

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Infrared and Raman Spectra of the Trimer and Tetramer of Phosponitridic Dichloride<sup>1</sup>

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The infrared spectra of  $(\text{PNCl}_2)_3$  and  $(\text{PNCl}_2)_4$  are given for the range from 260 to 5000 wave numbers for solutions in carbon tetrachloride or carbon disulfide and for the solid state. Raman spectra are also given for solutions in carbon tetrachloride and for the liquid state. An interpretation of the data strengthens the belief that the molecule  $(\text{PNCl}_2)_3$  has  $D_{3h}$  symmetry. An assignment of fundamental frequencies by class is made for fourteen of the seventeen active fundamentals and certain frequencies are further designated as modes of vibration originating in the skeleton or  $\text{PCl}_2$  groups. The symmetry of  $(\text{PNCl}_2)_4$  is shown to be either  $D_{4h}$  or  $D_{2d}$ . The data are more in accord with the selection rules for  $D_{4h}$  than  $D_{2d}$ , but do not unequivocally exclude the  $D_{2d}$  symmetry. Only a few class and group assignments are made for this compound.

## Introduction

From electron diffraction studies<sup>2</sup> the structure proposed for  $(\text{PNCl}_2)_3$  is a cyclic configuration similar to benzene, but consisting of alternating phosphorus and nitrogen atoms. In addition, each phosphorus is bonded externally to two chlorine atoms. A similar eight-membered ring is proposed<sup>3</sup> for  $(\text{PNCl}_2)_4$ .<sup>4</sup> The infrared spectra for III and IV were previously reported<sup>5</sup> without discussion of the molecular structure. The Raman spectrum of III was published some years ago.<sup>6</sup> The present report increases the range of the infrared spectrum, gives the Raman spectra of the pure liquids as well as carbon tetrachloride solutions, and discusses the data in regard to the probable molecular structure.

## Experimental

Infrared spectra from 5000 to 450  $\text{cm}^{-1}$  were obtained on the prism instrument previously described.<sup>7</sup> The range from 550 to 260  $\text{cm}^{-1}$  was studied with a Perkin-Elmer Model 12C equipped with a 30° CsBr prism. The Raman spectrograph used was an Applied Research Laboratory commercial instrument which has three 60° flint glass prisms as the dispersing element and both photographic and photoelectric recording. The resolving power of this instrument is listed as 3  $\text{cm}^{-1}$  and the dispersion as 87  $\text{cm}^{-1}$  per mm. at 4358 Å.

The samples were prepared by the procedure of Schenk and Romer<sup>8</sup> and were vacuum distilled directly into the Raman tube for that phase of the work. The samples were maintained in the liquid state while obtaining the Raman spectrum by surrounding the sample tube with another glass tube around which was wound a loose spiral of nichrome wire. There was no mass polymerization from the heat<sup>6</sup> but the background was fairly large indicating slight decomposition or polymerization.

Polarization measurements were semi-quantitative since no special effort was made to correct for convergence error. Also, some of the bands were too weak to measure their intensities accurately and only visual estimates of their polarization were made. The observed depolarization factors for the depolarized lines of  $\text{CCl}_4$  were 0.88, 0.90 and 0.77 so that one could be reasonably certain that other observed values for strong lines were fairly accurate. Nevertheless, the lines are only indicated as polarized (p) or depolarized (dp) with questionable weak lines so indicated.

## Results and Discussion

The infrared spectra of both compounds from

- (1) Nomenclature follows that outlined in *Chem. Eng. News*, **30**, 4515 (1952).
- (2) L. Brockway and W. Bright, *THIS JOURNAL*, **65**, 1551 (1943).
- (3) J. Ketelaar and T. de Vries, *Rec. trav. chim.*, **58**, 1081 (1939).
- (4) Hereafter  $(\text{PNCl}_2)_3$  referred to as III and  $(\text{PNCl}_2)_4$  as IV.
- (5) L. Daasch and D. Smith, *Anal. Chem.*, **23**, 853 (1951).
- (6) A. Ficquelmont, M. Magat and L. Ochs, *Compt. rend.*, **208**, 1900 (1939).
- (7) J. Rud Nielsen, F. Crawford and D. Smith, *J. Opt. Soc. Am.*, **37**, 296 (1947).
- (8) R. Schenk and G. Romer, *Ber.*, **57B**, 1343 (1924).

