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X-ray Crystallography of the Phenyltriphosphonitriles.
III. The Crystal Structure of 2,2,4,4,6,6-Hexaphenylcyclotriphosphazatriene

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The crystal structure of 2,2,4,4,6,6-hexaphenylcyclotriphosphazatriene, $(C_6H_5)_6P_3N_3$, has been determined from three-dimensional Patterson, Fourier, and difference syntheses, and has been refined by least squares to an R index of 0·054 for 2900 observed reflections. The space group is $P\bar{1}$, $Z=2$, and the cell constants are $a=11·778$, $b=14·130$, $c=9·761$ Å, $\alpha=96°51'$, $\beta=107°25'$, $\gamma=89°32'$. The cyclotriphosphazene ring, P_3N_3, has an irregular slight chair form. The six chemically equivalent P–N bonds are statistically equal in length (mean, 1·597 Å), as are the six P–C bonds (mean, 1·804 Å). The mean bond angles are 103·8° for C–P–C, 117·8° for N–P–N, and 122·1° for P–N–P. The average C–C bond length in the aromatic phenyl rings is 1·379 Å. The results are compared with available data for other trimeric phosphonitriles, and some systematic effects of the relative electronegativities of the ligands on bond lengths and angles are discussed.

Introduction

The crystal and molecular structures of $(C_6H_5)_2Cl_4P_3N_3$ and of $(C_6H_5)_4Cl_2P_3N_3$ have been described by Mani, Ahmed & Barnes (1965, 1966). In both of these cyclotriphosphazenes the two P–N bonds of some P–N–P segments of the P_3N_3 ring have significantly different lengths depending upon the relative electronegativity of the pairs of substituents on the two P atoms. Thus, when the substituents are different, *viz.* PCl_2–N–$P(C_6H_5)_2$ the P–N bond on the more strongly electronegative (Cl, Cl) side is shorter (1·555 Å) than the one on the side of the phenyl groups (1·612 Å), whereas when both are the same, *viz.* either PCl_2–N–PCl_2 or $P(C_6H_5)_2$–N–$P(C_6H_5)_2$ the P–N bonds have equal lengths (1·578 Å in each case). Furthermore, the cyclotriphosphazene ring, P_3N_3, deviates from planarity in both compounds by 0·08 to 0·09 Å, but has a slight chair form in the diphenyl, and a slight (distorted) boat form in the tetraphenyl, derivative. The present investigation completes the series with a description of $(C_6H_5)_6P_3N_3$, and provides accurate data for correlation with the previous results. The corresponding trimeric phosphonitrilic fluoride $(F_6P_3N_3)$ has been studied by Dougill (1963), the chloride $(Cl_6P_3N_3)$ by Pompa & Ripamonti (1959), Giglio (1960), Wilson & Carroll (1960), and the bromide $(Br_6P_3N_3)$ by Giglio & Puliti (1967), and the structure of diphenyltetrafluorocyclotriphosphazene, $(C_6H_5)_2F_4P_3N_3$, has been described by Allen, Paul & Moeller (1967).

Crystal data

Crystals of 2,2,4,4,6,6-hexaphenylcyclotriphosphazatriene are very thin, colourless, triclinic prisms. No

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extraneous diffraction effects were observed as in the case of the dichlorotetraphenyl compound (Mani, Ahmed & Barnes, 1966). The unit-cell constants are $a=11·778$, $b=14·130$, $c=9·761$ Å $(\sigma=0·002$, in each case), $\alpha=96°51'$, $\beta=107°25'$, $\gamma=89°32'$ $(\sigma=5'$, in each case), $U=1538·24$ Å^3, F.W. 597·58, D_m(flotation in aqueous potassium iodide solution) $=1·28_7$ g.cm^{-3} at 22°C, $Z=2$, $D_c=1·290$ g.cm^{-3}, μ(Cu) $=19·9$ cm^{-1}, μ(Mo) $=2·3$ cm^{-1}, $F(000)=624$.

The space group is $P\bar{1}$. Although the mean values $\langle|E|\rangle$ and $\langle|E^2-1|\rangle$ obtained from the distribution of the normalized structure amplitudes are between those calculated for $P1$ and $P\bar{1}$, $|E|>3$ for 0·27% of the reflections, $|E|>2$ for 3·93%, and $|E|>1$ for 25·8%, which are comparable with 0·3%, 5%, and 32%, respectively, calculated by Karle, Dragonette & Brenner (1965) for centrosymmetric space groups (0·01%, 1·8%, and 37·0%, respectively for non-centrosymmetric space groups). Furthermore, the Patterson synthesis shows P–P Harker peaks at $2x,2y,2z$.

Data collection

The crystal employed for data collection was 0·25 mm in length and 0·22 × 0·08 mm in cross-section. It was attached to a glass fibre and mounted on a eucentric goniometer head. A preliminary survey of the reciprocal lattice by precession methods showed that the crystal class was triclinic, and established the reciprocal and direct cell constants with reasonable accuracy. The goniometer head was then transferred to a General Electric XRD-5 manual diffractometer and the crystal was adjusted so that the a axis (its longest dimension) was along the φ axis of the goniostat. The reciprocal cell constants were then remeasured with Ni-filtered Cu radiation $(\lambda, K\alpha_1=1·54050$ Å, $K\alpha_2=1·54434$ Å), a 1° take-off angle, and a 0·02° slit for all but the weak reflections for which the slit width was increased to

0·05°. The parameters b^*, c^*, and α^* were measured at $\chi = 0°$ with b^* and c^* in the equatorial plane. The arcs were adjusted to bring a^* along the φ axis and thus into the equatorial plane for direct measurement at $\chi = 90°$. The angles β^* and γ^* were measured on the χ circle by suitable adjustments of φ to bring the planes a^*c^* and a^*b^*, respectively, into the plane of the χ circle. All measurements, therefore, could be made without remounting the crystal and the final values of all parameters were very close to those obtained from the preliminary precession survey. Only the high-angle reflections were employed for the reciprocal-cell lengths.

Intensity data were collected from the same crystal on the same instrument but with Nb-filtered Mo radiation. The integrated intensities were measured by the moving-crystal moving-counter method (Furnas, 1957) with 2° scans over 2θ. The background was measured separately for each reflection along its Laue streak at the start, and again at the end, of the 2θ scan. The tube current was reduced by a known amount for the strong reflections, the intensity of the 200 reflection was recorded at regular intervals of time for scaling purposes, and most of the weak reflections were measured more than once to improve their counting statistics. All intensities were placed on the same scale and 1/Lp corrections were applied to the net counts. Absorption corrections for Mo radiation were considered to be negligible and, therefore, were not applied.

Data collection was restricted to the sphere $\sin \theta/\lambda = 0·65$ because very few reflections were observable at higher 2θ values and, of 7042 possible reflections within the range covered, only 2900 (41·2%) had intensity values above threshold.

