[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN AND THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Structure of the Trimer of Phosphonitrile Chloride, $P_3N_3Cl_6$

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This electron diffraction study was undertaken in order to elucidate the structure of the trimer of phosphonitrile chloride, $P_3N_3Cl_6$. A reaction between phosphorus pentachloride and ammonia producing the phosphonitrile chloride series of compounds was discovered over one hundred years ago.[2] Since that time several other methods of preparation have been reported, and numerous investigations have been made of the physical and chemical properties of the resulting products.[3] The favored method of preparation involves the use of ammonium chloride as the ammonolytic reagent, and results in a series of polymers having the formula $(PNCl_2)_x$, where x may be 3, 4, 5, etc., reaching a hundred or more. The lower molecular weight compounds are believed to be cyclic while the higher ones, which may be rubber-like in character, have been shown to be long chains.[4] The trimer is the most abundant product of the reaction, forming nearly 50% of the mixture, although the amount depends on the precise method of preparation. The determination of the atomic arrangement and bond distances existing in this molecule was executed, and values are reported for the interatomic distances and bond angles. Our results are compared with those found by X-ray and crystallographic analysis of the trimer and tetramer.[5] The structures proposed by the various investigators are discussed.

Experimental

The phosphonitrile chloride was prepared using essentially the method of Schenck and Römer,[6] which seemed to be the most convenient laboratory method. However, some slight changes were introduced into their procedure. The reaction proceeds according to the equation $PCl_5 + NH_4Cl \rightarrow PNCl_2 + 4HCl$ and is carried out in the presence of *sym*-tetrachloroethane.

Four hundred and fifty grams of phosphorus pentachloride was added to a reaction flask containing 500 ml. of *sym*-tetrachloroethane (b. p. 144–145°) and 130 g. (16% excess) of finely ground, dry ammonium chloride. The phosphorus pentachloride was not all dissolved at the beginning of the reaction, but this offered no difficulty, as the reaction product is extremely soluble. No provision was made for stirring the reactants since the evolution of hydrogen chloride was found to give sufficient agitation. The mixture was heated under reflux for eighteen hours with the condenser connected to an "Anhydrone" drying tube and thence to a hydrogen chloride absorbing system. At the end of this time the solution was allowed to cool, and the excess ammonium chloride filtered off. The clear yellowish solution was then vacuum distilled at 20 mm. in order to remove the solvent. Both this distillation and the previous heating were carried out in an all-glass system. After allowing the distillation residue to cool overnight, a yellowish-brown slush was obtained, which consisted of crystalline phosphonitrile chloride trimer and tetramer and more highly-polymerized material in the form of an oil. The crystals were separated by filtering the mixture through a light wad of glass-wool. Approximately 115 g. of the crude crystals and 107 g. of oil were obtained in this manner. *sym*-Dichloroethane was found to possess a satisfactory temperature coefficient of solubility, and the crude crystals were recrystallized three times from this solvent. A 35% yield of pure white material was obtained.[7]

Pure trimer was separated from the mixed crystals by vacuum distillation of 50 g. of the product at 11 mm. pressure. An all-glass system made for the vacuum distillation of solids was used, and 25 g. of material boiling at 116–118° (11 mm.) was collected. Upon redistillation 18 g. of the trimer was secured with the b. p. 116–117°. The molecular weight was determined by measuring the depression of the freezing point in benzene and found to be 343 ($M_{\text{calcd.}}$ = 347). The melting point of this sample was 113.8°. This has been reported as 114°[8] and 114.9°.[7] This product was employed in the electron diffraction measurements.

The electron diffraction photographs were prepared using a camera distance of 100 mm. and an electron wave length of 0.0592 Å. with the sample heated to temperatures ranging from 120° to 135°. Diffraction rings were observed out to s values of nearly thirty. Measurements were made by three observers and the averaged s_0 values ($= 4\pi (\sin \theta/2)/\lambda$) are given in Table I. The appearance of the photographs is fairly represented by the curve G in Fig. 1.

The radial distribution function, $D(r) \doteq \Sigma c_k (\sin s_k r)/s_k r$, was calculated with twenty-three

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(1) Present address: The Kendall Company, Boston, Mass.

(2) Liebig and Wöhler, *Ann.*, **11**, 139 (1834).

(3) Audrieth, Steinman and Toy, *Chem. Rev.*, **32**, 109 (1943): an excellent review of the earlier work on these compounds.

(4) Meyer, Lotmar and Pankow, *Helv. Chim. Acta*, **19**, 930 (1936).

