

515. Phosphonitrilic Derivatives. Part II.* The Structure of Trimeric Phosphonitrilic Chloride.†

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The structure of trimeric phosphonitrilic chloride, $(\text{PNCl}_2)_3$, has been determined by means of two-dimensional Fourier and difference syntheses followed by three-dimensional least-squares refinement. The structure is composed of discrete molecules each of which is made up of an almost flat six-membered ring of alternate phosphorus and nitrogen atoms with two chlorine atoms attached to each phosphorus atom. The bond lengths within the ring are considered as all being equal in length although they vary from 1.57 to 1.61 Å. The bond angles within the ring vary from 118.33° to 120.93° but are not significantly different.

VERY little structural work has been done in the phosphonitrilic field of compounds. The crystal structure of $(\text{PNCl}_2)_4$ has been worked out by Ketelaar and de Vries.¹ Bode² was unable to carry out an accurate structural analysis of $(\text{PNBr}_2)_3$ because the positions of nitrogen atoms could not be observed on electron-density maps. The chloride trimer,

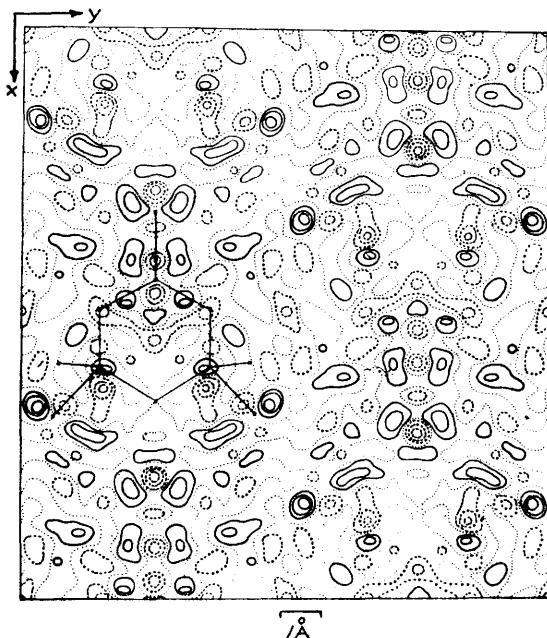


FIG. 1. Final $hk0$ difference map. The contours are drawn at $\frac{1}{2}$ -electron intervals, the dashed lines are negative values and the dotted lines are contours of zero electron density.

$(\text{PNCl}_2)_3$, has been studied by Brockway and Bright³ by electron diffraction. Only models with a planar ring were tried. The cyclic nature of $(\text{PNCl}_2)_3$ has been confirmed by Daasch,⁴ who studied the infrared and Raman spectra.

An accurate crystal structure was required as part of a study of the binding in phosphonitrilic compounds. In the present work two-dimensional refinement of the three axial projections has been followed by a three-dimensional diagonal least-squares refinement.

* Part I, preceding paper.

† While this work was in progress, Pompa and Ripamonti published a paper (*Ric. Sci.*, 1959, **29**, 1516) on the same subject.

¹ Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.

² Bode, *Angew. Chem.*, 1949, **61**, No. 11, 438.

³ Brockway and Bright, *J. Amer. Chem. Soc.*, 1943, **65**, 1551.

⁴ Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403.

Crystal Data.— $(\text{PNCl}_2)_3$, $M = 347.8$, orthorhombic, $a = 14.15 \pm 0.02$, $b = 12.99 \pm 0.02$, $c = 6.19 \pm 0.01$ Å, $U = 1138$ Å³, $D_m = 1.99 \pm 0.03$ (by flotation), $Z = 4$, $D_c = 2.02$, $F(000) = 672$. Cu- K_α radiation, single-crystal rotation and oscillation photographs. Space-group, $Pnma$ (D_{2h}^{16} , No. 62) or $Pna2$ (C_{2v}^9 , No. 33). The structure analysis confirmed that the correct space-group is $Pnma$. The implied symmetry of the molecule was assumed to be m rather than $\bar{1}$.

FIG. 2. Final $0kl$ difference map. The contours are drawn at $\frac{1}{2}$ -electron intervals, the dashed lines are negative values and the dotted lines are contours of zero electron density. The position of only one molecule is shown.

