

Chemistry. — *The Structure of Tetra- and Tri-Phosphonitrile-Chloride.*
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§ 1. *Tetra-Phosphonitrile-Chloride*¹⁾: $(PNCl_2)_4$ crystallizes from benzene in beautiful colourless crystals which, in most cases, are tabular parallel to opposite faces of $\{110\}$. They are very lustrous, yielding sharp reflections.

Tetragonal-bipyramidal; apparently holohedral.

$$a : c = 1 : 1.5492 \text{ to } 1.5508.$$

Forms observed: $m = \{110\}$, predominant, yielding splendid reflections; $a = \{100\}$, narrower than m , but also very well reflecting; $r = \{101\}$, rather well developed and lustrous. The habitus of the crystals is prismatic along the c -axis. (Fig. 1).

Angular Values: Observed: Calculated:

$m : r = (110) : (101) =^* 70^\circ 6'$	—
$r : r = (101) : (011) = 39 48$	$39^\circ 48'$
$a : r = (100) : (101) = 61 9$	$61 13\frac{1}{2}$
$r : r = (101) : (101) = 57 42$	$57 33$
$m : m = (110) : (1\bar{1}0) = 90 1$	$90 0$
$m : a = (110) : (100) = 44 59$	$45 0$

No distinct cleavability was observed.

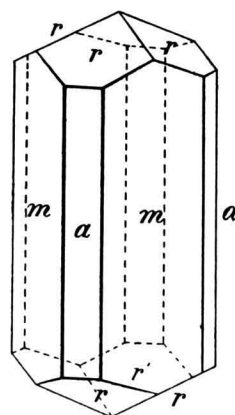


Fig. 1. *Tetraphosphonitrile-chloride.*

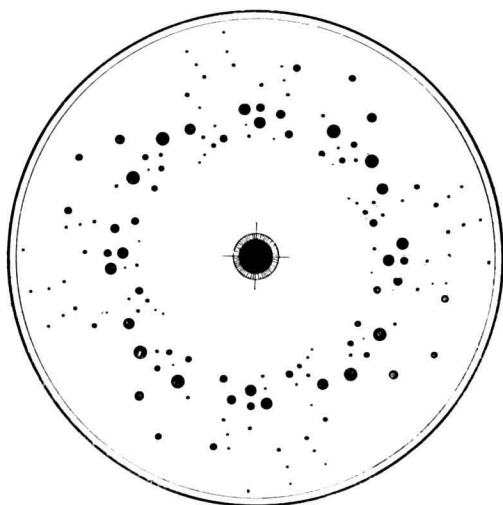


Fig. 2. LAUE-Pattern on (001) of *Tetraphosphonitrile-Chloride.* (Stereographical Projection.)

Although the aspect of the crystals is quite holohedral, the hemihedral symmetry is clearly proved by a LAUE-pattern (tungsten: 40 K.V.) on (001) : no vertical symmetry-planes are present, the image only showing a tetrad axis. As all faces of r are equally well developed, the presence of a horizontal plane of symmetry, however, is most probable; the tetragonal-bipyramidal symmetry C_{4H} , attributed to this compound, proves to be in perfect agreement with the other results of the spectrographical analysis.

¹⁾ R. SCHENCK and G. RÖMER, Ber. d.d. chem. Ges., **57**, (1924), 1351. W. GRIMME, Inaug. Dissert. Münster, (1926).

§ 2. Some rotation-spectrograms round [001] and [110] as axes of rotation were prepared. copper- x -radiation being used as luminous source.

1. *Rotation-spectrograms round [001]*. The crystal was oscillated through different angles (about 30°), the incident X -ray-pencil including different angles with the direction of the a -axis. The well developed spectrogram showed a principal spectrum and two or three accessory spectra. The most intensive spots were:

In the principal spectrum: (620) (10); (220) (9); (510) (7); (310) (7); (040) (8); (750) (6); (530) (5); (420) (4); (110) (4); (640) (4).

In the first acc. spectrum: (101) (10); (310) (7); (311) and (411) (7); (511) (7); (201) (6); (211) (6); (441) (6); (541) (6); (611) (6); (651) (6); (211) and (411) (5); (321) (5); (221), (331), (431) and (811) (4).