(5) (a) Jaeger and Bentema, *Proc. Acad. Sci. Amsterdam*, **35**, 756 (1932); (b) Renaud, *Ann. chim.*, (11) **3**, 445 (1935); (c) Ketelaar and deVries, *Rec. trav. chim.*, **58**, 1081 (1939).

(6) Schenck and Römer, *Ber.*, **57**, 1343 (1924).

(7) Steinman, Schirmer and Audrieth, THIS JOURNAL, **64**, 2378 (1942), report a yield of this order for a preparation which involves no solvent.

(8) Stokes, *Am. Chem. J.*, **19**, 782 (1897).

terms using the coefficients c_k based on estimated intensities and an exponential damping factor. The resulting curve has its best resolved strong peaks at 4.18, 4.80 and 1.96 Å. (Fig. 1). The other peaks are probably subject to considerable errors introduced by the use of a series in place of the integral in the distribution function.

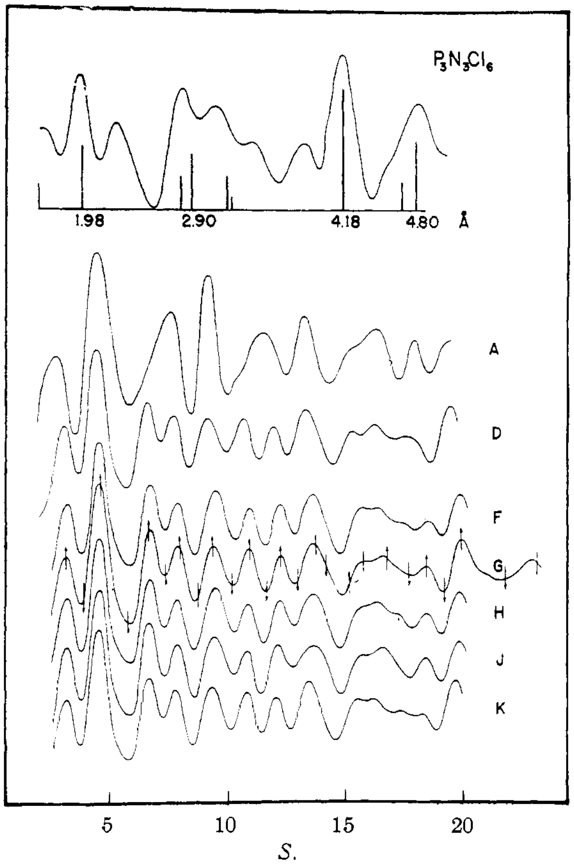


Fig. 1.

The most probable interpretation of the radial distribution results is afforded by a model in which the phosphorus and nitrogen atoms are placed in alternate positions in a six-membered plane ring with two chlorine atoms attached to each phosphorus atom. For eight models of this type (D to K, inclusive, Table II) intensity curves were calculated using the standard expression with the atomic scattering factors made proportional to the atomic numbers. The largest coefficient in the intensity function, then, belongs to a non-bonded P–Cl term at 4.2–4.3 Å. if the P–Cl bond is set at 2.0 Å. and the P–N bond at 1.66 Å. The next largest term is Cl–Cl near 4.8–4.9 Å. The three more reliable peaks in the distribution curve are easily identified for this kind of model.

Table I

Observed and Calculated Maxima and Minima

Max.	Min.	C_k	S_0	S_G/S_0	S_k/S_0
1			3.24		
2		48	4.72	0.981	0.960
	3	−36	5.81	1.019	.998
3		73	6.68	1.006	1.000
	4	−54	7.39	0.999	0.985
4		25	7.99	.994	.976
	5	−58	8.76	.990	.973
5		80	9.39	1.003	.994
	6	−55	10.21	1.003	.991
6		40	10.94	1.001	.991
	7	−32	11.67	0.996	.983
7		23	12.26	.999	.982
	8	−69	12.99	.991	.975
8		105	13.73	.996	.981
9			15.17		
10		108	16.79	.992	
	11	−63	17.71	1.011	
11		64	18.44	1.002	
	12	32	19.21	0.996	.980
12		64	19.92	1.001	.988
	13	−62	21.78	0.995	
13		48	23.13	.991	
	14	−28	24.52		
14		26	26.03		
15		10	29.46		
		Average		0.998	0.984
		Average dev.		.006	.008
	P_1–Cl_{21},[a] Å.			4.172	4.172
	Cl_{11}–Cl_{21}, Å.			4.820	4.782
	P_1–Cl_{11}, Å.			1.956	1.968

[a] These three distances are associated with the **strongest** scattering terms.

