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The Crystal Structure of Compounds with (N-P)_n Rings.
VIII.* Dichlorotetrakispropylaminocyclotriphosphazatriene Hydrochloride,
N₃P₃Cl₂(NHPrⁱ)₄. HCl

BY N. V. MANI† AND A. J. WAGNER

Laboratory of Structural Chemistry, The University, Bloemensingel 10, Groningen, The Netherlands

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The compound N₃P₃Cl₂(NHPrⁱ)₄.HCl crystallizes in the triclinic space group *P*1̄, with unit-cell dimensions *a* = 10·445 (4), *b* = 14·117 (4), *c* = 9·658 (3) Å, α = 104·76 (10), β = 100·09 (10), γ = 70·12 (10)°. The crystal structure was solved by Patterson and Fourier methods from the intensities of 2785 observed independent reflexions, measured with Mo radiation on an automatic three-circle diffractometer. The structure was refined by block-diagonal least-squares analysis to an index *R* of 0·067. The crystal structure consists of positive ions [N₃P₃Cl₂(NHPrⁱ)₄H]⁺ and negative ions Cl⁻. In the cyclophosphazene moiety the substituents at the phosphorus atoms are arranged geminally and the extra proton is linked to the ring nitrogen atom between the P(NHPrⁱ)₂ groups. The six-membered ring is slightly boat-shaped and considerably distorted compared with the regular six-membered rings of known cyclotriphosphazenes. The P-N ring bond lengths in the segment (PrⁱHN)₂PNHP(NHPrⁱ)₂ are 1·666 (5) Å and the exocyclic P-N bond lengths are 1·609 (5) Å. The P-N ring bonds in the segments Cl₂PNP(NHPrⁱ)₂ have lengths 1·558 (5) and 1·583 (5) Å, the shorter bonds being located near the PCl₂ group. The P-N-P ring angle in the segment (PrⁱHN)₂PNHP(NHPrⁱ)₂ is 131·7 (3)° and the N-P-N ring angles at the phosphorus atoms of this segment are 107·5 (2)°. The two other P-N-P ring angles are 125·4 (3)° and the third N-P-N ring angle is 120·1 (2)°. The anion Cl⁻ is coordinated by the ring >NH group of one cation, at a distance of 3·19 Å, and by four exocyclic >NH groups of two other cations, at distances ranging from 3·31 to 3·36 Å.

Introduction

Addition compounds of cyclophosphazenes with various Lewis acids have been known for some time. One group is exemplified by the adducts of amino derivatives with hydrochloric acid. The bonding between the Lewis base and the Lewis acid in these compounds has been studied by infrared and ¹H nuclear magnetic resonance (n.m.r.) techniques (Moeller & Kokalis, 1963) and by basicity measurements (Feakins, Last & Shaw,

1964). The results of these studies point to a ring nitrogen atom as the basic centre of the phosphazene molecule.

We have completed an X-ray diffraction study of the compound N₃P₃Cl₂(NHPrⁱ)₄.HCl. Our results (Mani & Wagner, 1968) confirm the conclusions from the earlier physico-chemical work. Furthermore, the present work shows what the detailed structure of the phosphazene molecule is, and which of the ring nitrogen atoms is the basic centre.

In general the nature of the cyclophosphazene addition compounds will depend both on the phosphazene base and on the Lewis acid concerned. An example, where the Lewis acid is not bonded to a particular ring

* Part VII: Zoer & Wagner (1970).

† Present address: Department of Chemistry, Michigan State University, East Lansing, Michigan 48823, U.S.A.

atom but situated above the ring and bonded to more than one nitrogen atom, has recently been reported by Trotter, Whitlow & Marsh (1969) in the crystal structure of N₆P₆(NMe₂)₁₂.CuCl₂.

Experimental

A sample of the compound N₃P₃Cl₂(NHPrⁱ)₄.HCl was kindly provided by Professor R. A. Shaw of Birkbeck College, London. Crystals suitable for the determination of the unit-cell dimensions and for the measurement of the intensities were obtained by recrystallization from a light petroleum-chloroform (3:1) mixture.