Structure determination

The positions of the three P and three N atoms in the asymmetric unit were determined from a 3-D sharpened Patterson synthesis with a sharpening function of $2 \sin 2\theta/(1 + \cos^2 2\theta)$. The R index calculated for these atoms alone, with an assumed $B = 2·5$ Å^2, was 0·43. All thirty-six C atoms were located from the first Fourier synthesis which was evaluated with 2592 reflections whose phases appeared to be decided by the contributions of the P and N atoms. The R index for this first trial structure (hydrogen atoms excluded) was 0·18, which dropped to 0·09 after three cycles of block-diagonal anisotropic least-squares refinement. The positions of twenty-nine of the thirty H atoms were found from a difference synthesis computed at this stage. After two more cycles of refinement but with all H atoms included (the unlocated one in its theoretical position), the R index for the observed reflections was reduced to 0·072. The sites of the twenty-nine H atoms were redetermined from a second difference synthesis but, after three more refinement cycles, the R index was about the same (0·065) although there was noticeable improvement in the geometry of the molecule. The shifts in the last cycle were less than 0·2σ for most of the parameters, and less than 0·4σ for the remainder. The weighting function was $w^{-1} = 1 + [(|F_o| - 55)/45]^2$, with $|F_o|$ in the range 5·0 to 172·1.

Although differences among chemically equivalent bonds and angles were below the significance level, or in the possibly significant range, the importance of the results prompted attempts to reduce all apparent discrepancies by the use of other weighting schemes. Three cycles of refinement, therefore, were computed with one based on counting statistics (Hall & Ahmed, 1968), and three more with those of Hughes (1941), but the results were approximately the same as before.

Finally, about 300 weak reflections were remeasured, and three further cycles of refinement were carried out with a weighting function, $w^{-1} = 1 + [(|F_o| - 50)/40]^4$, so that the weights were nearly equal in the medium range of $|F_o|$, but were very much reduced for the higher and lower values. The shifts in the last cycle were less than
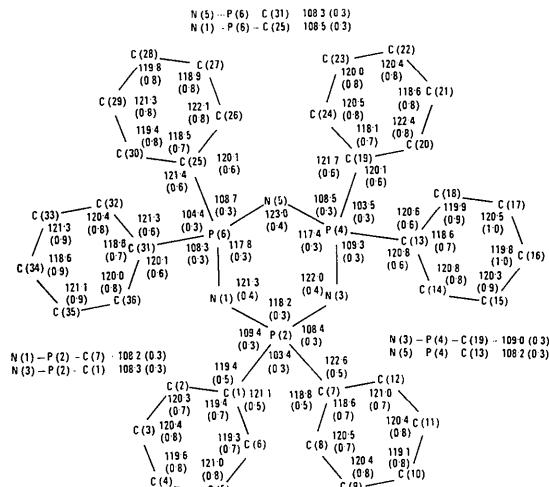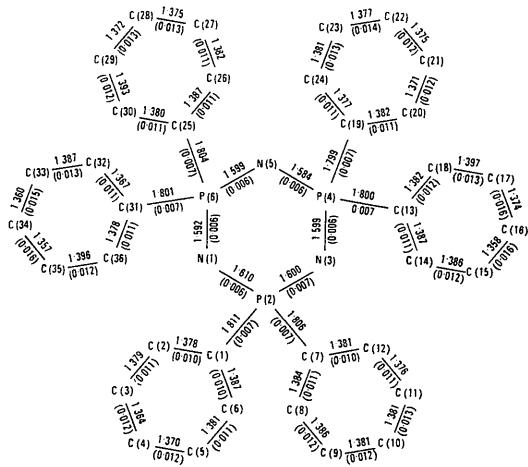

Fig. 1. Bond lengths (Å) and bond angles (°); e.s.d.'s in parentheses.

0·1σ for most of the parameters and less than 0·3σ for the others. The final R index for all observed reflections was 0·054.

The scattering factors employed in the calculations were those derived by Hanson, Herman, Lea & Skillman (1964).

Results

The final parameters, and their estimated standard deviations, of the P, N, and C atoms are shown in Table 1. Those of the H atoms, derived from the least-squares refinement, their e.s.d.'s, and the corresponding electron-density maxima, obtained from the second difference synthesis, are listed in Table 2, where each H atom has been assigned the same number as the C atom to which it is attached. All e.s.d.'s were calculated with the appropriate expression for least-squares refinement (*International Tables for X-ray Crystallography*, 1959, p.330), and then increased by 30% to allow for the omission of the unobserved reflections. The observed structure amplitudes, and the calculated structure factors for the parameters given in Tables 1 and 2, are tabulated in Table 3. For each of the 2900 observed reflections, the discrepancy $|\Delta F|$ is either $\leq 0·1|F_o|$ or $\leq F_{th}$, where F_{th} is the threshold amplitude. Of the unobserved reflections, $|F_c| \leq |F_{th}|$ for 4106 and $|F_{th}| < |F_c| \leq 1·5|F_{th}|$ for 36.

The bond lengths and bond angles, not corrected for thermal vibration, and their e.s.d.'s (Ahmed & Cruickshank, 1953, for bond lengths; *International Tables for X-ray Crystallography*, 1959, p.331 for bond angles), are shown in Fig.1. The C–H bond lengths are between 0·88 and 1·10 (mean, 0·99) Å. The six tetrahedral angles at each of the P atoms have a mean value of 109·3° in each case.

All intermolecular distances are greater than the sum of the corresponding atomic van der Waals radii; the shortest distances are N$\cdots$C, 3·583; N$\cdots$H, 3·23;

Table 1. *Fractional coordinates, vibration tensor components* (Å^2) *for the expression* $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl + \ldots)]$, *and their e.s.d.' s(all quantities* $\times 10^4$)

