the diphenyl compound; as mentioned previously (Mani, Ahmed & Barnes, 1965) the omission of any corrections for thermal vibrations may account to a small extent for the decrease in these values from that to be expected for an aromatic C-C bond.

The sixteen C-P-N angles vary from 106.6° to 111.8° (Fig. 2) and, therefore, cannot be considered as all equal; this is to be expected because they are not all chemically equivalent. Those angles which are chemically equivalent, however, differ by values which are not significant.

The mean values of chemically equivalent bonds and angles of particular interest, and their r.m.s. standard deviations, are listed in Table 6; corresponding values in the two molecules of the asymmetric unit have been included in the means. The last two columns have been reproduced from Table 6 of Mani, Ahmed & Barnes (1965) to facilitate comparison with data for diphenyltetrachlorocyclophosphazene. The designation of the types of bonds and angles is the same for both compounds but a distinction has been made between the P-N bond of type a' in $\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$ and type a in $(\text{C}_6\text{H}_5)_2\text{Cl}_4\text{P}_3\text{N}_3$, and between the P-N-P angle of type $\theta(1)'$ in the former and type $\theta(1)$ in the latter, because the ligands on the P atoms are phenyl groups in the first and chlorine atoms in the second. Thus, although the P-N bonds of types a' and a have the same length the P-N-P angles of types $\theta(1)'$ and $\theta(1)$ differ by 5.7°