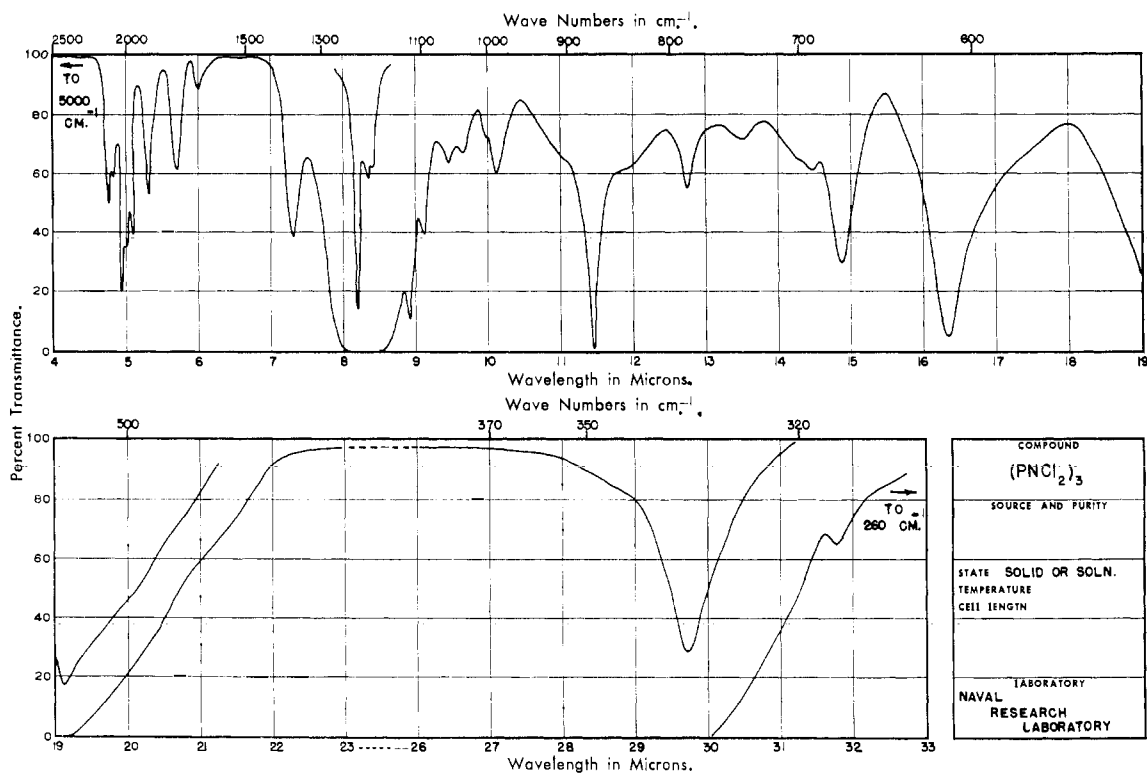
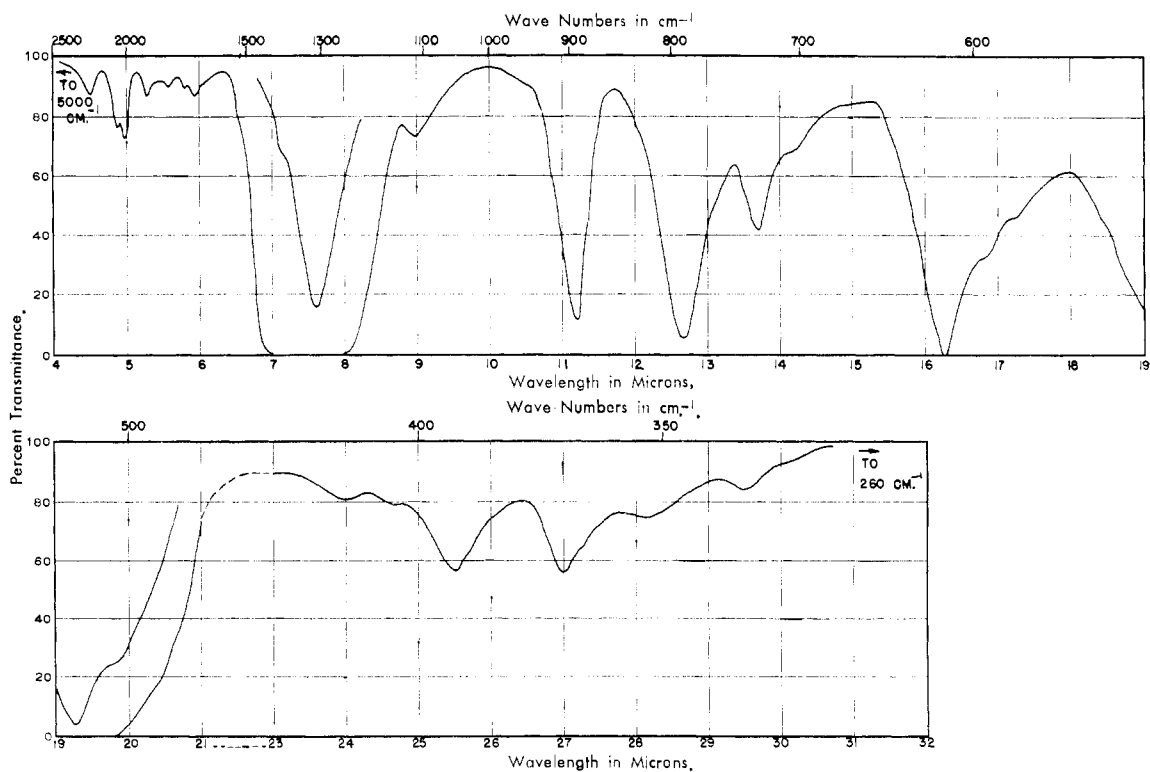
5000 to 260  $\text{cm}^{-1}$  (Figs. 1 and 2) are a composite of spectra obtained from saturated solutions of III and IV in carbon tetrachloride and carbon disulfide. The spectra in the solid state are the same as in solution. The wave numbers of the observed maxima in the infrared and Raman spectra are listed in Tables I and II and a partial vibrational assignment is given for each molecule. The Raman spectra of the liquids are the same as the solutions except where noted in the tables.