The crystal data are given in Table 1. The unit-cell dimensions were calculated by a least-squares procedure from θ values measured on Weissenberg photographs. Experimental details are given in Table 2.

Table 1. *Crystal data*

Compound	N ₃ P ₃ Cl ₂ (NHPr ⁱ) ₄ .HCl, $M=474.8$
Crystal system	Triclinic
Unit cell	$a=10.445(4)\text{ \AA}$ $b=14.117(4)$ $c=9.658(3)$ $\alpha=104.76(10)^\circ$ $\beta=100.09(10)$ $\gamma=70.12(10)$
Space group	$P\bar{1}$
Density	$D_m=1.20\text{ g.cm}^{-3}$ $D_c=1.22\text{ g.cm}^{-3}$ for $Z=2$
$F(000)$	500
$\mu(\text{Mo})$	5.5 cm^{-1}

The intensities were measured on a Nonius automatic three-circle single-crystal diffractometer. Details are included in Table 2. During the processing of the experimental data reflexions having a weight, based on counting statistics, less than 0.1 times the average weight of all reflexions were discarded. There remained 2785 independent reflexions with reliable intensities, which were corrected for Lorentz-polarization (Lp) effects and for absorption. The absorption correction factors were obtained with a computer program following the Busing & Levy (1957) scheme, which requires the crystal boundaries to be approximated by plane surfaces. Our data crystal was prismatic in shape having

dimensions $0.60 \times 0.31 \times 0.30$ mm and could be described by six bounding planes.

Structure determination

A three-dimensional Patterson synthesis was calculated, using 2785 independent $|F_o|^2$ values. From this vector map it was possible to identify the positions of the three phosphorus and three chlorine atoms. A structure factor calculation based on these atoms gave $R=0.53$. After initial least-squares refinement of the parameters of these atoms the F_o values of 2570 independent reflexions were used in a three-dimensional Fourier synthesis. All nitrogen and carbon atoms were located from the Fourier map. Their positional parameters and anisotropic thermal parameters were subsequently refined by least-squares to an index R of 0.072. After this a difference Fourier synthesis was calculated, which revealed the positions of the hydrogen atoms. In the final block-diagonal least-squares refinement (Cruickshank, 1961), based on the 2785 observed independent reflexions, the positions of all atoms were refined. Anisotropic thermal parameters were refined for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The function minimized was $\sum w[|F_o| - K|F_c|]^2$, where the weight w is given by $w=30/\{150 + |F_o|(1 + 0.00045|F_o|)\}$. The atomic scattering factors were taken from Moore (1963). In the last refinement cycle the shifts in the parameters were of the order of 0.5σ . The final value of the index R is 0.067.

The atomic coordinates are listed in Table 3 with their standard deviations as calculated by the least-squares program. Tables 4 and 5 give the thermal parameters of the heavier atoms and the hydrogen atoms respectively, with their standard deviations. Observed and calculated structure factors are compared in Table 6.

Description and discussion of the structure

In the crystal structure of N₃P₃Cl₂(NHPrⁱ)₄.HCl separate positive ions [N₃P₃Cl₂(NHPrⁱ)₄H]⁺ and negative ions Cl⁻ are present. In the cyclophosphazene moiety the substituents at the phosphorus atoms are arranged

Table 2. *Experimental details of unit-cell determination and intensity measurements*

Unit-cell determination:	
Method	Weissenberg photographs
Layer lines (and number of independent reflexions)	$hk0(88)$, $h0l(75)$, $0kl(67)$
Radiation	Cu K radiation, $\lambda(\alpha_1)=1.54051$, $\lambda(\alpha_2)=1.54433\text{ \AA}$
Calibration	NaCl reflexions, $a(\text{NaCl})=5.640\text{ \AA}$
Temperature	Room temperature
Intensity measurements:	
Method	Nonius automatic three-circle diffractometer
Radiation	Mo radiation, Zr filtered
Range	$(\sin \theta)/\lambda \leq 0.57\text{ \AA}^{-1}$, 3588 independent reflexions
Scanning method	$\theta-2\theta$
Scanning angle	$2.6-2.8^\circ$ in 2θ
Temperature	Room temperature

geminally and the extra proton is linked to the ring nitrogen atom between the $P(NHPr^i)_2$ groups. The fact that one of the nitrogen atoms in the ring is the basic centre, rather than one of the exocyclic nitrogen atoms or the π -electron cloud of the ring in general, is in agree-

ment with the observations from infrared and n.m.r. spectroscopy and from the basicity measurements. The fact that the ring nitrogen atom of the segment $(Pr^iHN)_2PNP(NHPr^i)_2$ is the basic centre rather than those of the segments $Cl_2PNP(NHPr^i)_2$ is in agreement