In the second acc. spectrum: (102) (10); (212) (6); (522) (5); (222) (5); (212), (302), (312), (322), (412), (432) and (512) (4).

In the third acc. spectrum: (313) (7); (443) (6); (223) (5).

2. *Rotationspectrograms round [110]*.

A principal spectrum and six or seven accessory spectra ordinarily were observed. The following indices-triplets corresponded to the most intensive spots ¹⁾.

In the principal spectrum: (111), (221), (333) and (443) (3); (002) (2); (114), (221), (223), (441), (550) and (770) (2).

In the first acc. spectrum: (101) (6); (102) (4); (212) (4); (321) (4); (541) (4); (542) and (762) (3); (761), (651) (4); (103), (651) (3).

In the second acc. spectrum: (311) (5); (201) (3); (313), (752), (642) (3); (312) (2); (112) and (111) (2); (750) (5); (640) (4).

In the third acc. spectrum: (301) (6); (212), (522), (411) (4); (741) (3); (632), (851) (4); (302), (213) and (304) (3).

In the fourth acc. spectrum: (221) (6); (311) (6); (223) (313) (4); (401) (402) and (621) (3); (620) (6); (310) (7); (511), (730) and (840) (3).

In the fifth acc. spectrum: (321) (8); (411) (6); (611) (6); (832) (4); (613), (322), (323) and (324) (3); (942), (721), (4); (412) (3).

In the sixth acc. spectrum: (510) (7); (420) (8); (331) (5); (511) (4); (333), (512) and (930) (3).

In the seventh acc. spectrum: (611) (10); (522) (4); (811), (812), (921), (434), (523) (3); (432) (3); (701), (702) and (703) (2); (524) (2).

¹⁾ The indices-triplets are indicated without the special algebraic signs of the spots observed, because only the total triplet $\{hkl\}$ is of interest.

From these spectrograms, the identity-distances were determined to be:

$$I_{[001]} = 5.9 \text{ \AA.}; \quad I_{[110]} = 15.4 \text{ \AA.}$$

The sum of the indices ($h+k$), as found with respect to these axes, proved to be always even. The real dimensions of the elementary cell, therefore, are: $a_0 = 10.9 \text{ \AA.}$; $c_0 = 5.9 \text{ \AA.}$

These values were corrected by means of a BRAGG-spectrogram on (110), — *calcite* being used as a standard-material. From the distances of the lines observed, $d_{(110)}$ proved to be: 15.26 \AA. ; so that the true values of a_0 and c_0 become:

$$a_0 = 10.79 \text{ \AA.}; \quad c_0 = 5.93 \text{ \AA.}$$

As the density of the crystals is: 2.18, the weight of the mass present within the elementary cell is: $1506 \cdot 10^{-24}$ grammes; as $(PNCl_2)_4$ weighs $765 \cdot 10^{-24}$ grammes, the mass indicated corresponds to: $P_8N_8Cl_{16}$.

The indices-triplets of the spots observed in the rotation-spectrograms were determined according to BERNAL's graphical method. It was proved that all triplets ($kk0$), for which ($h+k$) was odd, as well as all triplets ($00l$) for which l was odd, were absent. The space-group corresponding to the extinctions just mentioned is C_{4H}^4 . As the positions in the elementary cell of the other symmetry-classes to be taken into account here are, at the highest, *fourfold* positions, while $8P$ - $8N$ - and $16Cl$ -atoms must be placed within the cell, the phosphorus- and nitrogen-atoms were to be distributed over *two* non-equivalent, the chlorine-atoms even over *four* non-equivalent positions. This is most improbable and, therefore, it is safe to exclude all symmetry-classes without the horizontal plane of symmetry.

The space-group C_{4H}^4 is characterized by the presence of tetragonal screw-axes in $[001]_{00}$ and $[001]_{1/2, 1/2}$, dyad axes of rotation in $[001]_{1/2, 0}$ and $[001]_{0, 1/2}$, glidingplanes in $(001)_0$ and $(001)_{1/2}$ and 8 inversion-centra: $[1/4, 1/4, 0]$, $[1/4, 3/4, 1/2]$; etc.