**Interpretation of Trimer Data. Symmetry, Selection Rules and Assignment.**—An attempt will first be made to interpret the spectroscopic data on the basis of a molecule with  $D_{3h}$  symmetry. For this symmetry the fundamental modes of vibration divide as follows:  $4A_1' + 2A_2' + 1A_1'' + 3A_2'' + 6E' + 4E''$  where classes  $A_1'$  and  $E''$  are Raman active only,  $A_2''$  is infrared active only,  $E'$  is active in both infrared and Raman effects, and  $A_2'$  and  $A_1''$  are inactive in both effects. Since Class  $A_1'$  frequencies will be polarized, it is evident that three of the four  $A_1'$  frequencies are at 365, 670 and 785  $\text{cm}^{-1}$ . Another weak, polarized band was observed at 100  $\text{cm}^{-1}$  on one set of polarization records but the band is certainly not as strong as reported previously,<sup>6</sup> if, indeed, it is present at all. It will be noted also in Table I that there is disagreement with the previous work on the intensity and polarization of the 575  $\text{cm}^{-1}$  Raman line. It is at most only one-fourth as strong as 670  $\text{cm}^{-1}$  and has a semi-quantitative depolarization factor of 0.8.

The strong infrared bands at 1218, 885, 612, 522 and 336  $\text{cm}^{-1}$ , with coincident weak depolarized Raman lines, are undoubtedly  $E'$  vibrations. The strict strong-weak intensity relationship in the two effects indicates that the other possible  $E'$  vibration should likewise exhibit strong infrared absorption. Now there must be an overlapping of bands of different species at about 670  $\text{cm}^{-1}$  since the Raman line at 670  $\text{cm}^{-1}$  is definitely polarized and therefore Class  $A_1'$ , while there is a strong band at 672  $\text{cm}^{-1}$  in the infrared spectrum where  $A_1'$  is inactive. Keeping in mind the strong-weak relationship this infrared band is assigned to the remaining  $E'$  frequency.

Any other depolarized Raman lines must be class  $E''$  so that 162, 173 and 210  $\text{cm}^{-1}$  are surely of this class and the last  $E''$  frequency is probably at 575  $\text{cm}^{-1}$ , the only remaining depolarized line of any strength.

An assignment for the three vibrations of class  $A_2''$  is not apparent although one should only have to look for infrared active-Raman inactive bands.

Fig. 1.—Infrared spectrum of  $(\text{PNCl}_2)_3$ .Fig. 2.—Infrared spectrum of  $(\text{PNCl}_2)_4$ .

Another accidental overlapping class  $A_1'$  Raman band with an infrared band of medium intensity occurs at  $785 \text{ cm}^{-1}$ . The infrared band is assigned to an  $A_2''$  vibration. There are other bands in class  $A_2''$  at  $990 \text{ cm}^{-1}$  and above, which are be-

lieved to be overtones or combinations. The approximate "group" frequencies indicate that the two remaining  $A_2''$  fundamentals should be below the one just assigned, perhaps beyond the range of the infrared spectrum.

TABLE I  
 INFRARED AND RAMAN DATA ON  $(\text{PNCl}_2)_3$ 

Present work	Raman	Ref. (6)	Infrared	Assign.	Remarks <sup>a</sup>
100 (vw, P?)		100 (5.3, P)		A" (?)	Found on only one polarization record
162 (4, dp)		162 (4.6, dp)		E"	
173 (3, dp)		177 (4.5, dp)		E"	
210 (3, dp)		206 (4.0, —)		E"	
		312 (vw, —)	315 w		
340 (1, dp)		339 (2.7, dp)	336 s	E'	
365 (10, P)		366 (7.5, P)		A <sub>1</sub> '	Ring deformation; $\nu_3$
523 (0.5, —)		533 (1.2, dp)	522 vs	E'	Ring vibration; $\nu_{14}$
575 (1, dp)		585 (5.5, P)		E"	PCl <sub>2</sub> stretch; $\nu_{17}$
610 (0.5, —)		614 (1.0, —)	612 s	E'	$\nu_{13}$ (?)
670 (4, P)		672 (6, P)	672 s	A <sub>1</sub> ' and E'	PCl <sub>2</sub> vibrations; $\nu_2$ and $\nu_{13}$ (?)
		707 (vw, —)	690 vw		
			740 w		
785 (2, P?)			782 m	A <sub>1</sub> ' and A <sub>2</sub> "	$\nu_1$ and $\nu_8$
		885 (vw, —)	885 s	E'	Ring elongation; $\nu_{12}$
		940 (vw, —)	990 m		
			1040 vw		
			1060 vw		
			1092 m		
			1121 m		
			1200 m		
		1230 vw	1218 vs	E'	P=N valence; $\nu_{11}$
		1368	1310		
			1368		
			1660		
			1750		
			1880		
			1975		
			2025		
			2075		
			2095		

<sup>a</sup> See Table III for meaning of  $\nu_1$  to  $\nu_{20}$ .

**Group Frequencies.**—It is fortunate that certain molecular vibrations "concentrate" in a portion or group of the molecule. These group frequencies are effective tools in spectroscopy when the atomic masses participating in the vibration are much different from one another. One is not so fortunate as this in III and IV where the chlorine and phosphorus have comparable atomic masses and nitrogen has about one-third the atomic weight of either of these. In this case not much could be expected from group frequency correlations were it not for the well known fact that, in general, skeletal frequencies arising from cyclic structures have strong group characteristics.