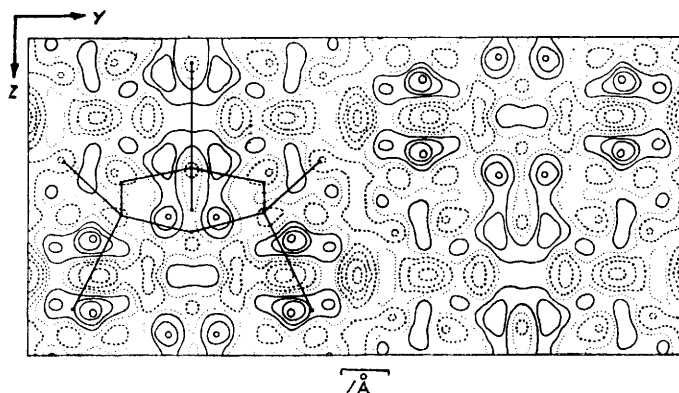
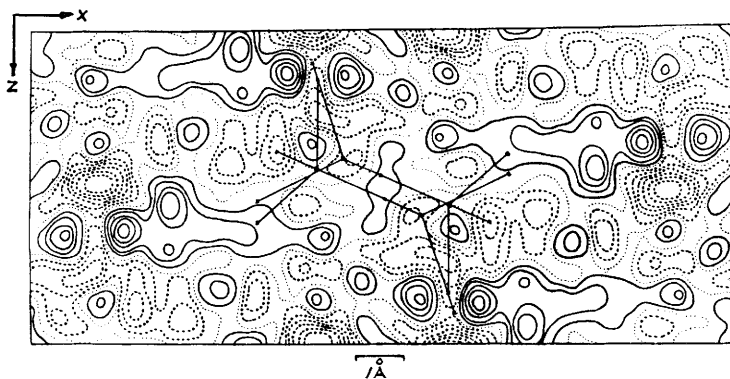


FIG. 3. Final $h0l$ difference map. The contours are drawn $\frac{1}{2}$ -electron intervals, the dashed lines are negative values and the dotted lines are contours of zero electron density.



Determination of Structure.—A study of the structure published for trimeric phosphonitric bromide² indicated that this, with minor changes, might serve as a starting point for the determination of the structure of $(\text{PNCl}_2)_3$.

(i) $hk0$ Projection: Structure factors calculated from co-ordinates obtained with the above consideration in mind agreed reasonably well with the observed values. The projection was refined by means of Fourier summations to an R value of 28%. A temperature factor of $B = 3.1$ Å², obtained from a plot of $\log \langle F_c \rangle / \langle F_o \rangle$ against $\langle (\sin \theta / \lambda)^2 \rangle$ was applied to all atoms; the angular brackets indicate mean values for a given $\sin \theta$ range. The refinement was carried further by means of difference syntheses; individual isotropic temperature factors were applied to all atoms.

The final discrepancy factor was $R = 10.6\%$. The final difference map is shown in Fig. 1.

(ii) $0kl$ Projection. The first structure factor calculation gave $R = 25\%$ and the

projection was refined steadily by means of difference syntheses to $R = 9.0\%$. Resolution was poor in this projection, and individual temperature factors were not applied to the atoms. The final difference map is shown in Fig. 2.

(iii) *h0l Projection.* The x and z co-ordinates obtained from the $hk0$ and the $0kl$ projections were used to calculate $h0l$ structure factors. The projection refined slowly and it was found impossible to reduce the discrepancy factor below 30%. Good agreement between F_o and F_c could be obtained by increasing the x fractional co-ordinates by 0.250 of the unit cell edge. This change in x did not alter the magnitudes of the F_c values for the $hk0$ projection, and the changes in signs of certain F_c values have been taken into account for the final $hk0$ map. Refinement, after change of the x co-ordinates, proceeded smoothly and the final R value was 8.2%. Once again resolution was poor; Fig. 3 shows the final difference map for the $h0l$ projection.

(iv) *Three-dimensional refinement.* The method of diagonal least squares was used for the refinement, and of the 847 observed structure factors 142 were given a weight of zero; the rest were given unit weight. It was later shown that omission of the 142 reflections did not make any appreciable difference to the results. This was done by including them in a cycle of the refinement. One refinement of the atomic co-ordinates was carried out

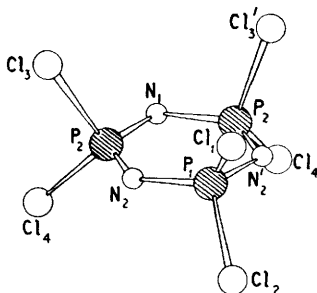


FIG. 4. The $(\text{PNCl}_2)_3$ molecule. The atoms P_1 , Cl_1 , Cl_2 , and N_1 lie on a mirror plane.