Table 3. *Final atomic coordinates with standard deviations in units of the last decimal in parantheses*

It is indicated to which heavy atoms the hydrogen atoms are bonded.

	x	y	z		x	y	z		
P(1)	0.7861 (2)	-0.4111 (1)	0.1499 (2)	N(5):	H(5)	0.704 (5)	-0.126 (4)	-0.072 (5)	
P(2)	0.6762 (2)	-0.2328 (1)	0.0378 (2)	C(7):	H(6)	0.365 (7)	-0.192 (5)	0.223 (8)	
P(3)	0.6531 (2)	-0.2370 (1)	0.3454 (2)	N(6)	H(7)	0.495 (5)	-0.160 (4)	0.506 (6)	
Cl(1)	0.9847 (2)	-0.4831 (2)	0.1910 (2)	C(10):	H(8)	0.927 (6)	-0.271 (4)	0.407 (6)	
Cl(2)	0.7188 (3)	-0.5322 (2)	0.0602 (3)	N(7):	H(9)	0.688 (6)	-0.133 (4)	0.554 (6)	
Cl(3)	0.4514 (2)	0.0542 (1)	0.2629 (2)	C(2)	H(10)	0.296 (7)	-0.235 (6)	-0.093 (8)	
N(1)	0.7705 (5)	-0.3480 (3)	0.0334 (5)		H(11)	0.303 (7)	-0.329 (5)	-0.237 (8)	
N(2)	0.6265 (5)	-0.1841 (3)	0.2029 (5)		H(12)	0.316 (7)	-0.220 (5)	-0.270 (7)	
N(3)	0.7211 (5)	-0.3572 (3)	0.2940 (5)	C(3)	H(13)	0.541 (8)	-0.330 (6)	-0.355 (9)	
N(4)	0.5500 (5)	-0.2270 (3)	-0.0841 (5)		H(14)	0.521 (13)	-0.430 (9)	-0.353 (13)	
N(5)	0.7492 (5)	-0.1582 (4)	0.0058 (5)		H(15)	0.670 (9)	-0.384 (6)	-0.263 (9)	
N(6)	0.5075 (5)	-0.2014 (4)	0.4100 (5)	C(5)	H(16)	0.849 (8)	0.003 (6)	0.033 (8)	
N(7)	0.7470 (5)	-0.1891 (4)	0.4767 (5)		H(17)	0.900 (9)	0.011 (6)	0.182 (9)	
C(1)	0.4929 (8)	-0.3117 (5)	-0.1543 (8)		H(18)	0.716 (9)	0.025 (7)	0.152 (10)	
C(2)	0.3398 (9)	-0.2642 (7)	-0.1926 (11)	C(6)	H(19)	1.082 (8)	-0.152 (6)	0.082 (9)	
C(3)	0.5642 (12)	-0.3777 (7)	-0.2840 (10)		H(20)	0.994 (9)	-0.122 (7)	-0.031 (10)	
C(4)	0.8624 (8)	-0.1279 (6)	0.0990 (7)		H(21)	1.010 (9)	-0.263 (7)	-0.006 (9)	
C(5)	0.8269 (11)	-0.0157 (8)	0.1312 (17)	C(8)	H(22)	0.382 (12)	-0.353 (9)	0.222 (12)	
C(6)	0.9939 (9)	-0.1803 (9)	0.0321 (13)		H(23)	0.426 (9)	-0.351 (7)	0.397 (10)	
C(7)	0.3772 (8)	-0.2029 (6)	0.3265 (7)		H(24)	0.253 (8)	-0.299 (6)	0.288 (8)	
C(8)	0.3523 (10)	-0.3028 (8)	0.3211 (15)	C(9)	H(25)	0.299 (14)	-0.048 (10)	0.400 (15)	
C(9)	0.2654 (8)	-0.1152 (8)	0.4005 (13)		H(26)	0.179 (8)	-0.106 (6)	0.334 (8)	
C(10)	0.8948 (7)	-0.2373 (6)	0.5069 (7)		H(27)	0.273 (12)	-0.120 (9)	0.508 (12)	
C(11)	0.9616 (8)	-0.1525 (8)	0.5656 (11)	C(11)	H(28)	0.920 (10)	-0.117 (8)	0.672 (11)	
C(12)	0.9243 (10)	-0.3128 (8)	0.6028 (11)		H(29)	0.910 (8)	-0.093 (6)	0.498 (8)	
N(2):	H(1)	0.569 (4)	-0.107 (3)		0.223 (5)	H(30)	1.070 (9)	-0.186 (7)	0.589 (10)
C(1):	H(2)	0.503 (5)	-0.358 (4)	-0.086 (6)	C(12)	H(31)	1.033 (9)	-0.339 (7)	0.614 (10)
N(4):	H(3)	0.499 (7)	-0.158 (6)	-0.094 (8)		H(32)	0.868 (8)	-0.265 (6)	0.695 (9)
C(4):	H(4)	0.899 (6)	-0.163 (5)	0.182 (7)		H(33)	0.868 (12)	-0.367 (9)	0.545 (13)