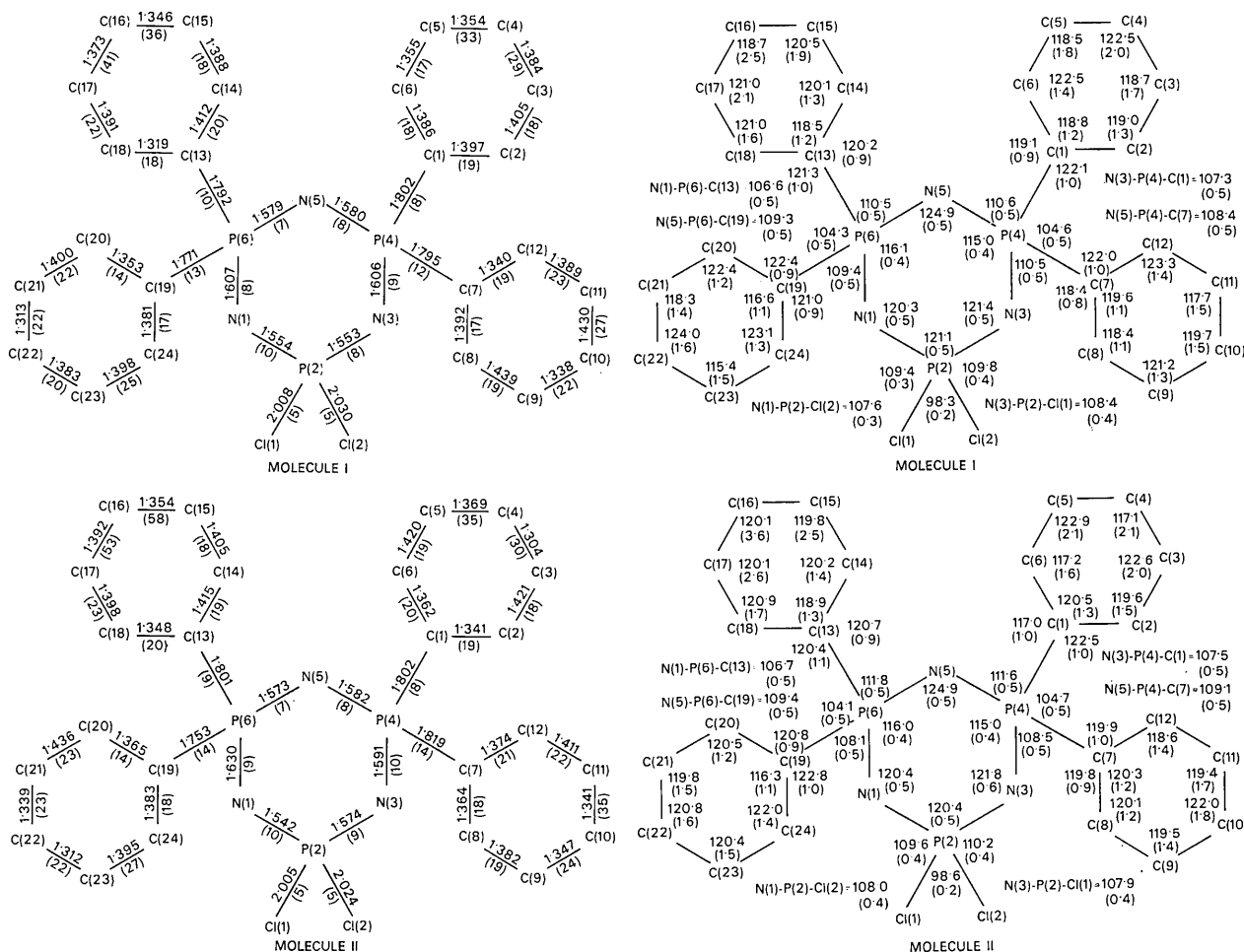


Fig. 2. Bond lengths (Å) and bond angles (°), with e.s.d.'s in parentheses, for the two molecules in the asymmetric unit.

There is also a difference of 1.8° between the mean values of the Cl-P-Cl angles of the type $\theta(5)$ in the two compounds. Both of these differences are statistically significant, and the difference (0.019 \AA) between the P-Cl bonds (type d) may also be significant. Otherwise the mean bonds and angles of the same types are in very good agreement in the two compounds.

Finally it may be noted that in the present structure, as in the previous one (Mani, Ahmed & Barnes, 1965), no intermolecular distances are less than van der Waals contacts.

Planarity of the rings

The equations for the mean planes through the cyclotriphosphazene, phenyl I [C(1) to C(6)], phenyl II [C(7) to C(12)], phenyl III [C(13) to C(18)], and phenyl IV [C(19) to C(24)] rings of the two molecules in the asymmetric unit, and referred to orthogonal axes, $x' = x + z \cos \beta$, $y' = y$, $z' = z \sin \beta$ are as follows:

Molecule I

- Phosphazene
 $0.6412x' - 0.5400y' + 0.5451z' - 3.9557 = 0$ (1)
- Phenyl I
 $0.5412x' - 0.7125y' - 0.4465z' - 2.2447 = 0$ (2)
- Phenyl II
 $0.7156x' + 0.2801y' + 0.6398z' - 4.7642 = 0$ (3)
- Phenyl III
 $0.6729x' - 0.5964y' - 0.4374z' - 5.3533 = 0$ (4)
- Phenyl IV
 $0.1935x' + 0.6927y' - 0.6947z' - 1.5696 = 0$ (5)

Molecule II

- Phosphazene
 $0.6427x' - 0.5408y' + 0.5427z' - 4.8286 = 0$ (6)
- Phenyl I
 $0.5445x' - 0.7314y' - 0.4104z' - 1.4979 = 0$ (7)
- Phenyl II
 $0.7241x' + 0.2468y' + 0.6433z' - 10.7759 = 0$ (8)
- Phenyl III
 $0.6457x' - 0.6245y' - 0.4390z' - 5.5710 = 0$ (9)
- Phenyl IV
 $0.1827x' + 0.6781y' - 0.7116z' - 6.5703 = 0$ (10)

Both cyclotriphosphazene rings are definitely non-planar, because $\chi^2 = 860$ for molecule I and $\chi^2 = 1074$ for molecule II, with $\nu = 3$ and $P \ll 0.001$ in both cases. Each has a slight boat form with considerable distortion because the members of every pair of opposite sides of the pseudo-hexagonal ring slope in opposite directions.

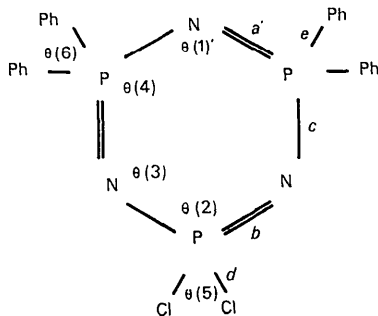
In molecule I, χ^2 for the phenyl rings varies from 3.6 to 8.0, while in molecule II it varies from 0.4 to 4.5. Deviations from the mean planes of the rings (equations 2 to 5; 7 to 10), however, are not statistically significant and all phenyl rings, therefore, must be considered as exactly planar.