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
N(1)	3795 (5)	1641 (4)	1201 (6)	426 (35)	349 (32)	600 (39)	93 (57)	518 (62)	27 (53)
P(2)	3727 (2)	2774 (1)	1599 (2)	348 (10)	299 (9)	377 (10)	124 (15)	333 (16)	−10 (14)
N(3)	2619 (5)	3170 (4)	2100 (7)	507 (38)	398 (34)	630 (42)	151 (61)	610 (66)	84 (57)
P(4)	1567 (2)	2480 (1)	2151 (2)	367 (10)	341 (9)	419 (11)	173 (16)	398 (17)	97 (16)
N(5)	1684 (5)	1371 (4)	1747 (6)	428 (35)	372 (34)	646 (42)	223 (59)	578 (64)	42 (54)
P(6)	2749 (2)	933 (1)	1196 (2)	315 (9)	285 (9)	392 (10)	146 (14)	311 (16)	25 (14)
C(1)	3796 (6)	3372 (5)	83 (7)	351 (37)	385 (38)	355 (38)	194 (61)	209 (62)	−93 (60)
C(2)	3409 (7)	4292 (5)	−8 (8)	656 (54)	437 (44)	578 (49)	348 (75)	588 (85)	127 (77)
C(3)	3471 (8)	4763 (5)	−1142 (9)	862 (64)	388 (44)	667 (55)	397 (80)	667 (98)	116 (84)
C(4)	3926 (8)	4329 (6)	−2180 (8)	707 (57)	684 (56)	525 (51)	364 (86)	490 (89)	−152 (90)
C(5)	4310 (8)	3413 (6)	−2099 (8)	751 (59)	692 (57)	479 (48)	223 (84)	663 (87)	0 (91)
C(6)	4245 (7)	2923 (5)	−980 (7)	615 (51)	484 (44)	390 (42)	152 (70)	485 (76)	86 (75)
C(7)	5080 (6)	3182 (4)	2998 (7)	442 (42)	335 (38)	394 (40)	130 (61)	358 (67)	25 (62)
C(8)	6162 (7)	2968 (6)	2767 (8)	495 (48)	682 (54)	431 (46)	150 (79)	214 (77)	40 (81)
C(9)	7220 (7)	3274 (7)	3811 (9)	499 (52)	1008 (74)	658 (60)	209 (105)	252 (92)	−21 (99)
C(10)	7208 (8)	3802 (6)	5092 (9)	639 (56)	703 (60)	576 (54)	464 (91)	−74 (89)	−122 (91)
C(11)	6127 (8)	4002 (6)	5330 (8)	933 (69)	613 (54)	383 (46)	175 (80)	205 (90)	−130 (96)
C(12)	5079 (7)	3702 (5)	4288 (8)	629 (52)	488 (47)	461 (46)	276 (74)	377 (80)	37 (77)
C(13)	1373 (6)	2670 (5)	3922 (8)	350 (41)	523 (45)	472 (44)	200 (72)	295 (69)	−57 (66)
C(14)	1685 (8)	1979 (6)	4856 (8)	707 (60)	731 (60)	442 (48)	96 (85)	134 (87)	−367 (94)
C(15)	1551 (9)	2130 (8)	6228 (9)	1019 (78)	1189 (85)	393 (51)	363 (107)	173 (100)	−821 (131)
C(16)	1092 (9)	2954 (9)	6672 (10)	831 (75)	1614 (110)	604 (64)	32 (134)	694 (115)	−176 (143)
C(17)	790 (9)	3653 (8)	5771 (11)	976 (83)	1415 (102)	687 (68)	−410 (131)	766 (124)	670 (145)
C(18)	912 (9)	3509 (7)	4382 (10)	951 (75)	940 (74)	574 (58)	165 (105)	563 (108)	520 (118)
C(19)	181 (6)	2848 (5)	988 (7)	462 (44)	472 (43)	416 (42)	204 (67)	413 (70)	242 (68)
C(20)	−873 (7)	2378 (6)	879 (9)	482 (48)	684 (56)	640 (54)	508 (89)	407 (83)	195 (81)
C(21)	−1946 (7)	2610 (6)	−28 (9)	487 (51)	809 (63)	608 (55)	256 (96)	98 (85)	199 (89)
C(22)	−1970 (8)	3342 (6)	−846 (9)	641 (59)	742 (62)	620 (57)	179 (96)	−66 (94)	496 (95)
C(23)	−934 (9)	3820 (6)	−767 (9)	952 (75)	631 (58)	622 (58)	537 (96)	−63 (105)	269 (103)
C(24)	136 (7)	3578 (5)	159 (8)	626 (55)	511 (48)	579 (52)	357 (80)	296 (85)	27 (81)
C(25)	2133 (6)	326 (5)	−610 (7)	365 (39)	403 (39)	437 (41)	243 (66)	318 (66)	−49 (63)
C(26)	2867 (7)	−175 (6)	−1298 (8)	475 (48)	764 (60)	489 (49)	−94 (86)	181 (79)	−36 (84)
C(27)	2440 (8)	−627 (7)	−2696 (9)	667 (59)	883 (67)	505 (52)	−127 (95)	417 (91)	−95 (100)
C(28)	1247 (8)	−586 (6)	−3422 (8)	714 (59)	737 (60)	405 (46)	−43 (83)	280 (85)	−279 (94)
C(29)	506 (7)	−103 (7)	−2752 (9)	475 (51)	994 (72)	616 (57)	374 (103)	63 (88)	67 (96)
C(30)	936 (7)	356 (6)	−1345 (8)	603 (55)	716 (57)	498 (50)	231 (86)	368 (85)	112 (88)
C(31)	3390 (6)	0 (5)	2269 (7)	508 (44)	322 (38)	416 (42)	126 (62)	441 (70)	186 (64)
C(32)	4592 (7)	−125 (6)	2705 (9)	582 (52)	580 (52)	716 (58)	439 (89)	473 (92)	287 (83)
C(33)	5071 (9)	−828 (7)	3571 (11)	780 (70)	939 (78)	918 (76)	610 (124)	258 (118)	706 (116)
C(34)	4365 (10)	−1412 (6)	4001 (10)	1355 (94)	572 (58)	645 (61)	421 (96)	452 (122)	531 (116)
C(35)	3169 (10)	−1302 (6)	3551 (10)	1422 (94)	365 (47)	721 (62)	399 (87)	863 (125)	83 (105)
C(36)	2668 (8)	−598 (6)	2682 (9)	761 (61)	531 (50)	724 (59)	611 (90)	569 (98)	−41 (88)

C···C, 3·464; C···H, 2·81; H···H, 2·32 Å, and none of the P atoms is less than 4·0 Å from any atom of a neighbouring molecule. The relationship between the two molecules in the unit cell, viewed along the normal to the mean planes of the P_3N_3 rings, is illustrated in Fig. 2.

Table 2. *Fractional coordinates* ($\times 10^3$) *and isotropic temperature factors* (Å^2) *of the hydrogen atoms, their e.s.d.'s, and observed electron densities* (e.Å^{-3})

	x	y	z	B	ϱ_o
H(2)	305 (5)	459 (4)	72 (6)	0·3 (1·3)	0·43
H(3)	315 (6)	539 (5)	−115 (7)	1·6 (1·5)	0·42
H(4)	395 (7)	459 (5)	−298 (8)	3·2 (1·9)	0·33
H(5)	452 (5)	309 (4)	−291 (7)	1·0 (1·4)	0·39
H(6)	451 (6)	225 (5)	−85 (7)	1·9 (1·6)	0·35
H(8)	620 (7)	262 (5)	189 (8)	3·8 (2·0)	0·33
H(9)	799 (6)	323 (5)	361 (8)	3·0 (1·8)	0·33
H(10)	795 (6)	392 (5)	591 (8)	2·9 (1·8)	0·36
H(11)	607 (6)	429 (5)	627 (8)	2·8 (1·8)	0·35
H(12)	434 (5)	381 (4)	439 (6)	0·9 (1·4)	0·34
H(14)	204 (6)	136 (5)	444 (8)	2·6 (1·7)	0·33
H(15)	177 (7)	165 (6)	697 (9)	4·9 (2·3)	0·33
H(16)	91 (8)	309 (7)	772 (10)	6·6 (2·7)	0·30
H(17)	46 (9)	430 (7)	608 (11)	7·9 (3·0)	0·25
H(18)	79 (7)	392 (5)	372 (8)	3·1 (1·9)	0·33
H(20)	−79 (6)	180 (5)	137 (7)	1·7 (1·6)	0·44
H(21)	−277 (7)	226 (5)	−10 (8)	3·5 (1·9)	0·35
H(22)	−266 (8)	359 (6)	−146 (10)	6·4 (2·7)	0·24
H(23)	−116 (7)	438 (6)	−126 (8)	4·0 (2·1)	0·31
H(24)	97 (6)	390 (4)	20 (7)	1·3 (1·5)	0·33
H(26)	370 (6)	−27 (5)	−71 (8)	2·9 (1·8)	0·41
H(27)	297 (7)	−96 (5)	−325 (8)	3·2 (1·9)	0·26
H(28)	94 (5)	−90 (4)	−446 (6)	0·2 (1·2)	0·35
H(29)	−26 (8)	−4 (7)	−319 (10)	6·6 (2·7)	0·31
H(30)	41 (6)	81 (5)	−85 (7)	1·7 (1·6)	0·32
H(32)	513 (6)	28 (5)	247 (7)	2·6 (1·8)	0·37
H(33)	593 (7)	−83 (6)	384 (9)	4·6 (2·2)	0·30
H(34)	475 (10)	−195 (8)	447 (12)	9·4 (3·4)	—
H(35)	263 (6)	−170 (5)	382 (7)	2·6 (1·7)	0·28
H(36)	181 (6)	−54 (5)	234 (8)	2·6 (1·7)	0·34
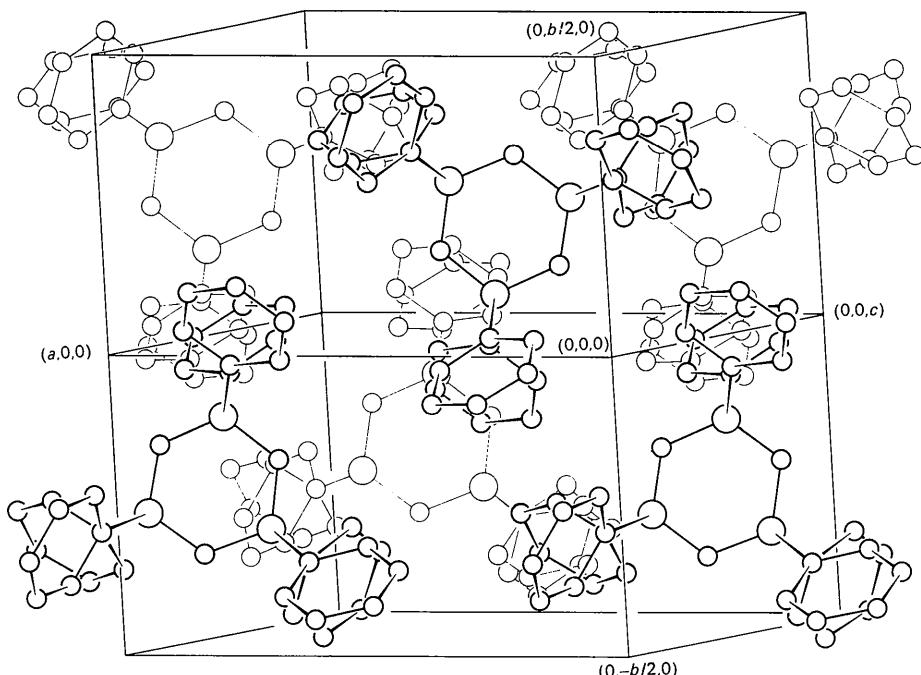
Fig. 2. Distribution of the molecules in the unit cell as viewed along the normal to the P_3N_3 rings.