§ 3. From the properties of the compound $(PNCl_2)_4$, more especially from its high stability on evaporation and in many reactions in which no depolymerisation appears to occur, it may safely be concluded that the molecules $P_4N_4Cl_8$ as such are really present within the structure of the crystalline compound. Now only two *twofold* positions are present here, — they having the parameters:

$$[0, 1/2, 1/4], [1/2, 0, 3/4] \quad \text{and} \quad [0, 1/2, 3/4], [1/2, 0, 1/4].$$

It is in one of these places, which properly are equivalent, that the centres of gravity of both molecules $P_4N_4Cl_8$ must be situated, the symmetry of each molecule, therefore, being S_4 . The *phosphorus*-atoms

then occupy, as well as the *N*-atoms, an eightfold position, while the *Cl*-atoms are distributed over two eightfold positions. As all atoms in the structure have three degrees of freedom, 12 parameters must be determined, so as to completely fix their positions. Tentatives will be made for the eventual calculation of these parameters.

§ 4. *Tri-Phosphonitrile-Chloride*: $(PNCl_2)_3$ crystallizes from ligroine in big, very lustrous, colourless crystals, which are perfectly developed. Their symmetry is rhombic-bipyramidal; the axial ratio is: $a:b:c = 0.9238 : 1 : 0.4397$.

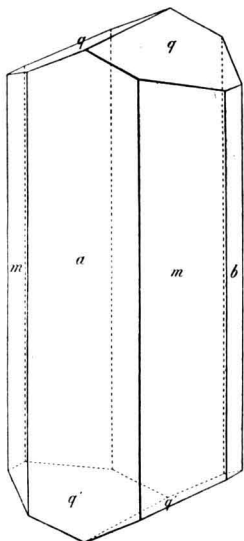


Fig. 3. *Tri-Phosphonitrile-Chloride*.

Forms observed: $a = \{100\}$, predominant, yielding very sharp reflections; $m = \{120\}$ ¹⁾, often equally well developed as a , but sometimes narrower, very well reflecting, just as $q = \{011\}$; $b = \{010\}$, narrower than m , more feebly reflecting, but very well measurable. The habitus of the crystals is prismatic, with elongation in the direction of the c -axis; commonly they are thick tabular plates parallel to a . (Fig. 3).

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : m = (100) : (120) =^* 61^\circ 34\frac{1}{2}'$		—
$q : q = (011) : (011) =^* 47 28^{\frac{1}{2}}$		—
$b : m = (010) : (120) = 28 25\frac{1}{2}$	$28^\circ 25\frac{1}{2}'$	$28^\circ 25\frac{1}{2}'$
$b : q = (010) : (011) = 66 16$	$66 16$	$66 16$
$m : q = (120) : (011) = 69 21$	$69 21$	$69 16$
$a : q = (100) : (011) = 90 0$	$90 0$	$90 0$

No distinct cleavability was observed; perhaps an imperfect cleavability parallel to (011) may be present.

On $\{100\}$ and $\{010\}$ the extinction is parallel and perpendicular to the c -axis. The crystals are optically-biaxial, the plane of the axes being $\{100\}$, with the c -axis as the first bisectrix. The optical axes seem to emerge almost perpendicular to the faces of $\{011\}$. The dispersion is weak, of rhombic character, with: $\rho < \nu$. The double refraction is strong and positive.

§ 5. A series of rotation-spectrograms round $[100]$, $[010]$ and $[001]$ were prepared, *copper- α* -radiation being used. The angle φ of oscillation was in all cases 30° .

1. *Rotation-spectrogram round $[100]$.*

A principal spectrum and six accessory spectra were observed. The most intensive images observed were the following:

In the principal spectrum: (040) and (080) (6); (083) , (051) , (041) , (020) , (081) and (092) (4); (060) , (061) , (074) and (093) (3).

¹⁾ The true indices $\{120\}$, in stead of $\{110\}$, follow from the spectrographical measurements.

In the first acc. spectrum: (160) (5); (171) (4); (120), (131) and (180) (3).

In the second acc. spectrum: (220) (5); (260), (242), (272), (253), (2.11.2) (2).

In the third acc. spectrum: (320) (10); (361) (7); (361) (6); (363) (5); (331), (340) and (360) (4); (341) (3).