The angles between the mean planes of corresponding rings in molecules I and II are 0.5° for phosphazene, 2.5° for phenyl I, 2.7° for phenyl II, 2.6° for phenyl III, and 2.0° for phenyl IV.

A projection of the dichlorotetraphenylcyclotriphosphazene molecule (excluding H atoms) along the nor-

Table 6. Mean values of the bond lengths (\AA) and angles ($^\circ$) in the dichlorotetraphenyl and diphenyltetrachloro cyclotriphosphazenes, and their r.m.s. standard deviations

Bond	Type	$\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$		$(\text{C}_6\text{H}_5)_2\text{Cl}_4\text{P}_3\text{N}_3$	
		Mean	$\sigma(\text{r.m.s.})$	Mean	$\sigma(\text{r.m.s.})$
P-N	a', a	1.578	0.008	1.578	0.005
P-N	b	1.556	0.009	1.555	0.005
P-N	c	1.609	0.008	1.615	0.005
P-Cl	d	2.017	0.005	1.998	0.002
P-C	e	1.792	0.011	1.788	0.006
Angle					
P-N-P	$\theta(1)', \theta(1)$	124.9	0.5	119.2	0.3
N-P-N	$\theta(2)$	120.7	0.5	119.7	0.3
P-N-P	$\theta(3)$	121.0	0.5	122.0	0.3
N-P-N	$\theta(4)$	115.5	0.4	115.2	0.2
Cl-P-Cl	$\theta(5)$	98.5	0.2	100.3	0.1
C-P-C	$\theta(6)$	104.4	0.5	104.4	0.3



mal to the mean plane of the cyclotriphosphazene ring is presented in Fig. 3. To facilitate direct comparison of the perpendicular distances of the atoms of molecules I and II from the planes of their respective cyclotriphosphazene rings the diagram has been constructed from the mean coordinates of corresponding atoms of the two molecules but the distances of each atom are shown in pairs, the top values are those for molecule I and the bottom ones are those for molecule II. It is apparent from Fig. 3 that each dichlorotetraphenylcyclotriphosphazene molecule has an approximate diad axis along a line through P(2) and N(5); this does not coincide, however, with the diad axis of the space group. The mirror plane through a nitrogen and a phosphorus atom in *para* positions, and through the two halogen atoms bonded to the phosphorus atom, which occurs in molecules of the corresponding hexahalocyclotriphosphazenes, $F_6P_3N_3$ (Dougill, 1963), $Cl_6P_3N_3$ (Giglio, 1960; Wilson & Carroll, 1960), and $Br_6P_3N_3$ (De Santis, Giglio & Ripamonti, 1962) is no longer present in either $Cl_4(C_6H_5)_2P_3N_3$ or $Cl_2(C_6H_5)_4P_3N_3$.

Comparison of the $Cl_2(C_6H_5)_4P_3N_3$ and $(C_6H_5)_2Cl_4P_3N_3$ molecules

For brevity the two molecules in the asymmetric unit of dichlorotetraphenylcyclotriphosphazene, $Cl_2(C_6H_5)_4P_3N_3$, will be referred to as molecules *A(I)* and *A(II)*, or collectively as molecule *A*, and the molecule of diphenyltetrachlorocyclotriphosphazene (Mani, Ahmed & Barnes, 1965) as molecule *B*.

Although the cyclotriphosphazene, P_3N_3 , ring in molecules *A* and *B* is only slightly, but significantly, non-planar, it has a puckered boat form (no two opposite sides are parallel, but slope in opposite directions) in

molecules *A(I)* and *A(II)*, whereas it has an almost regular (but slight) chair form in molecule *B*. The three types of P-N bond in molecule *B* also occur in molecule *A* (Table 6), and the previous discussion of special features of various segments and angles of the ring in molecule *B* (Mani, Ahmed & Barnes, 1965) also apply to molecule *A*. The only results to which attention need be drawn at this stage are the equality of the average P-N bond lengths of types *a* (molecule *B*) and *a'* (molecule *A*) in the segment P(4)-N(5)-P(6) where the ligands are chlorine atoms on P(4) and P(6) in molecule *B* but are phenyl groups in molecule *A*, and the increase in the mean angle P(4)-N(5)-P(6) from 119.2° for $\theta(1)$, molecule *B*, to 124.9° for $\theta(1)'$, molecule *A*.