Indeed, a comparison of the spectra of III with its esters<sup>5</sup>  $(\text{PN}(\text{OR})_2)_3$  clearly indicates that the E' vibration at 1218  $\text{cm}^{-1}$  is a ring vibration, preserved regardless of the mass attached to the phosphorus atom, and that those at 885 and 522  $\text{cm}^{-1}$  are likely to be ring vibrations also. Furthermore, the approximate motion for vibrations of this class suggests that a P=N stretching vibration (Table III) would be the only possibility for a frequency as high as 1218  $\text{cm}^{-1}$ .<sup>9</sup> The only other ring vibration that could come above 750  $\text{cm}^{-1}$  is the elongation mode which entails both stretching and de-

formation of the P=N bonds. Therefore, the 885  $\text{cm}^{-1}$  band is thought to arise from this mode. Except for the fact that symmetric PCl<sub>2</sub> stretch frequencies have in the past been below 800  $\text{cm}^{-1}$  (the 672 or 612  $\text{cm}^{-1}$  band probably accounts for this vibration), there is no basis on which the other three group frequencies given in Table III can be divided among the experimentally observed frequencies of this class.

In the class E" vibrations, the ring deformation mode is perpendicular to the plane of the ring (Table III) and experience has shown that these "out of plane" modes are usually found at very low frequencies. Likewise, the PCl<sub>2</sub> deformation and torsional modes will probably be at low frequencies. Therefore the three lowest depolarized Raman bands are assigned to these modes. The fourth vibration is described as an unsymmetrical, out of phase, PCl<sub>2</sub> valence vibration and consequently could come at a higher frequency (575  $\text{cm}^{-1}$ ).

The PCl<sub>2</sub> unsymmetrical, in phase, valence vibration is probably the only class A<sub>2</sub>" vibrational mode that might have a frequency as high as 782  $\text{cm}^{-1}$ . Thus, as mentioned previously, the bands at 990  $\text{cm}^{-1}$  and above 1092  $\text{cm}^{-1}$  which follow the A<sub>2</sub>" selection rules must be interpreted as combinations or overtones.

Class A<sub>1</sub>' has a "breathing" ring vibration (corresponding to P—N=P stretch) which might be expected above 1000  $\text{cm}^{-1}$  since the P=N stretch

(9) It might be pointed out that since the P=N bonds are very likely resonating around the ring of III, the absorption in the same region for organophosphorus compounds containing a P=O bond is indirect evidence that the P=O bond is likewise a resonating or polar bond.

TABLE II  
 INFRARED AND RAMAN DATA ON  $(\text{PNCl}_2)_4$ 

Raman	Infrared	Assignment ( $D_{4h}$ symmetry)	Remarks
137 (6, dp)			
158 (3, dp) <sup>a</sup>			
169 (8, dp)		$3E_g$	169 and 178 believed to be doublet although not well resolved
178 (8, dp)			
192 (5, dp)			
259 (4, dp)			
300 (0.5, —) <sup>b</sup>			
	339 vw		
350 (1.5, P) <sup>b</sup>	355 vw	$A_{1g}$	
	370 w		
	393 w		
404 (10, P)		$A_{1g}$	Raman line considerably broadened and peak intensity weakened in liquid spectrum
434 (4, P) <sup>a</sup>		$A_{1g}$	
512 (0.5, P?)	512 (shoulder)	$A_{1g}$	
	520 vs.	$E_u$	Ring vibration.
538 (5, P)		$A_{1g}$	
	579 w		
590 (5, dp)	590 w		
620 (0.5, —) <sup>a</sup>	615 vs	$E_u$	$\text{PCl}_2$ vibration
668 (0.5, —)			
725 (0.5, —) <sup>b</sup>	730 ms		
	790 s	$A_{2u}$	$\text{PCl}_2$ vibration
895 (1.0, dp?)	895 s	$B_{1g}$ and $E_u$	Ring vibration
	1315 vs	$E_u$	$\text{P}=\text{N}$ stretch
	1700 vw		
	1860 v.w.		
	2020 vw		
	2060 vw		
	2200 vw		