In the fourth acc. spectrum: (451) (5); (431) (4); (441), (452), (462), (443), (472), (441) and (492) (2).

In the fifth acc. spectrum: (531) (8); (542), (552), (543), (553), (563), (551), (571) and (581) (3).

In the sixth acc. spectrum: (651) (7); (621) and (641) (6); (631) (5); (632) and (643) (3).

The third and sixth spectra are somewhat stronger than the others.

$$I_{[100]} = 12.8 \text{ \AA}.$$

2. Rotation-spectrogram round [010].

A principal spectrum and six accessory spectra were observed. The most intensive spots were:

In the principal spectrum: (802) (8); (301) (4).

In the first acc. spectrum: (10.1.1) (5); (211), (313) and (811) (4); (611), (711) and (911) (3).

In the second acc. spectrum: (321) (5); (221), (621) and (721) (3).

In the third acc. spectrum: (931) (5); (531) (4); (331) and (431) (3).

In the fourth acc. spectrum: (10.4.1) (6); (641) (4); (10.4.0) (3).

In the fifth acc. spectrum: (651) (5); (451) (3).

In the sixth acc. spectrum: (360) (4); (361), (760), (761) and (960) (3).

From this spectrogram follows: $I_{[010]} = 14.0 \text{ \AA}$.

3. Rotation-spectrogram round [001].

A principal spectrum and three accessory spectra were observed. The most intensive spots were:

In the principal spectrum: (040) (8); (080) (5); (360), (440) and (020) (4); (460), (060) and (160) (3).

In the first acc. spectrum: (041) and (361) (8); (021) and (051) (6); (101) and (031) (5); (451) (4); (131), (011) and (071) (3).

In the second acc. spectrum: (332) (6); (662) (4); (552), (542), (232), (122), (132) and (152) (3).

In the third acc. spectrum: (363) (5); (323) and (253) (3).

From the distances between the principal and the successive accessory spectra follows: $I_{[001]} = 6.3 \text{ \AA}$. These values of $I_{[100]}$, $I_{[010]}$ and $I_{[001]}$ were now corrected by means of BRAGG-spectrograms, calcite being used as standard-material. On (100) a 4th and a 6th order, on (010) only a 4th order spectrum were observed, from which the spacings: $d_{(100)} = 12.94 \text{ \AA}$. and $d_{(010)} = 14.00 \text{ \AA}$. were calculated; so that: $I_{[100]} = 12.94 \text{ \AA}$.; $I_{[010]} = 14.00 \text{ \AA}$. and $I_{[001]} = 6.16 \text{ \AA}$. These values lead to the axial ratio: $a : b : c = 0.9243 : 1 : 0.4397$, which is, for $a : b$, in perfect agreement

with the ratio found by the goniometrical measurements. As the volume of the rhombic cell is: 1116.10^{-24} cm³ and its weight, according to STOKES' value: 1.98 for the density, is, therefore, 2210.10^{-24} grammes, the elementary cell contains a mass, corresponding to: $P_{12} N_{12} Cl_{24}$.

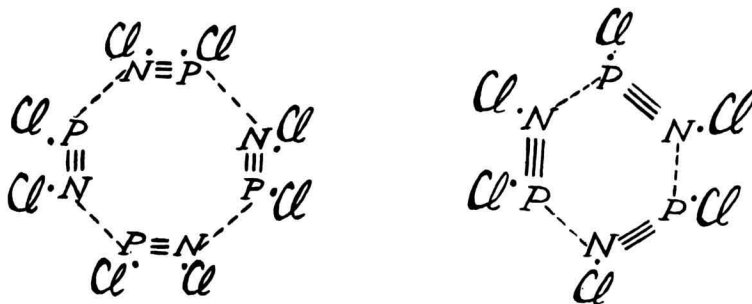
The fundamental cell is the *simple rhombic* one. Moreover, as extinction occurs for all triplets $\{hk0\}$, in which k is odd and for all triplets $\{h0l\}$ in which $(h+l)$ is odd, the space-group of the structure considered can easily be determined. If an interchange of the crystallographical axes be made in such a way ¹⁾, that: $a_0 = 14.00 \text{ \AA.}$; $b_0 = 6.16 \text{ \AA.}$ and $c_0 = 12.94 \text{ \AA.}$, the old index h now becomes l' , the old index k now becomes h' and the old index l now becomes k' . Therefore, intensities equal to zero, occur for all triplets $\{h'0l'\}$, if h' is odd and for all triplets $\{Ok'l'\}$, if $(k'+l')$ is odd; as no other extinctions occur ²⁾, the space-group must be V_H^{16} .

