Crystal and Molecular Structure of Nitrilohexaphosphonitrilic Chloride [2,2,3a,5,5,6a,8,8,9a-Nonachloro-2,2,5,5,8,8-hexahydro-1,3,4,6,7,9,9b-hepta-aza-2,3a,5,6a,8,9a-hexaphospha(3a,6a,9a,-P^V)phenalene]

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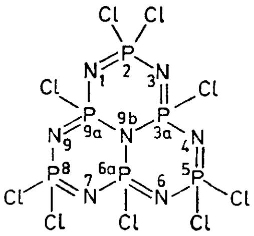
Crystals of the title compound are monoclinic, a = 19·817, b = 6·357, c = 29·897 Å, β = 99·38°, Z = 8, space group $C2/c$. The structure was determined by direct methods, and was refined by electron-density and full-matrix least-squares procedures to R 0·048 for 1947 observed reflections. $P_6N_7Cl_9$ has a non-planar condensed ring structure which shows small but significant deviations from C_{3v} symmetry. The structure can be interpreted as containing a set of three central weakened σ-bonds supplemented by π-bonds. These central P–N bonds, 1·723(6) Å, are longer than for any other phosphazene derivative hitherto reported. The remaining P–N bonds average 1·558(6) and 1·570(6) Å. The two types of P–Cl bonds have significantly different values, 2·004(3) and 1·980(3) Å.

NITRILOHEXAPHOSPHONITRILIC CHLORIDE ($P_6N_7Cl_9$) (I) was first discovered [1] in 1897 with the series $(NPCl_2)_n$, but its chemistry was not studied. The compound was again isolated and fully characterized during a study [2] of the chemistry of condensed ring phosphazene chlorides. Vibrational, mass, and ^{31}P n.m.r. spectra confirmed the condensed ring structure of the molecule.

(I)



The chemistry of $P_6N_7Cl_9$ is at present more limited than that of the ordinary cyclic chlorides. The introduction of the central nitrogen into the P_6N_6 ring system has a drastic effect on the properties of the molecule. Various substitution reactions were attempted on the condensed ring chloride.[2] When attempts at substitution of the chlorine are made with ring-activating groups (F, OMe), the tricyclic ring structure of the PN skeleton is destroyed. Reaction with deactivating groups (NMe_2) is less destructive, and only partial ring cleavage occurs, leading to the isolation of a compound in which the tricyclic PN skeleton has been lost, but in which some crosslinking of the ring is still apparent.

The differences between the condensed ring chloride and the ordinary cyclic phosphazene chlorides are therefore quite marked. The latter are stable to substitution, whereas the former is not. The physical and chemical properties of $P_6N_7Cl_9$ suggest that the reason for this lies in the weakness of the internal PN bond, which appears to be weaker than an exocyclic PCl bond.

The structure has been reported briefly [3] and a detailed description of the crystal structure analysis is now given.

EXPERIMENTAL

Crystal Data.—$P_6N_7Cl_9$, $M = 603·0$, monoclinic, $a =$ 19·817(5), $b = 6·357(2)$, $c = 29·897(6)$ Å, $\beta = 99·38(4)°$, $U = 3715·85$ Å^3, $D_m = 2·10$ g cm^{-3} (flotation), $Z = 8$, $D_c = 2·15$. Space group $C2/c$ (C_{2h}^6) from absent spectra: hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. Mo-K_α radiation, $\lambda = 0·71069$ Å; μ(Mo-K_α) = 18 cm^{-1}.

Crystals of $P_6N_7Cl_9$ from benzene are transparent plates, slightly elongated along b. The space group and initial unit-cell parameters were determined from precession and Weissenberg films. Accurate unit-cell parameters were later obtained by a least-squares treatment of 22 $\sin^2\theta$ (hkl) values measured on a General Electric XRD 6 diffractometer.

Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer using a θ—2θ scan at 2° min^{-1} in 2θ. All reflections with 2θ(Mo-K_α) $\leqslant 50°$ were measured. Two crystals were used for data collection. A check reflection was monitored every 30 reflections; approximately midway through the data collection the intensity of the check reflection had fallen off by 30% of its starting value. At this point a second crystal was used for the remainder of the data collection. The same check reflection was again monitored every 30 reflections and at the end of the data collection its intensity had again fallen off by 30% of its starting value. Lorentz and polarization corrections were applied and the structure amplitudes were derived. No corrections were made for absorption; the crystal dimensions were 0·4 × 0·4 × 0·2 and 0·4 × 0·3 × 0·2 mm., the maximum possible error in $|F_o|$ as a result of the absorption being *ca.* 9% with most errors much smaller than this value. Of the 3148 independent reflections, 1197 had intensities $< 2\sigma(I)$ above background, where $\sigma^2(I) = S + B + (0·05S)^2$, and S = scan count, and B = background. These reflections were classed as unobserved.

Structure Determination and Refinement.—The structure was solved by direct methods. Sixteen sets of signs for 217 reflections with normalized structure factor $|E| \geqslant 1·80$ were determined by a computer program which uses Sayre relationships in an iterative procedure.[4] The starting set of reflections is given in Table 1. One set of signs was outstanding in that the iteration procedure converged in two cycles to a set having the highest consistency index [4] (0·89)

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[1] N. H. Stokes, *Amer. Chem. J.*, 1897, **19**, 782.

[2] R. T. Oakley, M.Sc., Thesis University of British Columbia, 1970.

[3] W. Harrison, R. T. Oakley, N. L. Paddock, and J. Trotter, *Chem. Comm.*, 1971, 357.

[4] R. E. Long, Ph.D. Thesis, University of California, Los Angeles, 1965.

and approximately equal numbers of positive and negative signs. An E-map was computed using the 217 signed values of E from this set. The nine chlorine and six phosphorus atoms accounted for the fifteen highest peaks on the map. The seven nitrogen atom locations were then obtained from a difference Fourier. A re-examination of the E-map did show peaks at the nitrogen atom positions although there were larger, spurious peaks in the map. Refinement proceeded with full-matrix least-squares calculations, finally with all atoms having anisotropic temperature factors, the scattering factors of ref. 5 being used. Convergence was reached at R 0·048 for 1947 observed reflections. Four reflections (208, 40$\bar{8}$, 600, and 110) were omitted from the refinement because of suspected extinction errors. All reflections were given unit weights. Other weighting schemes were applied but showed no improvement in the consistency of $\Sigma w\Delta^2$ over ranges of $|F_o|$, or in R value. The final positional and thermal parameters are given in Tables 2 and 3. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20265 (5 pp., 1 microfiche).*

TABLE 1

Starting set reflections for $P_6N_7Cl_9$

h	k	l	$\|E\|$	
2	2	21	3·57	Origin determining
13	1	−10	4·78	
11	1	10	−4·50	
19	1	−22	3·82	
13	1	22	−3·69	
5	3	1	3·04	

TABLE 2

Final positional parameters (fractional) with standard deviations in parentheses

Atom	x	y	z
Cl(1)	0·1870(1)	0·6105(4)	0·0171(1)
Cl(2)	0·1601(1)	0·1361(5)	0·0200(1)
Cl(3)	0·0183(1)	0·8539(5)	0·0633(1)
Cl(4)	−0·1402(1)	0·1428(4)	0·1026(1)
Cl(5)	−0·1768(1)	0·6112(4)	0·1052(1)
Cl(6)	0·0012(1)	0·8479(5)	0·1816(1)
Cl(7)	0·1449(1)	0·1221(5)	0·2621(1)
Cl(8)	0·1855(1)	0·5867(5)	0·2754(1)
Cl(9)	0·1814(1)	0·7961(4)	0·1478(1)
P(1)	0·1407(1)	0·3987(4)	0·0505(1)
P(2)	0·0202(1)	0·5443(4)	0·0757(1)
P(3)	−0·0958(1)	0·4216(4)	0·1116(1)
P(4)	0·0161(1)	0·5387(4)	0·1747(1)
P(5)	0·1353(1)	0·3932(4)	0·2297(1)
P(6)	0·1497(1)	0·4957(4)	0·1419(1)
N(1)	0·0613(3)	0·4355(13)	0·0424(2)
N(2)	0·0624(3)	0·5199(11)	0·1305(2)
N(3)	0·1773(3)	0·3905(13)	0·1015(2)
N(4)	0·1733(3)	0·3761(13)	0·1873(2)
N(5)	0·0576(3)	0·4579(15)	0·2195(2)
N(6)	−0·0557(3)	0·4282(13)	0·1614(2)
N(7)	−0·0551(3)	0·4615(14)	0·0720(2)

