*Studies on Phosphonitrile Chlorides by their Pure Quadrupole Spectra**

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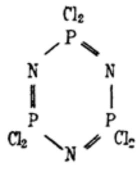
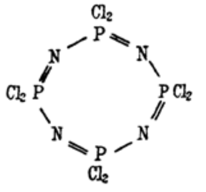
A group of phosphonitrile chlorides $(PNCl_2)_n$ have been known so far[1], where n is the degree of polymerization and is three or above. Of these, the trimer is the most ordinary compound and has been thought to form a plane ring[2], composing of nitrogen and phosphorus atoms alternatively. On the contrary, the tetramer has been shown to have a puckered ring and two kinds of chlorine atoms attached to the same phosphorus atom[3].



Trimer



Tetramer

We therefore examined the pure quadrupole spectra due to Cl^{35} of these two compounds and considered the states of their chlorine atoms, comparing the resonance absorption frequencies or absorption lines with each other.

Experimental

Preparation of Samples.—Phosphonitril chlorides were prepared by heating phosphorus pentachloride and ammonium chloride in *sym*-tetrachloroethane[4]. After the product was freed from ammonium chloride, solvent, and rubber-like residue, it was fractionally distilled at about 13 mmHg. The most part of the product was distilled off at about 127°C and this fraction was used as the sample of the trimer (m. p. 114°C). The fraction at 185–190°C was about one-tenth of the trimer, showing m. p. of 121–124°C. Thus it was used as the tetramer (m. p. 123.5°C), for a small content of impurities does not affect the absorption frequency, though they make the line width broader.

Apparatus.—To measure the absorption frequencies, we used the spectrometer reported in the previous paper[5], which was improved on a few points. For instance, a variable condenser of small capacity was connected parallel to the tank circuit of the main oscillator for the purpose of band spread, and its graduations were corrected every time by the crystal oscillator. By this method, the absorption frequency of potassium chlorate $KClO_3$ was found to be 28.147 Mc. at 14°C, which was in good agreement with the value of Wang et al.[6], taking the temperature effect into consideration.

Results and Considerations

The absorption frequencies of phosphonitrile chlorides were found at room temperature as shown in Table I. The experimental error was assumed to be several kc. in each case.

TABLE I

THE RESONANCE ABSORPTION FREQUENCIES DUE TO Cl^{35} IN PHOSPHONITRILE CHLORIDES $(PNCl_2)_n$ (287°K)

Compound	$(PNCl_2)_3$	$(PNCl_2)_4$
Frequency (Mc./sec.)	27.630	27.265
	27.704	28.124
	27.834	28.182
	27.903	28.616

It is noticed that both compounds show four kinds of frequencies. This fact seems to be curious in the case of the trimer $(PNCl_2)_3$, for six chlorine atoms of this molecule might be equivalent in the solid as well as in the vapor phase[2], and only one absorption frequency is to be expected. Otherwise, two or six kinds of frequencies may reasonably be expected, assuming slight distortion of P-Cl bonds or of the ring.

In the same way, two, four, and eight kinds may be probable in the case of the tetramer $(PNCl_2)_4$, for there are at least two kinds of chlorine atoms; that is, two chlorine atoms attached to the same phosphorus atom are at distances of 1.97 Å and 2.01 Å, respectively, according to the X-ray analysis[3].

The patterns of the spectra are illustrated in Fig. 1, where the intensity of each line is estimated roughly from the ratio of signal to noise. It is seen from this figure that

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four lines of the trimer are characterized by two kinds, the stronger and the weaker, whereas those of the tetramer are all of the same order. Consequently, it may be concluded that the stronger of the trimer and all of the tetramer are caused by two equivalent chlorine atoms in their molecules, and the weaker by only one. Thus, the four lines in each spectrum are concerned with the numbers of chlorine atoms in the corresponding molecules as $2+1+1+2=6$ and $2+2+2+2=8$, respectively.

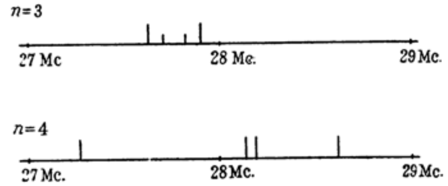

Fig. 1. The relative intensities of the absorption lines in $(PNCl_2)_n$.

However, it must be borne in mind that the intensity of the line in the pure quadrupole spectra is not always proportional to the amounts of the corresponding atoms, because it is affected also by the spin-lattice relaxation time and other factors[7].

The ionic character α of P-Cl bond may be assumed[8] by the relation $\alpha=1-\nu/\nu_0$, where ν is the measured absorption frequency of the compound and ν_0 is the absolute value of the coupling constant of atomic chlorine[9], 54.87 Mc.. Accordingly, the smaller is the frequency, the larger is the ionicity of the bond.

Several compounds which have P-Cl bonds and whose absorption frequences have been known are listed in Table II. From this table and Table I, it is seen easily that the ionicity of P-Cl bonds in phosphonitrile chlorides are closest to those of phosphorus oxychloride, taking account of frequancy increases, which presumably amount to several hundreds kc. at 77°K.

TABLE II

THE RESONANCE ABSORPTION FREQUENCIES OF SEVERAL COMPOUNDS WHICH HAVE P-Cl BONDS (77°K)

Compound	m. p. (°C)	Frequency (Mc./sec.)
PCl_3	−92	26.202[10] 26.107
$POCl_3$	1.4	28.9378[11] 28.9835
PCl_5	163	32.282[12] 32.384 32.63

Furthermore, two chlorine atoms in the trimer, corresponing to the absorption frequenty 27.630 Mc., are regarded as the most ionic of the six chlorine atoms, and they are to be replaced together to yield disubstituted compounds in place of monosubstituted compounds. In this way, the fact can be explained without difficulty that hydrolysis of the trimer gives triphosphonitrile dihydroxytetrachloride $P_3N_3(OH)_2Cl_4$ as a main product[13]. Trimeric phosphonitrilic acid $P_3N_2(OH)_6$ is unstable, whereas tetrameric phosphonitrilic acid $P_4N_4(OH)_8 \cdot 2H_2O$ is so stable that various hydrolytic intermediates have not been obtained[1]. However, these are likely to be isolated by controlled hydrolysis, for the absorption lines of the tetramer are widely spaced. Studies on the chemical behaviour of the phosphonitrile chlorides and their derivatives are now in progress, in connection with the results of the pure quadrupole spectra.

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