Table 3. *Observed structure amplitudes and calculated structure factors* ($\times 10$)

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

[Multi-column table of reflection indices (K) with observed structure amplitudes (FO) and calculated structure factors (FC), organized by H and L layer lines.]

Table 3 (cont.)

Table 3 (cont.)

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The table consists of multiple columns of crystallographic structure-factor data, each column group headed by $H=$, $L=$ values, with columns of k, F_O, F_C.

k	FO	FC

(Extensive numerical structure-factor listings arranged in many parallel columns, organized under successive $H=$, $L=$ headings such as $H= 2, L= 7$; $H= 3, L= 7$; $H= 4, L= 7$; $H= 5, L= 7$; $H= 8, L= 7$; $H= 9, L= 7$; $H= 10, L= 7$; $H= 11, L= 7$; $H= 12, L= 7$; $H= 13, L= 7$; $H= 14, L= 7$; $H= 2, L= 8$; $H= 3, L= 8$; $H= 4, L= 8$; $H= 5, L= 8$; $H= 6, L= 8$; $H= 7, L= 8$; $H= 8, L= 8$; $H= 9, L= 8$; $H= 10, L= 8$; $H= 11, L= 8$; $H= 12, L= 8$; $H= 13, L= 8$; $H= 14, L= 8$; $H= 1, L= 9$; $H= 2, L= 9$; $H= 3, L= 9$; $H= 5, L= 9$; $H= 6, L= 9$; $H= 7, L= 9$; $H= 9, L= 9$; $H= 11, L= 9$; $H= 12, L= 9$; $H= 13, L= 9$; $H= 14, L= 9$; $H= 0, L= 10$; $H= 1, L= 10$; $H= 2, L= 10$; $H= 3, L= 10$; $H= 4, L= 10$; $H= 5, L= 10$; $H= 6, L= 10$, each followed by rows of index k and observed/calculated structure factors F_O and F_C.)

Table 3 (*cont.*)