The other two types of models considered were a plane ring having one chlorine attached to each ring atom and an open chain of alternating phosphorus and nitrogen atoms with the chlorine atoms attached in various ways. Neither of these types shows reasonable agreement with the radial distribution curve. In a ring model with distributed chlorines the biggest term in the scattering function corresponds to a Cl–Cl separation of 3.50 Å.; this term cannot be shifted to give agreement with any strong radial distribution peak without using impossible values for the bond lengths. Scattering curves were nevertheless calculated for three models of this type (A, B, C, Table II). The P–Cl bonds were set either at 2,00 Å. (the value observed in PCl_3, $POCl_3$, etc.) or at 2.09 Å., the sum of the single bond radii. The N–Cl bonds were made equal to 1.69 Å., the single bond value, while the P–N distance was 1.66 Å. All three curves showed faults similar to those of Model A in Fig. 1: thus, curve A shows only one maximum between 5.5 and 8.5 and only one between 10.0 and 13.0, although two are observed on each of these regions. Curves for the model of this type using other combinations of bond distances were not calculated because no combination was found to give even fair agreement with the strong radial distribution peaks. Similar difficulties arise in considering chain models and no scattering curves were calculated for chain models. We believe that both the ring models with distributed chlorine atoms and the chain model are highly improbable.

TABLE II

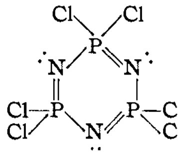
RING MODELS OF $P_3N_3Cl_6$

Model	P–Cl, Å.	P–N, Å.	N–Cl, Å.	PNP, °	P_1–Cl_{21}, Å.	Cl_{11}–Cl_{21} Å.
A[a]	2.00	1.66	1.69	125		
B[a]	2.00	1.66	1.69	125		
C[a]	2.09	1.66	1.69	125		
			ClPCl, °			
D	2.00	1.66	110	125		
E	1.95	1.66	110	125		
F	2.00	1.62	109$^3/_4$	120	4.18	4.80
G	1.96	1.63	108	120	4.18	4.83
H	2.00	1.61	107$^3/_4$	120	4.18	4.83
I	1.92	1.64	105	120	4.18	4.86
J	2.00	1.60	106	120	4.18	4.86
K	2.00	1.66	110	120	4.24	4.86

[a] In the first three models, one chlorine is attached to each of the nitrogen atoms and phosphorus atoms. The three chlorine atoms on phosphorus are displaced from the plane of the other atoms through an angle of 55°; in A and C all three chlorines lie on the same side while in B one chlorine is on the other side from the first two.

The eight scattering curves based on ring models with two chlorines on each phosphorus atom all show the correct number of maxima. In two of them (D and E) the ring angles, NPN and PNP, were 115 and 125°, respectively, but the rings were all regular (120° angles) in the remaining models of this type. The P–Cl distances were varied from 1.92 to 2.00 Å., the P–N distances between 1.60 and 1.66 Å. and the < ClPCl (which was normal to the ring) between 105 and 110°. The variations were combined in such a way to keep the two heaviest terms near 4.18 and 4.83 Å., as fixed by the radial distribution function. Curve G gives the best general agreement while F and K are almost as good. The photographs are not very clear in the region between 15 and 20 and the poor agreement with the peak observed at 15.17 is probably due to uncertain measurements. The other curves are inferior in producing the qualitative intensities of the sixth, seventh, and eighth maxima. In D the fifth maximum drops below the fourth and in E the sixth as well as the fifth is observed to be stronger than both its neighbors. The ratios of calculated and observed *s* values are shown in Table I for models G and K with the resulting values for the three strongest terms below 5.0 Å. indicated at the foot of the table. The final value for the most important terms and the bond distances are P_1–Cl_{21} (non-bonded) = 4.17 ± 0.04 Å., Cl_{11}–Cl_{21} = 4.82 ± 0.04 Å., Cl_{11}–Cl_{22} = 5.76 ± 0.05 Å., P–Cl (bond) = 1.97 ± 0.03 Å. and P–N (bond) = 1.65 ± 0.04 Å. The bond angles on the ring are 120 ± 3° and the <ClPCl is between 107 and 110°. All of the distances in the molecule below 5.0 Å. are shown by the vertical lines in the radial distribution curve in Fig. 1.