Table 4. *Parameters ($\text{\AA}^2 \times 10^{-4}$) of the anisotropic temperature factors*

$\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ with standard deviations in units of the last decimal in parantheses

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
P(1)	960 (13)	469 (8)	572 (10)	-26 (16)	306 (14)	281 (18)
P(2)	609 (9)	494 (8)	471 (9)	-300 (14)	318 (13)	69 (14)
P(3)	586 (9)	529 (8)	478 (9)	-238 (14)	292 (13)	147 (14)
Cl(1)	1168 (17)	1257 (17)	962 (15)	-1097 (27)	1036 (26)	621 (25)
Cl(2)	2444 (32)	623 (12)	1200 (18)	-1232 (32)	34 (23)	726 (38)
Cl(3)	1046 (13)	517 (8)	564 (9)	-99 (16)	327 (14)	368 (17)
N(1)	838 (33)	537 (27)	485 (27)	-94 (47)	231 (42)	263 (47)
N(2)	786 (33)	446 (24)	612 (28)	-94 (45)	345 (41)	331 (47)
N(3)	840 (35)	600 (29)	625 (31)	-173 (50)	516 (48)	281 (52)
N(4)	812 (34)	613 (29)	699 (33)	-668 (51)	565 (49)	-206 (52)
N(5)	759 (33)	758 (32)	496 (29)	-639 (53)	463 (48)	-20 (48)
N(6)	650 (30)	785 (32)	507 (29)	-469 (50)	211 (47)	135 (45)
N(7)	564 (30)	852 (34)	566 (30)	-303 (51)	230 (50)	86 (46)
C(1)	1088 (57)	849 (46)	1005 (55)	-1184 (86)	851 (81)	-693 (88)
C(2)	1103 (67)	1589 (83)	1946 (97)	-1630 (126)	2042 (149)	-1189 (128)
C(3)	2210 (111)	1015 (68)	1053 (71)	-1045 (141)	-155 (109)	-744 (140)
C(4)	1098 (55)	1082 (55)	771 (47)	-1280 (93)	308 (80)	-51 (80)
C(5)	1328 (88)	1141 (82)	3683 (189)	-1430 (144)	-934 (199)	582 (206)
C(6)	883 (65)	1980 (109)	2167 (124)	-1082 (137)	-109 (182)	-204 (141)
C(7)	723 (44)	1218 (59)	736 (46)	-784 (83)	560 (82)	-142 (70)
C(8)	1214 (81)	1254 (84)	2558 (153)	-1146 (138)	-329 (179)	-1008 (180)
C(9)	621 (51)	1588 (84)	2195 (115)	-349 (104)	272 (154)	62 (119)
C(10)	713 (45)	1150 (55)	825 (50)	-472 (79)	419 (82)	-26 (73)
C(11)	844 (58)	1485 (86)	1972 (99)	-1163 (117)	801 (146)	-495 (119)
C(12)	1290 (79)	1331 (81)	1512 (91)	-624 (129)	1368 (142)	-702 (134)

with what is expected from the large electronegativity of the chlorine atoms and from the electron releasing power of the secondary amino groups.