In both molecules *A* and *B* there appear to be significant differences among the lengths of the P-Cl bonds (Fig. 2 of the present paper, and Fig. 3 of Mani, Ahmed & Barnes, 1965), and in general, these bonds are longer than those reported by Wilson & Carroll (1960), 1.97 to 1.98 Å, and by Giglio (1960), 1.949 to 1.989 (mean, 1.967) Å for $Cl_6P_3N_3$. The distance between Cl(1) and Cl(2) bonded to P(2) in molecules *A(I)* and *A(II)* is 3.054 Å in each case; in molecule *B* it is 3.067 Å between Cl(1) and Cl(2) bonded to P(4) and 3.070 Å between Cl(3) and Cl(4) bonded to P(6); these distances are much less than a normal van der Waals contact of about 3.6 Å but are somewhat larger than the Cl to Cl separations of 2.87 Å in carbon tetrachloride and 2.92 Å in methylene chloride and in chloroform (Pauling, 1960). Also, the four N to Cl distances around P(2) in molecules *A(I)* and *A(II)* are 2.900 to 2.944 (mean, 2.917) Å and 2.899 to 2.962 (mean, 2.919) Å, respectively, while in molecule *B* they are 2.882 to 2.920 (mean, 2.906) Å around P(4) and 2.894 to 2.946 (mean, 2.909) Å around P(6); again these distances are much

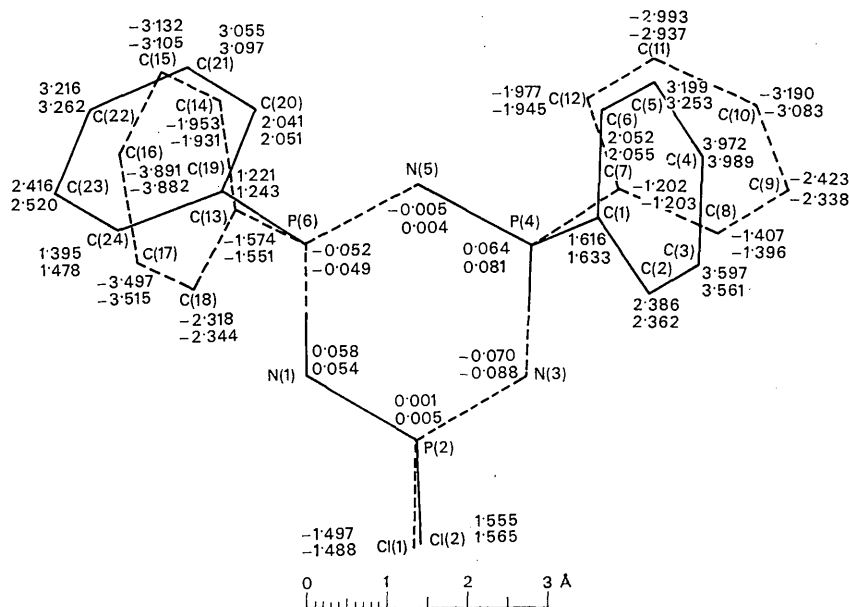


Fig. 3. The mean plane of the mean cyclotriphosphazene ring showing the perpendicular distances (Å) of the atoms from it for the two molecules in the asymmetric unit (top values, molecule I; bottom values, molecule II).

less than the sum (approximately 3.3 Å) of the van der Waals radii.

The angles among the mean planes of the phenyl rings are 84.4° between phenyls I & II and 88.8° between phenyls III & IV in molecule *A*(I), 87.1° and 89.6° for the corresponding pairs in molecule *A*(II) (Fig. 1) and 83.7° between phenyls I & II bonded to P(2) in molecule *B* [Fig. 2 of Mani, Ahmed & Barnes (1965)]; mean (all values), 86.7° ($\sigma = 2.6^\circ$). The planes of the two phenyl rings bonded to the *same* phosphorus atom, therefore, are almost perpendicular to each other in all cases.