K	FO	FC
H= -6, L= 10		
6	103•	46
7	106•	57
8	109•	-37
9	111•	-69
-1	147	125
-2	96•	9
-3	96•	-87
-4	145	142
-5	246	248
-6	110	107
-7	100•	-64
-8	102•	50
-9	104•	59
-10	106•	-89
-11	108•	-86
-12	111•	45
H= -7, L= 10		
0	128	135
1	97•	-54
2	170	-162
3	99•	30
4	101•	65
5	103•	-59
6	104•	-80
7	120	94
8	123	114
H= -7, L= 10		
-1	97•	30
-2	97•	-45
-3	146	150
-4	213	214
-5	99•	69
-6	137	-125
-7	101•	25
-8	103•	0
-9	170	-145
-10	107•	-37
-11	109•	51
H= -8, L= 10		
0	98•	63
1	116	113
2	100•	-43
3	142	-125
4	102•	45
5	104•	51
6	106•	-79
7	108•	-82
8	111•	53
H= -8, L= 10		
-1	92	-102
-2	99•	-6
-3	126	118
-4	122	-131
-5	198	-195
-6	102•	43
-7	103•	-51
-8	105•	-49
-9	107•	80
-10	109•	31
-11	111•	-6
H= -9, L= 10		
0	100•	-6
1	101•	51
2	102•	58
3	103•	39
4	104•	3
5	106•	61
6	108•	48
7	111•	-37
H= -9, L= 10		
-1	113	-101
-2	101•	-56
-3	101•	-54
-4	102•	-37
-5	103•	-46
-6	104•	-66
-7	105•	90
-8	141	117
-9	109•	-27
-10	111•	3
H= -10, L= 10		
0	103•	-66
1	103•	60
2	104•	-24
3	105•	-74
4	107•	48
5	127	112
6	110•	1
H= -10, L= 10		
-1	103	-110
-2	103•	80
-3	168	168
-4	104•	-19
-5	105•	-41
-6	140	134
-7	114	108
-8	109•	-70
-9	111•	-60
H= -11, L= 10		
0	106•	-62
1	106•	-38
2	107•	53
3	108•	-73
4	177	-164
H= -11, L= 10		
-1	106•	84
-2	106•	101
-3	107•	-39
-4	107•	-93
-5	108•	41
-6	109•	56
-7	111•	-107
H= -12, L= 10		
0	109•	81
1	109•	-33
2	110•	35
H= -12, L= 10		
-1	110•	40
-2	110•	-72
-3	103	-96
-4	110•	-15
-5	111•	8
H= 0, L= 11		
0	103•	7
1	104•	-59
2	105•	-60
3	106•	7
4	107•	-41
5	109•	-16
-1	105•	-6
-2	104•	23
-3	104•	34
-4	105•	20
-5	105•	-29
-6	105•	21
-7	107•	-2
-8	108	-93
-9	110•	-30
H= 1, L= 11		
0	105•	-48
1	106•	-46
2	107•	60
3	108•	33
4	109•	29
-1	106•	-28
-2	106•	-71
-3	106•	-27
-4	107•	-21
-5	107•	-5
-6	108•	49
-7	109•	20
-8	111•	51
H= -1, L= 11		
0	103•	41
1	104•	-50
2	105•	61
3	106•	18
4	108•	-68
5	109•	-57
6	111•	-15
-1	200	180
-2	103•	-3
-3	103•	-65
-4	103•	-6
-5	104•	100
-6	104•	-45
-7	139	-130
-8	107•	67
-9	115	88
-10	110•	-53
H= 2, L= 11		
0	107•	-27
1	108•	75
2	109•	69
-1	109•	-36
-2	108•	40
-3	109•	-2
-4	109	-113
-5	110•	5
-6	110•	13
-7	112•	-8
H= -2, L= 11		
0	125	134
1	103•	4
2	104•	-26
3	123	131
4	113	130
5	108•	-59
6	110•	-59
-1	102•	3
-2	164	-136
-3	102•	-14
-4	130	140
-5	103•	-27
-6	103•	-53
-7	104•	84
-8	99	91
-9	107•	9
-10	109•	12
H= 3, L= 11		
0	110•	57
-1	111•	-32
-2	111•	3
-3	111•	82
-4	111•	42
H= -3, L= 11		
0	101•	-29
1	102•	3
2	103•	-59
3	117	-90
4	106•	49
5	107•	98
6	109•	-46
7	111•	-20
-1	107	-109
-2	101•	-42
-3	101•	70
-4	101•	-19
-5	102•	-24
-6	103•	67
-7	104•	11
-8	105•	-18
-9	107•	-21
-10	109•	-63
H= -4, L= 11		
0	101•	4
1	102•	-22
2	103•	-29
3	104•	-49
4	106•	-93
5	107•	-17
6	109•	54
7	111•	-15
H= -4, L= 11		
-1	101•	83
-2	101•	59
-3	101•	78
-4	101	113
-5	102•	-17
-6	103•	-96
-7	104•	16
-8	105•	-30
-9	107•	-76
-10	109•	-15
H= -5, L= 11		
0	101•	85
1	96	97
2	103•	-11
3	104•	-19
4	106•	2
5	107•	-51
6	109•	-74
7	111•	-21
H= -5, L= 11		
-1	101•	-67
-2	101•	33
-3	143	129
-4	102•	-61
-5	165	-148
-6	145	117
-7	110	114
-8	105•	-49
-9	107•	7
-10	168	149
H= -6, L= 11		
0	120	-98
1	103•	-37
2	116	115
3	105•	31
4	106•	-68
5	108•	46
6	110•	79
H= -6, L= 11		
-1	102•	-9
-2	102•	36
-3	102•	-96
-4	149	-161
-5	115	94
-6	171	146
-7	105•	2
-8	106•	2
-9	108•	84
-10	110•	13
H= -7, L= 11		
0	103•	-41
1	104	-86
2	105•	-35
3	124	106
4	107•	37
5	109•	-41
6	111•	49
H= -7, L= 11		
-1	103•	39
-2	103•	-24
-3	103•	-57
-4	103•	98
-5	97	91
-6	104•	-19
-7	106•	-62
-8	107•	-31
-9	109•	-18
H= -8, L= 11		
0	98	84
1	105•	-15
2	106•	-38
3	107•	-4
4	109•	17
5	110•	-14
H= -8, L= 11		
-1	105•	42
-2	104•	-29
-3	104•	34
-4	105•	4
-5	105•	-88
-6	106•	-82
-7	107•	-67
-8	109•	-73
-9	110•	-46
H= -9, L= 11		
0	106•	62
1	107•	35
2	108•	-4
3	109•	17
4	111•	12
H= -9, L= 11		
-1	106•	-46
-2	106•	-59
-3	106•	-55
-4	107•	-54
-5	107•	17
-6	108•	-70
-7	109•	-43
-8	103	122
H= -10, L= 11		
0	109•	11
1	110•	19
2	110•	-86
3	111•	6
H= -10, L= 11		
-1	102	-90
-2	121	-101
-3	108•	80
-4	128	118
-5	109	-100
-6	110•	-9
H= -11, L= 11		
0	112•	-10
H= -11, L= 11		
-1	111•	-43
-2	111•	78
-3	130	129
H= 0, L= 12		
-1	110•	-38
-2	110•	-27
-3	124	100
-4	112•	11
H= -1, L= 12		
0	110•	-25
1	110•	-19
H= -1, L= 12		
-1	109•	50
-2	121	109
-3	110•	7
-4	110•	-44
-5	111•	33
-6	111•	54
H= -2, L= 12		
0	109•	54
1	109•	-61
2	110•	51
H= -2, L= 12		
-1	132	108
-2	109•	-58
-3	109•	-69
-4	109•	17
-5	110•	21
-6	110•	-7
-7	112•	-29
H= -3, L= 12		
0	108•	-16
1	109•	-34
2	109•	-48
3	111•	39
H= -3, L= 12		
-1	107•	-62
-2	108•	-71
-3	108•	-21
-4	108•	-7
-5	109•	36
-6	110•	48
-7	111•	11
H= -4, L= 12		
0	108•	-18
1	108•	-32
2	109•	-74
3	110•	-52
H= -4, L= 12		
-1	107•	-14
-2	107•	5
-3	108•	-41
-4	108•	37
-5	109•	69
-6	109•	-60
-7	111•	-78
H= -5, L= 12		
0	108•	105
1	108•	30
2	109•	-17
3	110•	-4
H= -5, L= 12		
-1	107•	64
-2	108•	-49
-3	132	119
-4	121	114
-5	133	-134
-6	110•	-80
-7	111•	57
H= -6, L= 12		
0	108•	-4
1	115	104
2	110•	58
3	111•	-7
H= -6, L= 12		
-1	137	-111
-2	108•	27
-3	108•	2
-4	144	-138
-5	109•	-65
-6	110•	39
-7	111•	71
H= -7, L= 12		
0	115	-98
1	109•	-29
2	110•	58
H= -7, L= 12		
-1	108•	8
-2	109•	-4
-3	109•	-68
-4	109•	-6
-5	110•	5
-6	111•	28
H= -8, L= 12		
0	110•	12
1	111•	-65
H= -8, L= 12		
-1	109•	62
-2	110•	23
-3	110•	59
-4	111•	7
-5	111•	-8
H= -9, L= 12		
-2	112•	22

Table 4. *Summary of the agreement between the chemically equivalent bonds* (Å) *and angles* (°)

Bond	Number	Range	σ(r.m.s.)	Mean	χ^2	*P* limits
P–N	6	1·584–1·610	0·006	1·597	10·65	0·10–0·05
P–C	6	1·799–1·811	0·007	1·804	2·11	0·95–0·50
Angle						
N–P–N	3	117·4–118·2	0·3	117·8	3·56	0·20–0·10
P–N–P	3	121·3–123·0	0·4	122·1	9·14	0·05–0·01
C–P–C	3	103·3–104·4	0·3	103·8	6·78	0·05–0·01
C–P–N	12	108·2–109·4	0·3	108·6	21·67	0·05–0·01

Discussion

Bond lengths and angles

All atoms of the same molecule of hexaphenylcyclotriphosphazene are crystallographically independent, whereas there is a plane of symmetry through a P···N diagonal and normal to the cyclotriphosphazene ring in the hexafluoro, hexachloro, and hexabromo analogues. The hexaphenyl derivative, therefore, has six crystallographically independent P–N bonds, while each of the three hexahalogen compounds has three only.