Fig. 1 shows the residual electron density distribution in the neighbourhood of the attached proton H(1) in the best plane through the ring atoms P(2), N(2) and P(3) and through the chloride ion Cl(3). In calculating this difference density the contribution from H(1) to the calculated structure factors was omitted. The deviations of the atoms from the best plane are indicated in the Figure. It is seen that the four atoms P(2), N(2), P(3) and Cl(3) lie in the same plane within experimental error and that H(1) is in this plane as well. N(2), H(1) and Cl(3) lie on a straight line; the angle N(2)–H(1)–Cl(3) is 179.0 (1.0)° and the distances are N(2)–H(1) = 1.04 (4), H(1)–Cl(3) = 2.15 (4) and N(2)···Cl(3) = 3.192 (4) Å.

Fig. 2 gives the arrangement of the positive and negative ions in the crystal. The chloride ion Cl(3) has short distances to five >NH groups belonging to three cyclophosphazene molecules. The coordination by these groups is approximately square-pyramidal. As indicated in the Figure Cl(3) is closest (3.19 Å) to the ring nitrogen atom N(2) and has somewhat larger distances (3.31–3.36 Å) to the four exocyclic nitrogen atoms N(4'), N(5'), N(6') and N(7'). The geometry of the Cl(3)···H–N contacts is given more fully in Table 7.

Figs. 3 and 4 show the bond lengths and valence angles in the cation [N₃P₃Cl₂(NHPⁱ)₄H]⁺. The six-membered ring is non-planar and has a slight boat conformation. The distances from the ring atoms to the best plane through the ring are given in Fig. 5. The dihedral angles of the ring bonds are also included in this Figure.

The P–N bonds in the ring are equal in pairs; the average lengths (and individual standard deviations) are 1.558 (5), 1.583 (5) and 1.666 (5) Å. In the segments P(1)–N(1)–P(2) and P(1)–N(3)–P(3), the difference in bond length (0.025 Å) is related to the electronegativity of the substituents; the shorter P–N bonds are found on the side of the more electronegative substituents. This dependence of bond length on electronegativity has also been observed in the molecular structures of N₃P₃Cl₂Ph₄ (Mani, Ahmed & Barnes 1966), N₃P₃Cl₄Ph₂ (Mani, Ahmed & Barnes, 1965) and N₃P₃F₄Ph₂ (Allen, Faught, Moeller & Paul, 1969). The P–N bonds in the segment P(2)–N(2)–P(3) are much longer than the other ring bonds, corresponding to the fact that this segment is phosphazane-like rather than phosphazene-like. The value of 1.666 Å is in good agreement with the P–N bond lengths found in the cyclophosphazanes (NH)₃P₃O₆Na₃·4H₂O (Olthoff, Migchelsen & Vos, 1965) and (NMe)₃P₃O₃(OMe)₃ (Ansell & Bullen, 1965).

The four exocyclic P–N bonds are equal within experimental error. Their average length 1.609 (5) Å is considerably shorter than that (1.67 Å) of the exocyclic P–N bonds in the aminocyclophosphazenes N₄P₄(NMe₂)₈ (Bullen, 1962) and N₆P₆(NMe₂)₁₂ (Wagner & Vos,

Table 5. Parameters (Å²) of the isotropic temperature factors $\exp[-B(\sin \theta/\lambda)^2]$ with standard deviations in parentheses