TABLE 3

Final thermal parameters. U_{ij} are the components of the thermal vibration tensors referred to axes a, b, and c ($\text{Å}^2 \times 10^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Mean $\sigma(U)$
Cl(1)	4·50	6·66	5·89	−1·02	1·46	0·86	0·13
Cl(2)	6·54	5·78	7·86	0·79	1·58	−1·44	0·15
Cl(3)	6·70	6·68	6·89	0·95	−0·14	1·06	0·15
Cl(4)	6·29	5·66	9·08	−1·37	−0·37	0·15	0·15
Cl(5)	3·19	7·14	6·21	1·18	0·43	0·44	0·14
Cl(6)	6·82	7·59	8·51	0·10	2·49	−2·64	0·16
Cl(7)	8·53	6·48	6·76	0·02	1·66	1·34	0·16
Cl(8)	4·97	8·05	5·02	−1·09	−0·11	−0·63	0·13
Cl(9)	4·06	7·35	8·37	−1·63	0·08	0·08	0·15
P(1)	2·26	5·61	3·67	0·27	0·60	0·02	0·11
P(2)	1·84	6·82	3·39	0·21	0·13	0·32	0·11
P(3)	1·83	5·67	4·05	−0·21	0·19	0·18	0·10
P(4)	1·83	7·46	3·40	0·20	0·27	−0·21	0·11
P)5)	2·36	6·79	3·46	0·24	−0·04	0·53	0·12
P(6)	1·75	6·97	3·58	0·23	0·14	0·34	0·11
N(1)	2·22	7·88	4·18	0·40	0·08	−0·02	0·37
N(2)	1·68	6·65	3·76	0·10	0·44	−0·13	0·33
N(3)	2·35	8·80	3·99	0·95	0·34	0·55	0·37
N(4)	2·46	8·52	3·99	0·86	0·17	0·47	0·37
N(5)	2·60	14·53	4·08	1·56	0·65	0·98	0·45
N(6)	2·47	8·77	4·11	−0·79	0·58	0·83	0·38
N(7)	2·18	10·92	3·57	−1·33	−0·22	−0·01	0·39

DISCUSSION

Figure 1 shows the molecule $P_6N_7Cl_9$ viewed down b. Bond lengths and angles, with their standard deviations, are given in Tables 4 and 5.