While the coplanarity of the ring might be questioned since no tests of staggered rings were made, the large number of molecular parameters make it impractical to test all the possibilities. The satisfactory agreement afforded by the coplanar model both with the radial distribution curve and between the calculated intensity curves and the photographs makes large deviations from such a model improbable. The coplanarity of the P–N bonds and the attachment of only two atoms to each nitrogen suggests that the molecule resonates between Kekulé-type structures like the following



I

The observed P–N distance, 1.65 Å., has just the value calculated for the Kekulé resonance using 1.80 and 1.61 Å. for the single and double bond distances of P–N.[9] The P–Cl distance, 1.97 Å., may be compared with the following values reported in other compounds: PCl_3, 2.00 Å.; $PFCl_2$, 2.02 Å.; $POCl_3$, 2.02 Å.; $POFCl_2$, 1.99 Å.; POF_2Cl, 2.01 Å.; PCl_5, 2.04 Å.; 2.11 Å.; PF_3Cl_2, 2.05 Å.[10] The variations among these values are not very significant (with the exception of the result for PCl_5) since the experimental uncertainties are 0.02–0.04 Å. The single bond radius sum

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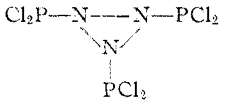
(9) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 154.

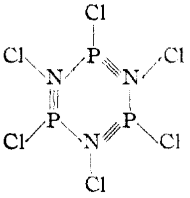
(10) L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938); L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935); reference 9, footnote on page 103.

is 2.09 Å. The previous suggestion that back coördination of an electron pair from chlorine usually occurs in P–Cl bonds with a decrease in the length below the single bond value applies also to the $P_3N_3Cl_6$ molecule.

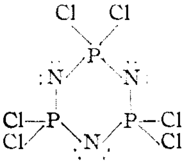
From his interpretation of purely chemical evidence, Wichelhaus[11] proposed II as the structure of the trimer, and this bonding has been offered as a possibility in the case of the hexaphenyl derivative.[12]



II



III



IV

Such a three-membered nitrogen ring is not known elsewhere in compounds which might be expected to allow its formation, as methyl azide, which has been shown to have a straight chain arrangement, for example. Structure II would not be expected to give a radial distribution of the type which we have found for this compound. The ring III possessing distributed chlorine atoms was suggested by Schenck and Römer,[6] but as we have demonstrated a model of this type does not give any reasonable agreement with the radial distribution curve. The use of pentavalent nitrogen in this formulation is not consistent with the generally accepted limitation of first row elements to four electron pairs in the valence shells. Single bond linkages between the P–N atoms of the ring (IV) have been postulated,[5a] but the resulting charge distribution is not very favorable. It is likely that IV is one of the less stable structures in a resonance hybrid consisting chiefly of the Kekulé analogs I.

The benzene-like ring was proposed first by Stokes[8,13] on the basis of an extensive investigation of the chemical properties, and other more recent workers[4,5c] employing X-ray techniques have concluded that resonance between single and double bonds acts to stabilize the larger phosphonitrile chloride polymers. Ketelaar and deVries[5c] studying the tetramer by X-ray analysis of the crystal structure report the P–N distance as 1.67 Å. and P–Cl (bonded) = 1.99 Å., almost the same in each case as we have found in the trimer. They favored a puckered ring for the tetramer having the angles PNP′ = 123° and NPN′ = 117° and report the angle Cl_1PCl_2 as 105°30′. The latter value is somewhat less than we have determined in the trimer, while the ring angles are within the range reported herein.

The coplanar ring structure having resonance of the Kekulé type and a non-distribution of the chlorine atoms adequately explains the stability and chemical properties of the phosphonitrile chloride trimer. For example, heating a sample of this highly purified $P_3N_3Cl_6$ for seventy-five hours at 210° failed to give any indication of ring rupture and subsequent polymerization into the higher molecular weight, rubber-like bodies. The products of the reaction between the trimer and water or ammonia are formed slowly and then with conservation of the ring structure. The favored resultants are those in which two or six chlorine atoms have been replaced by a like number of OH or NH_2 groups.

Summary

The structure of $(PNCl_2)_3$ has been shown by electron diffraction of the vapor to agree with a benzene-like ring of alternating P and N atoms with a separation of 1.65 ± 0.03 Å. The chlorine atoms are attached in pairs to the phosphorus atoms with P–Cl = 1.97 ± 0.03 Å. and $< ClPCl = 107–110°$.

Other proposed structures involving chlorine on nitrogen atoms, a three-membered nitrogen ring or an open chain of alternating phosphorus and nitrogen atoms lead to definite disagreements with the electron diffraction results.

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(11) Wichelhaus, *Ber.*, **3**, 163 (1870).

(12) Rosset, *Compt. rend.*, **180**, 750 (1925).

(13) Stokes, *Am. Chem. J.*, **18**, 629 (1896).