<sup>a</sup> Not observed on liquid spectrum, perhaps due to background or unresolved from broadened neighboring lines.  
<sup>b</sup> Raman line observed on liquid spectrum only.

vibration of class  $E'$  is at  $1218 \text{ cm}^{-1}$ . However, in benzene the  $A_{1g}$  breathing frequency ( $990 \text{ cm}^{-1}$ ) is much lower than the comparable  $E_u$  and  $E_g$  class  $\text{C}=\text{C}=\text{C}$  stretching frequencies which occur<sup>10</sup> at  $\sim 1500 \text{ cm}^{-1}$ . Likewise for III the polarized band at  $785 \text{ cm}^{-1}$  which is assigned to the  $A_1'$  breathing mode is lower than the  $E'$  infrared active ring frequencies which come at  $1218$  and  $885 \text{ cm}^{-1}$ . Of the three remaining polarized bands the one at  $670 \text{ cm}^{-1}$  is assigned to a  $\text{PCl}_2$  symmetric stretch vibration and the one at  $365 \text{ cm}^{-1}$  to the trigonal ring deformation. The doubtful band at  $100 \text{ cm}^{-1}$  may be the remaining  $\text{PCl}_2$  deformation vibration.

The group of bands on the low and high frequency sides of the very strong infrared band at  $1218 \text{ cm}^{-1}$  and the group of bands in the  $1650$  to  $2100 \text{ cm}^{-1}$  region have been purposely ignored in the discussion of the assignment. These high frequency bands are undoubtedly combinations and overtones. The list of such bands which could be active in the infrared for  $D_{3h}$  symmetry is quite lengthy so that suitable combinations are easily found. However, in view of the number of possible combinations it would add little support to the assignment of the fundamentals, especially when it is realized that some of the possible combinations include bands from the inactive  $A_2'$  and  $A_1''$  classes which are completely unknown for this molecule.

Nevertheless, a peculiarity for each of these groups of observed bands should be noted. Most of

(10) G. Herzberg, "Molecular Spectra and Molecular Structure, II," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 362-369.

 TABLE III  
 GROUP FREQUENCIES IN  $(\text{PNCl}_2)_4$ 

Class	Activity	Approximate motion
$A_1'$	R	$\nu_1$ Ring breathing
		$\nu_2$ Symmetrical $\text{PCl}_2$ stretch, in phase
		$\nu_3$ Trigonal ring deformation
		$\nu_4$ $\text{PCl}_2$ deformation, in phase
$A_2'$	I.A.	$\nu_5$ $\text{P}=\text{N}$ stretch (trigonal)
		$\nu_6$ $\text{PCl}_2$ wag, in phase (motion in plane of $\text{PCl}_2$ group)
$A_1''$	I.A.	$\nu_7$ $\text{PCl}_2$ torsion, in phase?
$A_2''$	I.R.	$\nu_8$ Unsymmetrical $\text{PCl}_2$ stretch, in phase
		$\nu_9$ Ring deformation (out of plane of ring)
		$\nu_{10}$ $\text{PCl}_2$ rock, in phase (motion perpendicular to plane of $\text{PCl}_2$ )
$E'$	R and I.R.	$\nu_{11}$ $\text{P}=\text{N}$ stretch in plane
		$\nu_{12}$ Ring elongation
		$\nu_{13}$ Symmetrical $\text{PCl}_2$ stretch, out of phase
		$\nu_{14}$ Ring deformation, in plane
		$\nu_{15}$ $\text{PCl}_2$ wag, out of phase (motion in plane of $\text{PCl}_2$ )
		$\nu_{16}$ $\text{PCl}_2$ deformation, out of phase
$E''$	R	$\nu_{17}$ $\text{PCl}_2$ unsymmetrical stretch, out of phase
		$\nu_{18}$ $\text{PCl}_2$ rock, out of phase?
		$\nu_{19}$ Ring deformation (out of plane of ring)
		$\nu_{20}$ $\text{PCl}_2$ torsion, out of phase?