with isotropic temperature factors obtained from the two-dimensional analysis. Anisotropic temperature factors were then obtained from axial zone data, and since the programme of the computer could only deal with seven anisotropic temperature factors with fixed orientations, simplifications were made. For the chlorine atoms, one vibration direction was taken to be along the P-Cl bond, a second perpendicular to it and parallel to the plane of the six-membered ring. For the phosphorus and nitrogen atoms forming the ring, two vibration directions were taken to be parallel to the plane of the ring, one of them towards the centre of the ring and the other perpendicular to it. The number of anisotropic temperature factors was reduced from eight to seven by assuming them to be the same for both phosphorus atoms. A three-dimensional refinement of the atomic co-ordinates and temperature factor values was carried out. At this stage the R factor was 14.9% and further refinement of part of the three-dimensional data showed that further improvements were not likely to occur. Only F values used in the refinement were used to calculate R .

Results.—The lettering in the tables corresponds to Fig. 4. Table 1 lists the final co-ordinates and temperature factors which were obtained from the least-squares refinement. The origin was taken at the centre of symmetry. The standard deviations of the atomic co-ordinates which are shown in Table 3 were calculated from the formula:

$$\sigma^2(x) = n^2 \sum |\Delta F|^2 / (m - s) \sum (\partial F / \partial x)^2$$

where n = fractional shift applied to the atoms, m = number of observations, and s = number of parameters. Other terms have their usual meaning. For P and Cl, $n = 1$, for nitrogen $n = \frac{1}{2}$.

Table 2 lists bond lengths and bond angles together with their respective standard

deviations calculated from formulæ given by Ahmed and Cruickshank.⁵ For angles across the mirror plane, the standard deviation of the half angle was calculated. A least-squares plane was calculated for the six-membered ring, and for this the phosphorus atoms were given twice the weight of the nitrogen atoms. The equation of the plane is:

$$-0.421(2)x - 0.006(7)y + 0.906(9)z - 0.420(9) = 0$$

The distances of the atoms from this plane are: P₁, +0.027 Å; N₁, -0.089 Å; P₂, +0.021 Å; N₂, +0.017 Å.

TABLE 1. Atomic co-ordinates in fractions of the cell edge and the temperature factors applied.

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>Bx</i>	<i>By</i>	<i>Bz</i>
P ₂	0.595(8)	0.144(2)	0.563(7)	1.6	1.9	3.5
N ₂	0.495(6)	0.143(3)	0.456(5)	2.5	3.8	6.3
Cl ₃	0.586(9)	0.069(7)	0.842(9)	3.4	6.0	5.6
Cl ₄	0.681(3)	0.054(7)	0.396(5)	2.7	5.3	5.5
N ₁	0.650(9)	0.250	0.604(1)	3.6	3.0	7.3
Cl ₁	0.318(7)	0.250	0.552(9)	2.3	4.8	4.7
Cl ₂	0.403(0)	0.250	0.097(8)	3.1	5.7	5.6
P ₁	0.442(0)	0.250	0.403(1)	1.6	1.9	3.5

TABLE 2. Bond lengths (in Å) and bond angles together with their respective standard deviations.

Bond	Bond length (<i>l</i>)	σ (<i>l</i>)	Angle	θ	σ (θ)
P ₁ -N ₂	1.61	0.017	P ₂ N ₂ P ₁	120.38°	0.75°
P ₂ -N ₂	1.57	0.017	N ₁ P ₂ N ₂	120.93	1.10
N ₁ -P ₂	1.60	0.011	Cl ₁ P ₁ Cl ₂	101.77	0.52
Cl ₁ -P ₂	1.98	0.013	Cl ₃ P ₂ Cl ₄	102.05	0.32
Cl ₂ -P ₁	1.97	0.013	N ₂ P ₁ N ₂ '	118.33	1.30
Cl ₃ -P ₂	1.98	0.008	P ₂ N ₁ P ₂ '	118.48	1.25
Cl ₄ -P ₂	1.97	0.008			

TABLE 3. Standard deviations (in Å) of the atomic co-ordinates.