The agreement among chemically equivalent bonds and angles in the hexaphenyl molecule is summarized in Table 4, where the values of χ^2 and *P* indicate clearly that the observed discrepancies among chemically equivalent bonds are not significant. Some of the observed differences among the chemically equivalent angles, however, are in the possibly significant range with a maximum deviation of 0·9° (σ=0·4). The thirty-six C–C bonds vary in length from 1·357 to 1·397 Å, with a mean of 1·379 Å which is virtually the same as that (1·377 Å) for the diphenyl and tetraphenyl molecules (Mani, Ahmed & Barnes, 1965, 1966). The difference of 0·015 Å between the mean C–C bond length in hexaphenylcyclotriphosphazene and 1·394 Å for a C–C aromatic bond (Sutton, 1965) can be attributed to the omission of thermal-vibration corrections in the present investigation.

Planarity of the rings

The equations for the unweighted mean planes through the cyclotriphosphazene and each of the six phenyl rings, calculated by the method of Blow (1960), and referred to orthogonal axes, x' along a, y' in the ab plane, and z' along c^* (where x',y',z' are in Å) are as follows:

Cyclotriphosphazene [N(1) to P(6)]

$$0{\cdot}2181x' - 0{\cdot}2209y' + 0{\cdot}9506z' - 1{\cdot}4521 = 0\,, \quad (1)$$

Phenyl I [C(1) to C(6)]

$$0{\cdot}7952x' + 0{\cdot}2866y' + 0{\cdot}5344z' - 4{\cdot}9672 = 0\,, \quad (2)$$

Phenyl II [C(7) to C(12)]

$$0{\cdot}1175x' + 0{\cdot}9046y' - 0{\cdot}4097z' - 3{\cdot}2246 = 0\,, \quad (3)$$

Phenyl III [C(13) to C(18)]

$$0{\cdot}8577x' + 0{\cdot}3622y' + 0{\cdot}3650z' - 2{\cdot}9562 = 0\,, \quad (4)$$

Phenyl IV [C(19) to C(24)]

$$0{\cdot}3685x' - 0{\cdot}5698y' - 0{\cdot}7345z' + 2{\cdot}9167 = 0\,, \quad (5)$$

Phenyl V [C(25) to C(30)]

$$0.3022x' + 0.8845y' - 0.3554z' - 1.4778 = 0 , \quad (6)$$

Phenyl VI [C(31) to C(36)]

$$0.1701x' - 0.5493y' - 0.8181z' + 0.9995 = 0 . \quad (7)$$

For these planes, $\chi^2 = 377$, 1·3, 2·3, 1·8, 1·1, 1·4, 2·9, respectively, and therefore only the atoms of the P_3N_3 ring deviate significantly from their mean plane; the six C atoms of each phenyl ring are coplanar within the accuracy of the present determination.

A projection of the molecule (excluding the H atoms) along a normal to plane (1) showing the perpendicular distances of the atoms from this plane is presented in
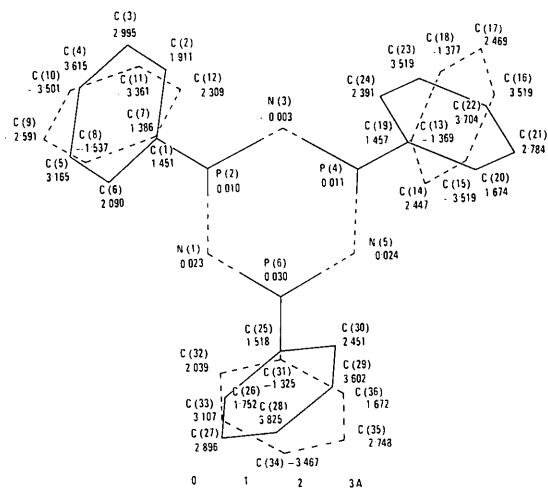
Fig. 3. Normal projection of the molecule onto the unweighted mean plane of the P_3N_3 ring, and distances (Å) of the atoms from it. E.s.d.'s of the normal distances are 0·002, 0·006 and 0·007 Å for P, N and C, respectively.

Fig. 3. The four atoms, N(1), P(2), P(4), N(5) are exactly coplanar while N(3) and P(6) are off this plane on opposite sides with P(6) at a greater distance (+0·072 Å) than N(3) (−0·031 Å). The P_3N_3 ring, therefore, has an irregular slight chair form with a mirror plane normal to the mean plane of the ring and through the P(6)···N(3) diagonal. The deviation from planarity cannot be attributed to intermolecular interactions because there are no abnormally short intermolecular distances. Each N atom, however, is situated approximately half way between two H atoms of the same molecule at distances which are slightly shorter than the sum (2·7 Å) of the van der Waals radii, thus N(1)···H(6), 2·62; N(1)···H(32), 2·65; N(3)···H(12), 2·60; N(3)···H(24), 2·55; N(5)··· H(14), 2·54; N(5)···H(30), 2·57 Å. The relatively even distribution of these distances, and the small, but significant, departure of the P_3N_3 ring from exact planarity, may be the result of weak intramolecular interactions between each N atom and the two nearest H atoms.

The dihedral angles between the cyclotriphosphazene ring and each of the six phenyl rings vary from 51·7 to 63·0°, with a mean of 57·5°, compared with mean values of 54·4° in the tetraphenyldichloro, and 51·8° in the diphenyltetrachloro molecules. Those between each pair of phenyl rings attached to the same P atom vary from 80·9 to 82·3°, with a mean of 81·6°, compared with mean values of 87·5 and 83·7° in the other two derivatives, respectively. Finally, the dihedral angles between pairs of adjacent phenyl rings which are cis with respect to the P_3N_3 ring vary from 69·4 to 82·4°, with a mean of 75·8°, compared with a mean of 86·4° in the two molecules of the asymmetric unit of the tetraphenyldichloro compound.

Residual electron-density distribution

A difference synthesis evaluated at the end of the refinement, and with all atoms subtracted, shows a
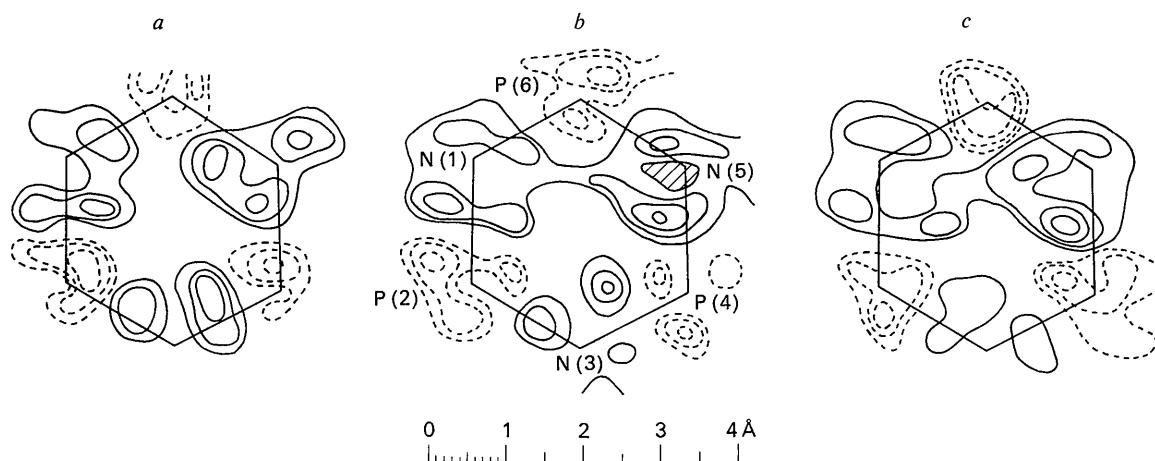