the peaks about the  $1218 \text{ cm}^{-1}$  band are symmetrically placed. That is, there are bands at  $\pm 95$  ( $\pm 3$ )  $\text{cm}^{-1}$  and  $\pm 154$  ( $\pm 4$ ). In addition, on the low frequency side there are absorptions at  $126$  and  $178 \text{ cm}^{-1}$  from the  $1218 \text{ cm}^{-1}$  maximum. What may be of significance is that the  $95$ ,  $154$  and  $178 \text{ cm}^{-1}$  values are close to the three lowest Raman frequencies and the bands may be the combinations  $1218 \pm X$ , where  $X$  takes on the above values.

The other group of frequencies,  $1650$  to  $2100 \text{ cm}^{-1}$ , can also be explained as combinations but the peculiarity is the concentration of the bands in these regions to the exclusion of the  $1400$  to  $1750 \text{ cm}^{-1}$  and  $2100$  to  $5000 \text{ cm}^{-1}$  regions. The three singlets and two doublets are definitely reminiscent of a similar group of bands in substituted benzenes which occur in about the same part of the spectrum.

**Interpretation of the Tetramer Data. Symmetry, Selection Rules and Structure.**—The structure of IV has been studied previously using X-ray diffraction methods.<sup>3</sup> These studies show that the structure is probably an eight-membered ring similar to III but with the ring now puckered into a sort of skewed "tub" structure with  $S_4$  symmetry. However, as shown in Table IV the tetramer with this symmetry should display 11 polarized and 21 depolarized Raman lines and in addition there should be 10 coincidences between the Raman and infrared spectra. The spectroscopic data in Table II, summarized in Table IV, shows that the symmetry is higher than  $S_4$  in the liquid or solution media because the total number of observed bands and coincidences is so much less than calculated for  $S_4$  symmetry. It is possible, of course, that in the

solid state crystal forces distort the molecule into the lower symmetry.

TABLE IV  
SELECTION RULES FOR POSSIBLE TETRAMER STRUCTURES

Symmetry	Raman fundamentals		Infrared fundamentals	Coincidences
	Polarized	Depolarized		
$S_4$	11	21	10	10
$C_{4v}$	5	16	15	15
$D_{2d}$	6	14	16	10
$D_{4h}$	4	11	9	0
Obsd. <sup>a</sup>	5	8	10 w to s + 2 vw below 1350 cm. <sup>-1</sup>	6

<sup>a</sup> Four additional very weak Raman lines were observed but their polarization was not measured.

The possible structures of higher symmetry are drawn in Fig. 3, along with an  $S_4$  structure. The symmetry  $C_{4v}$  need not be considered for the structure of an isolated, stationary molecule in the crystal since the site group must be a subgroup of both the molecular symmetry<sup>11</sup> and the space group symmetry<sup>12</sup> and  $C_{4v}$  does not have  $S_4$  as a subgroup. Although the molecule could attain this symmetry in solution and in the liquid state the number of observed coincidences is much less than required for  $C_{4v}$  symmetry (Table IV). This leaves symmetries  $D_{2d}$  and  $D_{4h}$  as possibilities. In  $D_{2d}$  and  $D_{4h}$  symmetries any polarized Raman lines should have no coinciding infrared bands because Class  $A_1$  is inactive in the infrared spectrum for both these symmetries. Thus, eliminating as accidental those coincidences between polarized Raman lines and infrared bands, there are four other coincidences. On this basis alone one might be inclined to eliminate the symmetry  $D_{2d}$  which requires ten coincidences. However, the fact that the infrared spectrum extends to only 260 cm.<sup>-1</sup> makes it impossible to be certain that there are not infrared bands coincident with some of the six depolarized Raman lines below 260 cm.<sup>-1</sup>. On the other hand, if  $D_{2d}$  symmetry were assumed, some of these depolarized bands would, without doubt, prove to be in class  $B_1$  since there are four depolarized Raman active bands in this class which would have to be included in the assignment for the Raman spectrum. The observed coincidences, therefore, could not possibly number ten. In any case, with the data available the  $D_{2d}$  symmetry requires six more coincidences to be displayed whereas  $D_{4h}$  requires four observed coincidences to be accidental. The  $D_{4h}$  structure is at least less in conflict with this portion of the data than  $D_{2d}$ .