H(1)	2.9 (1.0)	H(18)	13.1 (2.9)
H(2)	3.8 (1.3)	H(19)	10.3 (2.5)
H(3)	10.6 (2.2)	H(20)	13.4 (3.0)
H(4)	9.3 (1.7)	H(21)	10.6 (2.9)
H(5)	3.7 (1.1)	H(22)	11.0 (4.3)
H(6)	5.7 (2.1)	H(23)	14.1 (3.0)
H(7)	5.3 (1.3)	H(24)	8.8 (2.3)
H(8)	5.2 (1.5)	H(25)	17.5 (5.2)
H(9)	5.8 (1.6)	H(26)	9.9 (2.3)
H(10)	11.9 (2.2)	H(27)	16.4 (4.2)
H(11)	6.1 (2.1)	H(28)	14.9 (3.5)
H(12)	7.2 (1.8)	H(29)	9.4 (2.4)
H(13)	12.6 (2.7)	H(30)	14.8 (3.1)
H(14)	17.5 (4.7)	H(31)	12.7 (3.1)
H(15)	11.9 (2.7)	H(32)	10.0 (2.6)
H(16)	10.3 (2.2)	H(33)	17.8 (4.7)
H(17)	12.8 (2.7)		

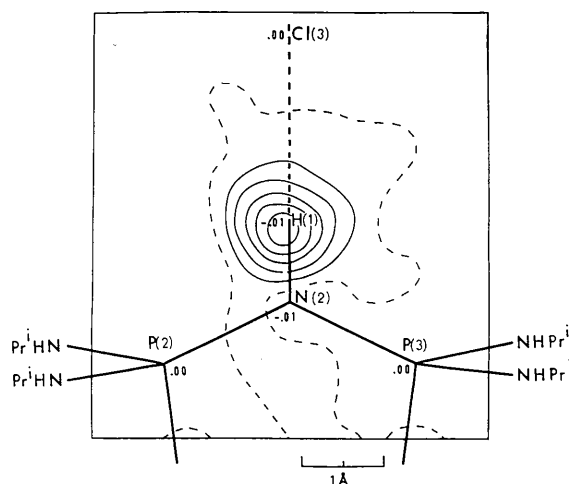


Fig. 1. Residual electron density distribution in the best plane through P(2), N(2), P(3) and Cl(3). H(1) contribution to F_c omitted. Contours at 0.1 e.Å⁻³, beginning at 0.15 e.Å⁻³ (dotted). Equation of the best plane, referred to the orthogonal axes a^* , $c \times a^*$ and c with X , Y and Z measured in Å units: $0.8405X + 0.5350Y + 0.0859Z = 5.005$. The numbers in the Figure are the deviations (Å) of the atoms from this plane.

1968). The exocyclic P–N bonds in the present structure have a large amount of double bond character, due to delocalization of the lone electron pairs on the atoms N(4), N(5), N(6) and N(7). The delocalization is induced by the positive charge on N(2). It should be noted that the coordination of the Cl⁻ ion by >NH groups, discussed above, is in agreement with a spreading of this charge to the exocyclic nitrogen atoms.

The P–Cl, N–C and C–C bonds have the expected lengths, except for the bond C(4)–C(5) which is somewhat short. This may be related to the large value of the parameter U_{33} of the atom C(5). The N–H bond lengths range from 0.94 to 1.04 Å and the C–H bond lengths from 0.97 to 1.15 Å.

Most valence angles in the ion [N₃P₃Cl₂(NHPⁱ)₄H]⁺ have the expected values. The angles around P(1) are comparable to those in halogenocyclotriphosphazenes

Table 6. Observed and calculated structure factors
The columns are k , $10F_o$ and $10F_c$.

Table with multiple columns containing numerical data for structure factors. The columns are labeled with k, 10Fo, and 10Fc. The data is organized in a grid-like format with various numerical values and some text labels like 'k, 10Fo' and '10Fc' interspersed within the columns.