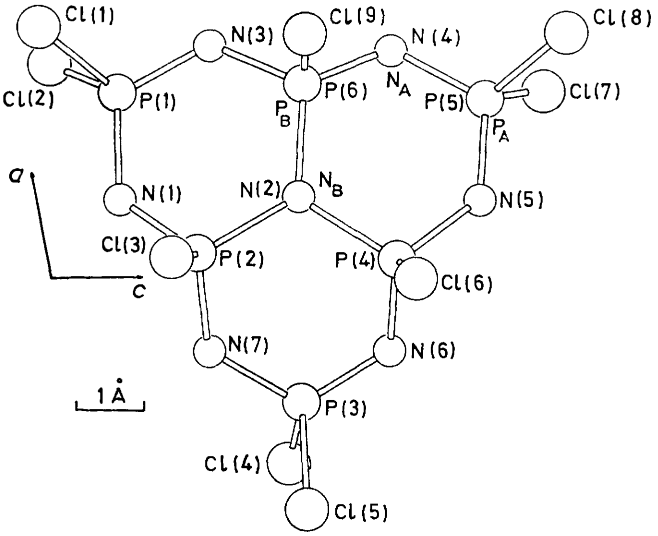

FIGURE 1 The $P_6N_7Cl_9$ molecule

TABLE 4

Bond distances (Å), with standard deviations in parentheses

P(1)–Cl(1)	1·989(3)	P(4)–Cl(6)	2·002(4)
P(1)–Cl(2)	1·971(3)	P(4)–N(2)	1·733(6)
P(1)–N(1)	1·570(5)	P(4)–N(5)	1·540(7)
P(1)–N(3)	1·579(6)	P(4)–N(6)	1·579(6)
P(2)–Cl(3)	2·002(4)	P(5)–Cl(7)	1·970(4)
P(2)–N(1)	1·550(7)	P(5)–Cl(8)	1·982(3)
P(2)–N(2)	1·720(6)	P(5)–N(4)	1·581(6)
P(2)–N(7)	1·569(6)	P(5)–N(5)	1·575(6)
P(3)–Cl(4)	1·977(3)	P(6)–Cl(9)	2·009(4)
P(3)–Cl(5)	1·990(3)	P(6)–N(2)	1·716(5)
P(3)–N(6)	1·569(6)	P(6)–N(3)	1·554(7)
P(3)–N(7)	1·558(7)	P(6)–N(4)	1·560(7)

The $P_6N_7Cl_9$ molecule shows small but crystallographically significant deviations from C_{3v} symmetry.

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[5] ' International Tables for X-Ray Crystallography, 'vol. III, Kynoch Press, Birmingham, 1962, pp. 202—207.

This may be due to crystal packing forces, since its ^{31}P n.m.r. spectrum in solution (two equal signals at $-20·2$ and $+3·5$ p.p.m. relative to H_3PO_4) requires the molecule to have three-fold symmetry.

The central nitrogen atom is nearly coplanar with its neighbours, the deviation of N(2) from the P(2),P(4),P(6) plane being 0·04 Å (Table 6). The three five-atom segments, typically P(2),N(7),P(3),N(6),P(4), are also roughly planar, but the molecule as a whole deviates strongly from planarity, the N,P,N planes at the bridgehead making a mean angle of 49·0° with the central P(2),P(4),P(6) plane (Table 6).

TABLE 5

Bond angles (deg.) with standard deviations in parentheses

Cl(1)–P(1)–Cl(2)	101·5(1)	N(5)–P(4)–N(6)	113·8(4)
Cl(1)–P(1)–N(1)	110·7(3)	Cl(7)–P(5)–Cl(8)	101·9(1)
Cl(1)–P(1)–N(3)	109·3(3)	Cl(7)–P(5)–N(4)	108·3(3)
Cl(2)–P(1)–N(1)	108·7(3)	Cl(7)–P(5)–N(5)	109·7(3)
Cl(2)–P(1)–N(3)	109·0(3)	Cl(8)–P(5)–N(4)	110·2(3)
N(1)–P(1)–N(3)	116·5(3)	Cl(8)–P(5)–N(5)	109·7(3)
Cl(3)–P(2)–N(1)	108·3(3)	N(4)–P(5)–N(5)	116·1(3)
Cl(3)–P(2)–N(2)	104·8(3)	Cl(9)–P(6)–N(2)	102·9(3)
Cl(3)–P(2)–N(7)	109·2(3)	Cl(9)–P(6)–N(3)	109·5(3)
N(1)–P(2)–N(2)	110·3(3)	Cl(9)–P(6)–N(4)	110·0(3)
N(1)–P(2)–N(7)	113·6(4)	N(2)–P(6)–N(3)	110·8(3)
N(2)–P(2)–N(7)	110·2(3)	N(2)–P(6)–N(4)	111·4(3)
Cl(4)–P(3)–Cl(5)	101·3(1)	N(3)–P(6)–N(4)	111·8(4)
Cl(4)–P(3)–N(6)	107·4(3)	P(1)–N(1)–P(2)	125·9(4)
Cl(4)–P(3)–N(7)	108·4(3)	P(2)–N(2)–P(4)	119·0(3)
Cl(5)–P(3)–N(6)	110·5(3)	P(2)–N(2)–P(6)	119·8(3)
Cl(5)–P(3)–N(7)	109·7(3)	P(4)–N(2)–P(6)	121·0(3)
N(6)–P(3)–N(7)	118·1(3)	P(1)–N(3)–P(6)	124·8(4)
Cl(6)–P(4)–N(2)	104·5(3)	P(5)–N(4)–P(6)	123·4(4)
Cl(6)–P(4)–N(5)	107·8(4)	P(4)–N(5)–P(5)	128·6(4)
Cl(6)–P(4)–N(6)	108·7(3)	P(3)–N(6)–P(4)	123·2(4)
N(2)–P(4)–N(5)	111·4(3)	P(2)–N(7)–P(3)	127·3(4)
N(2)–P(4)–N(6)	110·1(3)		