Atom	(<i>x</i>)	(<i>y</i>)	(<i>z</i>)	Atom	(<i>x</i>)	(<i>y</i>)	(<i>z</i>)
P ₂	0.0045	0.0048	0.0050	N ₁	0.0190	—	0.0229
N ₂	0.0163	0.0157	0.0187	Cl ₁	0.0081	—	0.0092
Cl ₃	0.0065	0.0062	0.0060	Cl ₂	0.0089	—	0.0084
Cl ₄	0.0059	0.0060	0.0064	P ₁	0.0092	—	0.0105

Description.—A clinographic projection of the structure is shown in Fig. 5 and from this it can be seen that the crystal is composed of discrete molecules held together by van der Waals forces. The van der Waals contacts are between chlorine atoms or between chlorine atoms and nitrogen atoms. Between the chlorine and nitrogen atoms situated on mirror planes, a normal van der Waals separation of 3.2 Å is attained by displacement of the nitrogen atom out of the mean plane of the ring and away from the chlorine atom. The non-planarity of the ring is thought to be due to crystal forces, and in the gaseous phase the ring would probably be planar. The molecular geometry has been calculated and the results are given in Table 2. The bonds within the ring are to be considered as being of all the same length; the difference between the shortest and the longest is 0.04 Å, but the standard deviations of the nitrogen atoms are large and hence no significance can be attached to the difference between bond lengths. The angles within the ring are all equal. The P-Cl bonds are not significantly different in length from one another. The Cl-P-Cl planes are perpendicular to the plane of the ring, and the Cl-P-Cl angles of 101.77° and 102.05° are significantly less than 109.47°.

⁵ Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 385.

Discussion.—The most notable features of the structure are the equality and shortness of the P–N bonds, the close approximation to planarity of the ring, and the equality of the angles within it. The equality of the P–N bonds excludes the possibility of alternate single and double bonds. The length is very much shorter than the 1.8 Å expected for a single bond between phosphorus and nitrogen on using Pauling's values⁶ of covalent radii and the 1.78 Å found in the crystal structure of monosodium phosphoramidate.⁷ This implies that the bond order is greater than unity. The average angle at the

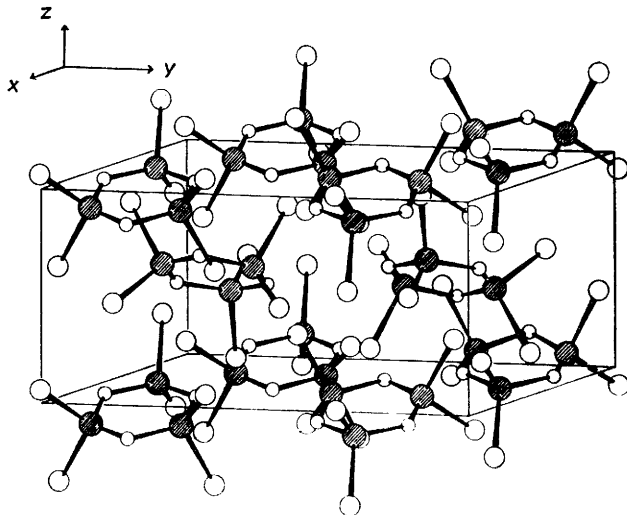


FIG. 5. A clinographic drawing of a unit cell and contents. ●, P atoms, ○, Cl atoms, o, N atoms.

nitrogen atoms is 119.4°; since the deviation from 120° is so small, the bond cannot be strengthened appreciably by charge transfer in the sense P⁺N⁻.

All these features suggest aromatic character. The ring differs, however, from that in benzene in that the formation of π -bonds requires the use of a *d*-orbital at the phosphorus atom. Such orbitals have different symmetries from the *p*-orbitals responsible for the π -bonds in benzene; the consequences of this difference have been explored by Craig and Paddock.^{8,9}

EXPERIMENTAL

Small crystals, whose dimensions in any direction did not exceed 0.10 mm., were obtained by recrystallising the compound from light petroleum (b. p. 60–80°). The compound has an appreciable vapour pressure at room temperature and it was necessary to seal the crystals inside thin-walled quartz tubes. Weissenberg photographs were taken by the multiple film technique. Intensities were estimated visually, a calibrated strip being used. No absorption corrections were made. In structure-factor calculations, James and Brindley's scattering factor curves¹⁰ for phosphorus and chlorine, and McWeeny's scattering factor curve¹¹ for nitrogen were used.

The three-dimensional diagonal least-squares refinement was carried out at the Ferranti Computer Service Centre by Dr. H. J. Milledge (née Grenville-Wells) to whom we are grateful for useful advice concerning the refinement.

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⁶ Pauling, "Nature of the Chemical Bond," 2nd edtn., Cornell University Press, New York, 1948, p. 164.

⁷ Hobbs, Corbridge, and Raistrick, *Acta Cryst.*, 1953, **6**, 621.

⁸ Craig and Paddock, *Nature*, 1958, **181**, 1052.

⁹ Craig, *J.*, 1959, 997.

¹⁰ James and Brindley, *Phil. Mag.*, 1931, **12**, 81.

¹¹ McWeeny, *Acta Cryst.*, 1951, **4**, 513.