§ 6. Also in the present case it is feasible to suppose, that the complex molecule: $(PNCl_2)_3$ is preserved in the crystal-structure; then its centre of gravity must occupy a *fourfold* position in the cell.

In the group V_H^{16} there are two fourfold positions without a degree of freedom; the molecule occupying them, in that case has the proper symmetry: C_i ; moreover, there is one fourfold position available with two degrees of freedom, the corresponding symmetry of the occupying molecule now being C_s . A molecule $(PNCl_2)_3$, however, cannot be centrally symmetrical; so that only the other alternative remains. The co-ordinates of the centres of gravity of the four molecules then are ³⁾:

$$[0, u, v]; [1/2, 1/2 - u, \bar{v}]; [0, 1/2 + u, 1/2 - v]; [1/2, \bar{u}, 1/2 + v].$$

§ 7. As to the structure of the molecules $(PNCl_2)_4$ and $(PNCl_2)_3$ we can finally make the following remarks. SCHENCK and RÖMER have, for both compounds, proposed a *cyclic* structure of the kind:

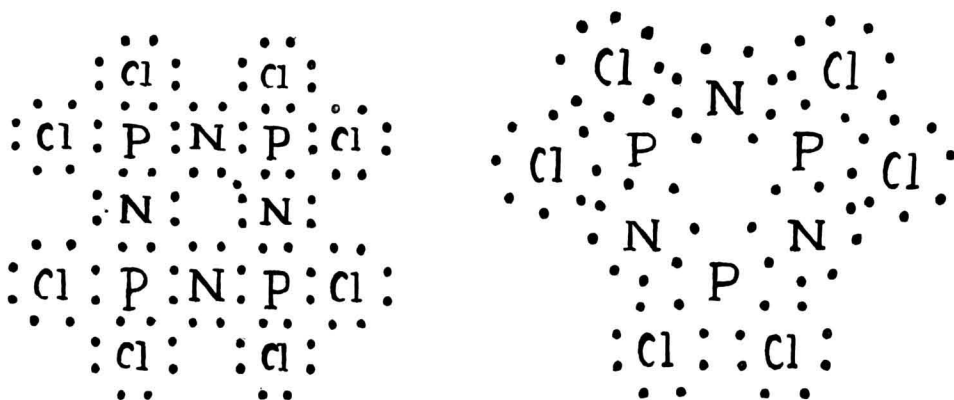


¹⁾ This corresponds to a rotation of the crystals through 90° round the c -axis, followed by the same rotation round the previous b -axis. The symbols of the faces thus become: $a = \{001\}$, $b = \{100\}$, $q = \{110\}$ and $m = \{201\}$, with: $a' : b' : c' = 2.2727 : 1 : 2.1006$.

²⁾ H. MARK, *Die Verwendung der Röntgenstrahlen*, etc., (1926), p. 389.

³⁾ R. W. G. WYCKOFF, *The Analytical Expression*, etc., Washington, (1922), p. 64.

In so far as the different indication of the bonds between the *P*- and *N*-atoms is really supposed simultaneously to express a difference in the way of linkage between these atoms, we here can state that, at least with respect to the second formula, the experience gained in this investigation cannot be reconciled with that formula. For the proper symmetry C_s of the molecule involves the presence of a symmetry-plane, and the latter makes it necessary that at least one of the phosphorus-atoms be linked to the two adjacent nitrogen-atoms in a quite *identical* way. Only if *all* these atoms were situated *in* this plane of symmetry, its presence would not interfere with the linkages mentioned; but this is impossible in connection with the dimensions of the elementary cell. Perhaps an electronic linkage of the following kind:



could be considered as in better agreement with the facts observed and our modern views. As soon as the right parameters of the atoms in this arrangement shall be calculated, we hope to return to this interesting problem about the constitution of these remarkable compounds.

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