TABLE 6

Equations of planes in the form $lX' + mY + nZ' = p$, where X', Y, and Z' are in Å referred to axes a, b, and c^*, and angles (deg.) between the planes. N(2) is displaced from plane (1) by 0·04 Å (5σ)

Plane	Atoms	l	m	n	p
(1)	P(2),P(4),P(6)	0·1080	0·9936	0·0329	3·5145
(2)	N(1),P(2),N(7)	−0·1986	0·6979	−0·6881	0·8720
(3)	N(5),P(4),N(6)	−0·5073	0·6982	0·5051	5·2649
(4)	N(3),P(6),N(4)	0·8004	0·5752	0·1778	4·3698

(1)—(2)	49·5
(1)—(3)	49·0
(1)—(4)	48·6

The thermal parameters (Table 3) are largest in the b direction. This may be partly the result of the omission of an absorption correction, but the values suggest that the most significant vibration is that of the molecule as a whole normal to the mean molecular plane. The molecule is not however a rigid body, as the parameters for the outer nitrogen atoms indicate a further intramolecular out-of-plane motion of these atoms; the central nitrogen atom parameters are similar to those of the phosphorus atoms to which it is bonded, so that the central region of the molecule appears to be rigid. The chlorine atoms appear to have additional vibrations normal to the P–Cl bonds, as might be expected. It is difficult to make a detailed analysis of these complicated motions, but approximate bond length corrections based on a riding model are *ca.* 0·01—0·02 Å for all bonds except the central PN bonds, where the corrections are zero. Since these corrections are approximate it seems appropriate to base discussion mainly on the uncorrected values.

The non-central PN bonds fall into two classes, the P_AN_A type and the P_BN_A type (see Figure 1); although the differences between individual values are not always significant (Table 4), the mean values of 1·572 and 1·559 Å respectively (corrected means $1·58_2$ and $1·56_6$ Å), in comparison with the single-bond length of 1·77 Å,[6] suggest slightly greater π-character in the P_BN_A bonds. This conclusion is unchanged when allowance is made for differences in σ-hybridization.[7]

Probably the most significant feature of the structure is the length of the central PN bonds (P_BN_B type), 1·723 Å, longer than for any other phosphazene derivative previously reported. In tetrameric[8] and hexameric[9] phosphazene dimethylamides, $[PN(NMe_2)_2]_{4,6}$, the average exocyclic PN bond lengths are 1·68 and 1·67 Å respectively. Thus the exocyclic PN bond in these molecules is stronger than the P_BN_B bond in $P_6N_7Cl_9$, even though the environments of the nitrogen atoms in the dimethylamides deviate more from planarity. The delocalization of the lone pair on the central nitrogen in $P_6N_7Cl_9$, suggested by its planar configuration, would seem to be real, since the base strength of this compound in aqueous sulphuric acid is less than that of the monocyclic $N_6P_6Cl_{12}$. It therefore seems probable that the π-bonding from the central atom is normal. The non-planarity of the molecule and the length of the central bonds has been attributed[3] to the σ-bonding requirements. In a general sense, such pairs of bonds as N(2)–P(2)–Cl(3) are equivalent to an exocyclic pair such as Cl(4)–P(3)–Cl(5), and the relation between the angles N(2)–P(2)–Cl(3) and N(7)–P(2)–N(1) is close to that expected for two pairs of equivalent orbitals based on an ($s + 3p$) set, as it is in monocyclic phosphazene derivatives. Detailed geometrical calculation[10] shows this requirement to be incompatible with a planar configuration of the P–N bonds at P(2); shorter central bonds would be achieved if the configuration were planar, but the bridgehead P–Cl bond would then be formed from a pure p-orbital at phosphorus. Some compromise between the σ- and π-requirements is indicated by the small ring-angles at nitrogen (125·5°) and phosphorus (116·9°); in $N_5P_5Cl_{10}$ their mean values are 148·6 and 118·4° respectively.[11] The interpretation of the structure of $P_6N_7Cl_9$ as containing a set of three