Fig. 4. Residual electron-density distribution (a) at +0·4 Å from the mean plane of the P_3N_3 ring, (b) in the plane of the P_3N_3 ring, (c) at −0·4 Å from the mean plane of the P_3N_3 ring; first contour at ±0·1 e.Å^{-3}, then at intervals of ±0·05 e.Å^{-3}.

residual electron-density distribution of less than ± 0.25 e.Å^{-3} $[\sigma(\Delta\varrho)=0.09]$. The largest positive concentrations occur on, or near, the P–N bonds close to the sites of the N atoms, and on some of the P–C bonds near the sites of the C atoms, while the largest negative ones appear near the sites of the three P atoms. Three sections (in the mean plane of the P_3N_3 ring and at ± 0.4 Å from it) are shown in Fig. 4. The residual concentrations of electron density near the sites of the N atoms may be indicative of delocalization of the lone pair of electrons of each of these atoms as previously mentioned (Mani, Ahmed & Barnes, 1965, p.697) in connection with the diphenyltetrachloro derivative.

Effects of the ligands on the cyclotriphosphazene ring

The electronegativities of the ligands on the phosphonitrilic trimers, $(R_2PN)_3$, where $R=C_6H_5$ (present paper), Br (Giglio & Puliti, 1967), Cl (Pompa & Ripamonti, 1959; Giglio, 1960; Wilson & Carroll, 1960), F (Dougill, 1963), are 2·5 (for C), 2·8, 3·0, 4·0, respectively, and cover half of the electronegativity scale of Pauling (1960, p.93). The effect of the ligands' electronegativity on the P–N bond lengths, the exocyclic R–P–R angles, and the internal N–P–N and P–N–P angles is shown in Fig. 5 [(a), (b) and (c), respectively], where the circles represent the weighted mean values and the vertical lines designate their e.s.d.'s. (The results of Giglio, 1960, and Wilson & Carroll, 1960, have been combined for R=Cl.) It is clear from Fig. 5(a) that an increase in the ligands' electronegativity results in a systematic decrease in the P–N bond length, which can be accounted for by more efficient overlap of the orbitals of the P and N atoms with a consequent increase in the P–N bond strength and total bond energy. At the same time, there is a systematic decrease in the exocyclic R–P–R angle (103·8, 102·6, 102·1, 99·2°) as demonstrated in Fig. 5(b). This is accompanied by a tendency for the internal N–P–N angle to increase (117·8, 117·2, 119·2, 119·4°) and the P–N–P angle to decrease (122·1, 122·4, 121·6, 120·5°), as illustrated in Fig. 5(c), but these changes are neither systematic nor uniform, although the average internal angle in each P_3N_3 ring remains very close to 120° regardless of R [see the dotted line in Fig. 5(c)]. Consequently, the P_3N_3 ring has a *slight* chair form when $R=C_6H_5$, Br, or Cl, and becomes planar when $R=F$.

In the cyclotriphosphazenes with mixed substituents, the two P–N bonds in a P–N–P segment are, in general, dependent on the relative electronegativities of the two pairs of substituents on the two bordering P atoms of the segment. When the two pairs of ligands are the same, the two intermediate P–N bonds are of equal lengths (as in the $(R_2PN)_3$ molecules). However, when the two pairs of ligands are different, the P–N bond on the side of the P atom with the more electronegative pair of substituents is appreciably shorter than that on the other side, but the overall mean of both bonds decreases as the overall mean electronegativity of both pairs of ligands increases.

In $(C_6H_5)_2Cl_4P_3N_3$ (Mani, Ahmed & Barnes, 1965) the mean P–N bond length is 1·555 Å on the Cl,Cl side, and 1·613 Å on the C_6H_5,C_6H_5 side, of N in the same P–N–P segment; the average electronegativity of all four ligands is $\frac{1}{2}(3·0$ for Cl $+2·5$ for C)$=2·75$, and the mean of both bond lengths is 1·584 Å shown as cross (1) in Fig. 5(a). In $(C_6H_5)_4Cl_2P_3N_3$ (Mani, Ahmed & Barnes, 1966) the corresponding mean bond lengths are 1·556 and 1·609 Å, respectively, and the overall mean is 1·582 Å shown as cross (2) in Fig. 5(a). In $(C_6H_5)_2F_4P_3N_3$ (Allen, Moeller & Paul, 1968) they are 1·537 (F,F replacing Cl,Cl) and 1·599 Å, respectively, and the overall mean is 1·568 Å shown as cross (3) in Fig. 5(a); the average electronegativity in this case is $\frac{1}{2}(4·0$ for F $+2·5$ for C)$=3·25$. All three crosses, (1), (2), (3), are within $\pm 0.001_5$ Å of the 'P–N bond length *versus* electronegativity' curve.
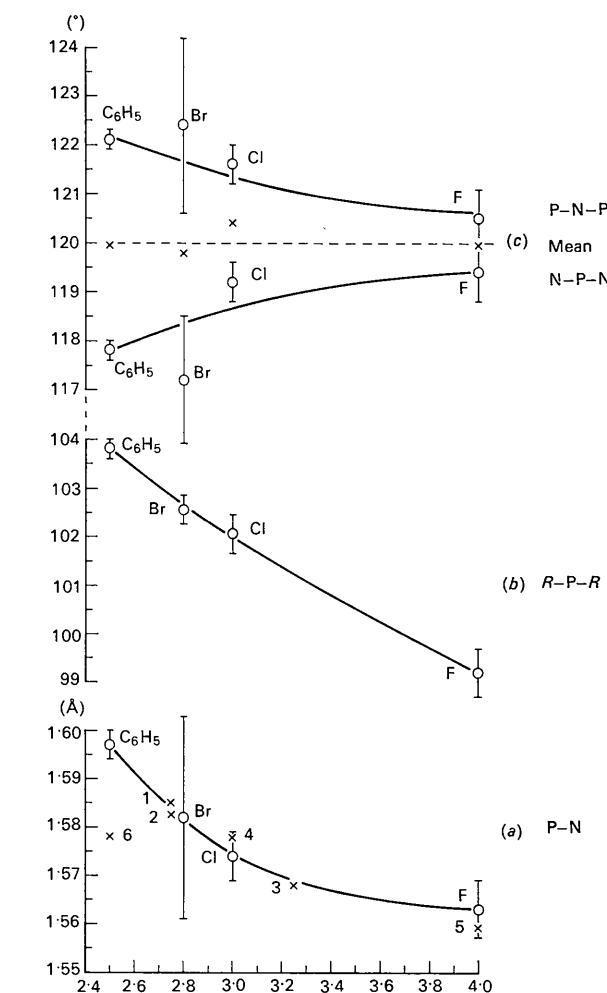


Fig. 5. Graphs of (a) P–N bond lengths (Å), (b) R–P–R bond angles (°) and (c) N–P–N and P–N–P bond angles (°) *versus* the mean electronegativity of the substituents when R = C_6H_5, Br, Cl, F in the trimeric phosphonitriles $(R_2PN)_3$. Vertical lines represent e.s.d.'s of weighted means. See text for crosses (1) to (6).