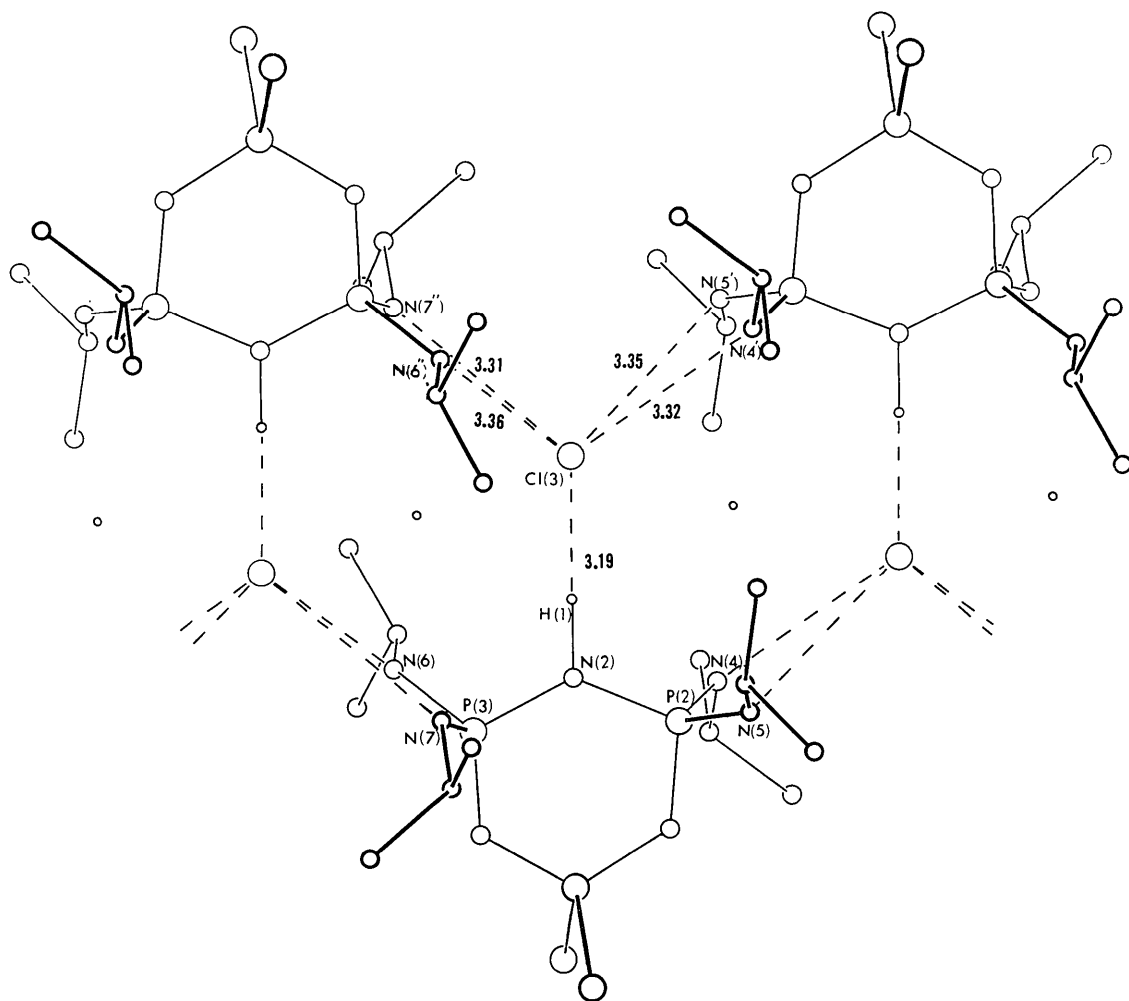


Fig. 2. Arrangement of the positive and negative ions and coordination of the chloride ion Cl(3) by $>NH$ groups. The structure is projected along an axis with direction cosines 0.7437, 0.5894, 0.3156 with respect to the orthogonal axes a^* , $c \times a^*$ and c . Primed atoms are related to the atoms at x, y, z by the operation $(1-x), -y, -z$ and doubly primed atoms by the operation $(1-x), -y, (1-z)$.