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[9] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 1423.

[10] N. L. Paddock, personal communication.

[11] A. W. Schlueter and R. A. Jacobson, *J. Chem. Soc. (A)*, 1968, 2317.

weakened σ-bonds supplemented by π-bonds has been supported by a study of other properties.[3]

The P–Cl bonds also show an interesting feature. The P_B–Cl type bonds, 2·002—2·009(4), mean 2·004(3) Å (corrected mean 2·02$_5$ Å), are significantly longer than the P_A–Cl type bonds, 1·970—1·990, mean 1·980 Å (corrected mean 1·99$_7$ Å). These P_A–Cl type bonds appear to be longer than P–Cl bonds found in other phosphazenes, *cf.* 1·989(4) Å for both the 'tub'[12] and 'chair'[13] conformations of $N_4P_4Cl_8$, 1·961(8) Å in $N_5P_5Cl_{10}$,[11] and 1·975(10) Å in $N_3P_3Cl_6$,[14] although recent electron diffraction results[15] for the latter compound report the P–Cl bond lengths as 2·006(7) Å. A possible explanation for the increased length of the P_B–Cl type bonds may be that atoms P(2), P(4), and P(6) are involved in relatively strong π-bonding to three nitrogen atoms with a resultant decrease in the π-bonding in the P_B–Cl bond. In the case of P_A–Cl bonds, each phosphorus atom is involved in π-bonding with only two nitrogen atoms, thus allowing more extensive π-interaction with the chlorine atoms.

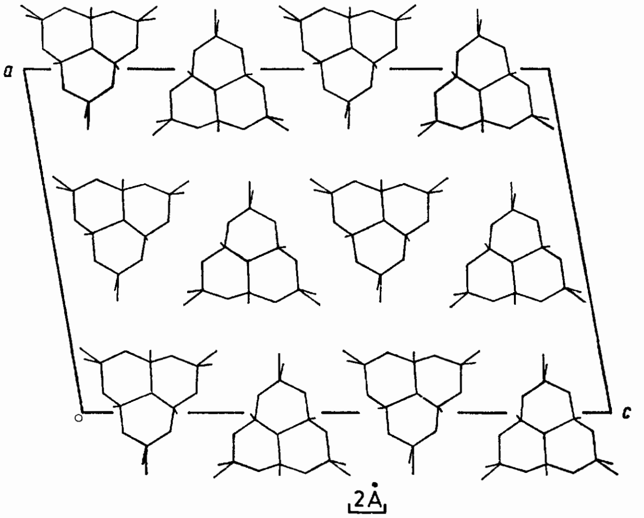

FIGURE 2 Projection of the structure of $P_6N_7Cl_9$ along *b*

The packing arrangement viewed down the *b* axis is shown in Figure 2. The closest non-bonded, intermolecular contacts are: N · · · N 3·149, Cl · · · Cl 3·354, N · · · Cl 3·380, N · · · P 3·637, and Cl · · · P 3·894 Å. The Cl · · · Cl distance of 3·354 Å is considerably shorter than the van der Waals separation of 3·60 Å. However this shortening is quite common.[16]

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[1/1123 *Received, 2nd July*, 1971]

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