In the P–N–P segment of the P_3N_3 ring in $(C_6H_5)_2Cl_4P_3N_3$, where all four substituents on the P atoms are Cl atoms, the two P–N bonds have the same length, 1·578 Å $(\sigma_m = 0·003_5)$, and in the corresponding segment in $(C_6H_5)_2F_4P_3N_3$ the two bonds also have equal lengths, 1·559 Å $(\sigma_m = 0·01)$; these two bond lengths are shown as crosses (4) and (5) in Fig. 5(a) and are off the curve by only 0·003 and 0·004 Å, respectively.

All the aforementioned results are consistent in confirming that the mean P–N bond length in a P–N–P segment is uniformly dependent on the average electronegativity of the four substituents on the two P atoms bordering the segment. This rule, however, does not appear to be directly applicable when the four substituents are similar and *less* electronegative than the remaining two ligands of the P_3N_3 ring. Such a configuration occurs in the $(C_6H_5)_4Cl_2P_3N_3$ molecules, where the two P–N bonds in the $P(C_6H_5)_2$–N–$P(C_6H_5)_2$ segment are 1·580, 1·579 Å in molecule I, 1·582, 1·573 Å in molecule II, and the overall mean is 1·578 Å $(\sigma_m = 0·004)$ which is significantly shorter than the value of 1·597 Å $(\sigma_m = 0·003)$ for the mean P–N bond length in $(C_6H_5)_6P_3N_3$ by 0·019 Å $(t = 3·8)$; see cross (6) in Fig. 5(a). Furthermore, the P–N–P angle in this segment

Fig. 6. The weighted mean P–C and P–Cl bond lengths (Å) *versus* the overall mean electronegativity of the six substituents in the molecules of (A) hexaphenyl-, (B) tetraphenyldichloro-, (C) diphenyltetrachloro-, and (D) hexachlorocyclotriphosphazene; e.s.d.'s of means indicated by vertical lines.

is 124·9° $(\sigma_m = 0·4)$ which is appreciably larger than the corresponding value of 122·1° $(\sigma_m = 0·2)$ in $(C_6H_5)_6P_3N_3$. According to Craig & Paddock (1962), however, an increase in this angle is indicative of increased migration of the lone-pair electrons of the N atoms. This may account for both observed features (short P–N bonds, and large P–N–P angle) of the $P(C_6H_5)_2$–N–$P(C_6H_5)_2$ segment in $(C_6H_5)_4Cl_2P_3N_3$. It is noteworthy also that the mean length of the adjacent P–N bonds, which have the P atoms of this segment in common, is 1·609 Å so that the overall mean value of the P–N bonds in, and adjacent to, the segment is 1·594 Å which is less than the P–N bond length in $(C_6H_5)_6P_3N_3$ by only 0·003 Å. The tendency of the P atoms in a N–$P(C_6H_5)_2$–N–$P(C_6H_5)_2$–N segment to gain electrons from the adjacent N atoms, therefore, appears to be the same in $(C_6H_5)_4Cl_2P_3N_3$ as in $(C_6H_5)_6P_3N_3$ but is not distributed uniformly in the former, presumably because of the greater electronegativity of the pair of Cl atoms on the third P of the P_3N_3 ring compared with that of the pair of C_6H_5 groups in the hexaphenyl derivative. It would be interesting to find out if these features occur in $(C_6H_5)_4F_2P_3N_3$.

Finally, in the phenylchlorocyclotriphosphazene series, $(C_6H_5)_xCl_yP_3N_3$, where $x = 0, 2, 4, 6$, $y = 6, 4, 2, 0$, and $x + y = 6$, the P–C and P–Cl bond lengths, particularly the latter, appear to be influenced by the mean electronegativity $[\frac{1}{6}(x \times 2·5$ for C $+ y \times 3·0$ for Cl$) = 2·50$ when $x = 6, y = 0$; 2·67 when $x = 4, y = 2$; 2·83 when $x = 2, y = 4$; 3·00 when $x = 0, y = 6]$ of all six ligands. Thus, the weighted mean P–C bond length is 1·804 Å $(\sigma_m = 0·003)$ in $(C_6H_5)_6P_3N_3$, 1·792 Å $(\sigma_m = 0·004)$ in $(C_6H_5)_4Cl_2P_3N_3$, and 1·788 Å $(\sigma_m = 0·004)$ in $(C_6H_5)_2Cl_4P_3N_3$, and the weighted mean P–Cl bond length is 2·017 Å $(\sigma_m = 0·003)$ in $(C_6H_5)_4Cl_2P_3N_3$, 1·998 Å $(\sigma_m = 0·001)$ in $(C_6H_5)_2Cl_4P_3N_3$, and 1·973 Å $(\sigma_m = 0·004)$ in $Cl_6P_3N_3$. These results are shown graphically in Fig. 6 where the P–R bond lengths (R = C, Cl) have been plotted against the overall mean electronegativity of the six ligands. Both the mean P–C and the mean P–Cl bond lengths decrease regularly with increasing average electronegativity of all the exocyclic groups.

Further analysis and interpretation of the results of the crystal structure investigations of the cyclotriphosphazenes is left to those actively engaged in molecular orbital theory.

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Crystal Structure of N-Salicylideneglycinatoaquocopper(II) Tetrahydrate

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N-Salicylideneglycinatoaquocopper(II) tetrahydrate, $[Cu(C_9H_7NO_3).(H_2O)].4H_2O$, crystallizes in the monoclinic space group $C2/c$, with eight formula units per unit cell, of dimensions, $a=10\cdot721$, $b=17\cdot769$, $c=13\cdot895$ Å, $\beta=94\cdot71°$. Intensity data were collected on a diffractometer with Mo $K\alpha$ radiation. The molecular structure of the complex is essentially the same as that found by other workers in N-salicylideneglycinatoaquocopper(II) hemihydrate. The environment of the copper(II) ion is a square pyramid, with four short and one long coordination bond. The crystal structure of the tetrahydrate is entirely different from that of the hemihydrate; the complexes are not bound together by coordination bonds, but are connected by nine hydrogen bonds to form a three-dimensional network. The bond distances of N–C(3) of the salicylaldimine residue and C(2)–N of the glycine residue are $1\cdot302$ Å and $1\cdot461$ Å respectively. A comparison on these bonds of the related compounds was also made in relation to the transamination reactions.

Introduction

Kishita, Nakahara & Kubo (1964) prepared complexes from copper(II) ion and N-salicylideneglycine at various temperatures. Below 10°C they obtained N-salicylideneglycinatoaquocopper(II) tetrahydrate $[Cu(C_9H_7NO_3).(H_2O)].4H_2O$ (SGCT) and above 30°C they obtained the hemihydrate (SGCH). The structures of the complexes were discussed on the basis of the magnetic susceptibility. The value of the magnetic moment obtained, $1\cdot86$ Bohr magnetons, suggested that the copper(II) ions were separated from each other so as not to permit appreciable spin interaction between them.

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In this laboratory the crystal structure of SGCH was established (Ueki, Ashida, Sasada & Kakudo, 1967) and it was found that the complex had a five-coordinated square pyramid configuration. In the structure the fifth weak coordination bond is formed by the 'free' carboxyl oxygen atom of an adjacent complex. Therefore, the crystal structure of SGCT, especially the hydrogen bonding system of the free crystallization water molecules [water molecules which do not coordinate to the copper(II) ion] and the coordination configuration of the copper(II) ion, were of much interest.

Since this complex is expected to be a catalytic intermediate in the non-enzymatic transamination reactions (Eichhorn & Marchand, 1956: Longenecker & Snell, 1957), the bond distances concerning the nitrogen atom are also of interest.