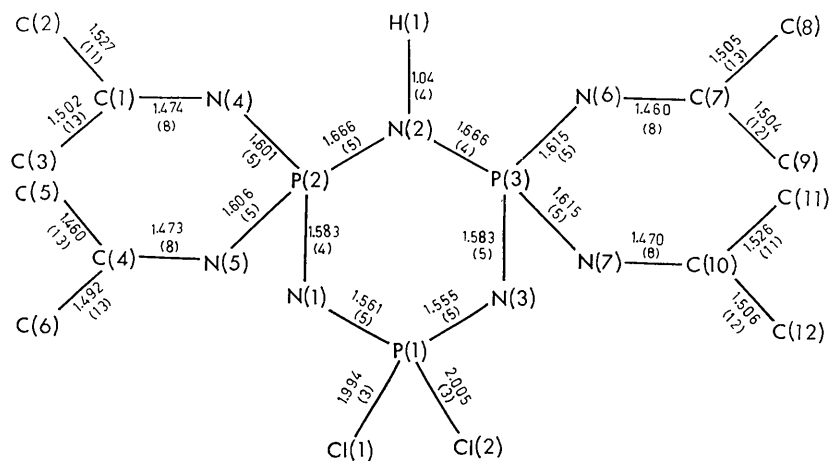
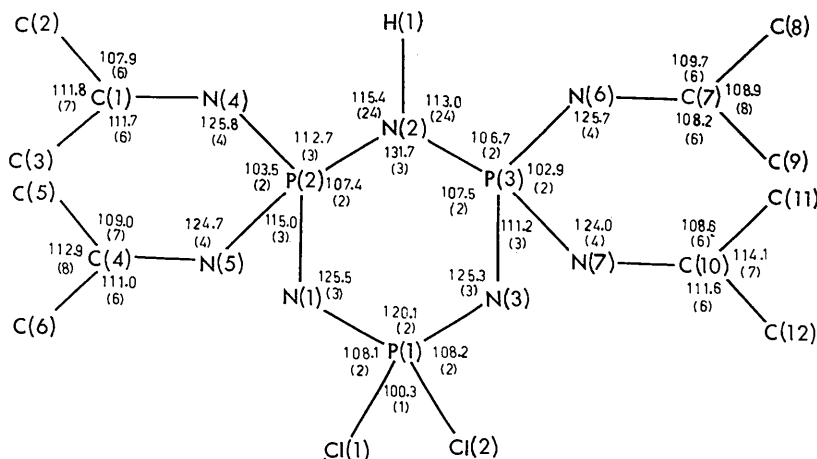


Fig. 3. Bond lengths. Standard deviations in units of the last decimal are in parentheses.



N(1)-P(2)-N(4)	111.2(3)	Cl(1)-P(1)-N(3)	109.5(2)	N(3)-P(3)-N(6)	116.0(3)
N(2)-P(2)-N(5)	107.1(2)	Cl(2)-P(1)-N(1)	108.8(2)	N(2)-P(3)-N(7)	112.6(3)

Fig. 4. Valence angles. Standard deviations in units of the last decimal are in parentheses.

Table 8. Some intramolecular non-bonded distances between isopropylamino groups at the same side of the ring plane

N(5)···N(7)	4.68 Å	N(4)···N(6)	4.78 Å
C(4)···C(10)	4.51	C(1)···C(7)	4.74
C(4)···C(11)	4.52	C(2)···C(7)	4.83
Other C····C	≥4.85	Other C····C	≥5.01

vant intramolecular non-bonded distances are given in Table 8 and show no unacceptably short values.

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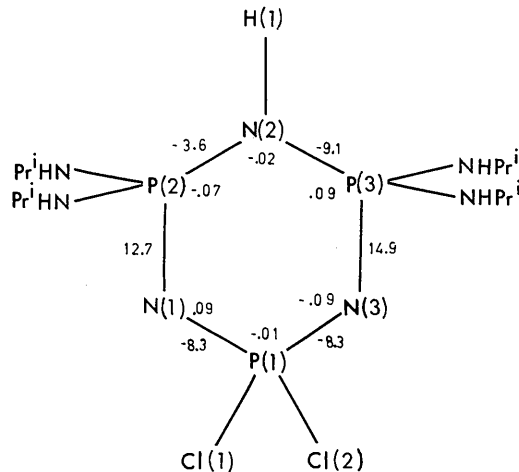


Fig. 5. Deviations of the ring atoms from the best plane through the ring and dihedral angles of the ring bonds. Equation of the best plane, referred to the orthogonal axes a^* , $c \times a^*$ and c with X , Y and Z measured in Å units:

$$0.8496X + 0.5085Y + 0.1399Z = 5.164.$$

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