It is also of interest to note that the angle between the mean planes of phenyls I & IV is 85.5° in molecule *A*(I) and 84.0° in molecule *A*(II), while that between the mean planes of phenyls II & III is 88.0° in molecule *A*(I) and 88.2° in molecule *A*(II); mean (all values), 86.4° ($\sigma = 2.0^\circ$). Thus, the two *cis* phenyl rings which are bonded to *different* phosphorus atoms (Fig. 1) also are approximately perpendicular to each other. Finally, the mean planes of phenyls I & III are nearly parallel to each other [angle phenyl I-phenyl III = 10.1°, molecule *A*(I), and 8.7°, molecule *A*(II)], whereas the mean planes of phenyls II & IV are almost perpendicular to each other [angle phenyl II-phenyl IV = 83.6°, molecule *A*(I), and 80.9°, molecule *A*(II)].

The configuration of the four bonds to the same phosphorus atom is of special interest. Thus, the angles between the planes X-P-X (where X = Cl or C) and the planes N-P-N with the same phosphorus atom in common are 88.8°, 88.6°, and 88.5° at P(2) in molecules *A*(I), *A*(II), and *B*, respectively; they are 88.1°, 88.8°, and 89.0° at P(4), and 88.5°, 88.7°, and 89.0° at P(6). The mean of all values is 88.7° ($\sigma = 0.3^\circ$), and the planes X-P-X and N-P-N, therefore, are nearly normal to each other in all cases. Furthermore, although the exocyclic X-P-X angles are different from the value for a tetrahedral angle and also depend on whether X is Cl or C, the mean of each pair of an X-P-X and its opposite N-P-N angle varies only from 109.5° to 110.2°, with an overall mean of 109.8° when X is C, and 109.9° when X is Cl, neither of which is significantly different from the tetrahedral angle of 109.4°. The tetrahedron around P, however, is severely distorted by the pseudo-hexagonal cyclotriphosphazene ring as shown by the fact that when the ligands are two Cl atoms, the mean N-P-N angle is 120.2° (range, 119.7° to 121.1°) while the mean Cl-P-Cl angle is only 99.4° (range, 98.3° to 100.4°), and with two phenyl groups as ligands the mean N-P-N angle is 115.5° (range, 115.0° to 116.1°) and the mean C-P-C angle is 104.4° (range, 104.1° to 104.7°). Furthermore, the effect of the ligands on the cyclotriphosphazene ring is to reduce the hexagonal angle of 120° by about 5° when a pair of Cl atoms is replaced by a pair of the larger phenyl groups with a corresponding increase of about 5° in the X-P-X angle. The increase in the mean angle

P(4)-N(5)-P(6) by almost 6° in molecule *A* may have the effect of reducing strain in the cyclotriphosphazene ring resulting from the decrease in the angles N(1)-P(6)-N(5) and N(3)-P(4)-N(5), although the decrease from 120° in the single angle N(1)-P(2)-N(3) in molecule *B* appears to have had a lesser effect on the other internal angles of the ring except for a possibly significant increase in the adjacent angles P(2)-N(1)-P(6) and P(2)-N(3)-P(4).

The configurations of the phenylchlorocyclotriphosphazene molecules, therefore, appear to be governed by a number of factors, namely, tetrahedral bonds to the phosphorus atoms *versus* a planar hexagonal cyclotriphosphazene ring, the effect of the ligands on the P-N bond lengths and on the internal N-P-N angles of the ring, van der Waals interactions between the two ligands on each phosphorus atom in addition to those between the ligands and the closest nitrogen atoms of the ring, and, of course, packing considerations in the structures of the crystals of the individual compounds.

The nomenclature adopted throughout this and the preceding paper (Mani, Ahmed & Barnes, 1965) is essentially that of Shaw, Fitzsimmons & Smith (1962).

The programs of Ahmed, Gabe, Mair & Pippy (1963) for the IBM 1620 computer were employed in the present investigation. The original crystals were supplied by Dr R. A. Shaw, Birkbeck College, London, and were subsequently recrystallized under various temperature conditions in our laboratory. Grateful acknowledgment is made to Mrs M. E. Pippy for assistance with the computations, and to the staff of the N.R.C. Computation Centre for their cooperation.

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