Considering the Raman data only, the total number of depolarized bands seems to indicate a  $D_{4h}$  structure.  $D_{2d}$  requires 14,  $D_{4h}$  requires 11; and there are only eight definitely depolarized bands with a possibility of four others, if all the very weak lines prove to be depolarized. The five polarized bands are intermediate in number between the required four for  $D_{4h}$  and six for  $D_{2d}$ .

(11) Molecular symmetry is used here to mean the symmetry of an isolated molecule, not the "apparent" molecular symmetry deduced from X-ray intensity measurements. The X-ray measurements may indicate molecular symmetries higher than the site group symmetry in such cases as tunneling or random occupation of alternate orientations.

(12) R. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

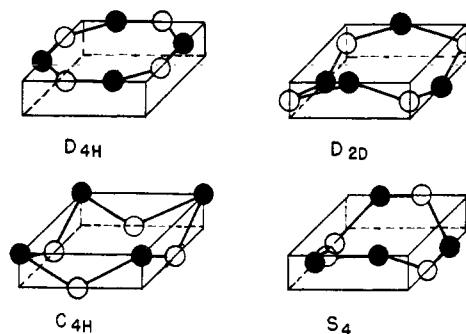


Fig. 3.—Possible structure for  $(PNCl_2)_4$ .

The infrared absorption spectrum between 260 and 1350 cm.<sup>-1</sup> (about the upper limit for possible fundamentals) has six strong bands, four weak, and two in the very weak category. Here again ignorance of the 0–260 cm.<sup>-1</sup> region is a handicap but  $D_{4h}$  structure with nine infrared fundamentals fits the available infrared data much better than  $D_{2d}$  with sixteen infrared active fundamentals. In summation, the available spectroscopic data favor the structure with  $D_{4h}$  symmetry although they do not eliminate  $D_{2d}$  symmetry.

One other bit of evidence would favor the planar  $D_{4h}$  structure even in the crystal. The X-ray studies<sup>3</sup> which indicated a molecular structure with  $S_4$  symmetry also contained the information that the P=N distances around the ring were equal. Resonance in the ring of IV was postulated to account for this equality of P=N distances and for the remarkable chemical stability of the ring in IV. However, a common requirement for what is apparently resonance of a high order is that the structure involved in the resonance must be planar,<sup>13</sup> and for this molecule the planar structure has  $D_{4h}$  symmetry.

**Group Frequencies and Class Assignments.**—The infrared spectra of III and IV are strikingly similar, there being only two strong bands at 336 and 672 cm.<sup>-1</sup> in III which have no counterparts in IV. Likewise the strong depolarized Raman lines below 250 cm.<sup>-1</sup> in III are almost matched by lines in IV. Using this similarity and the selection rules for  $D_{4h}$  symmetry<sup>14</sup> a partial assignment by class is given for IV in Table II. There are two class  $E_u$  ring vibrations, one of which corresponds to P=N stretch and the other to a ring distortion (Fig. 4). In cyclooctatetraene<sup>10</sup> the corresponding vibrations have the frequencies 1635 and 1399 cm.<sup>-1</sup>. The infrared bands at 1315 and 895 cm.<sup>-1</sup> in IV would be logical choices.<sup>15</sup> The  $PCl_2$  stretching vibration of class  $E_u$  comes at 615 cm.<sup>-1</sup> and one of the remaining ring vibrations at 520 cm.<sup>-1</sup>.

Lippincott<sup>16</sup> lists another frequency in cyclooctatetraene as being concentrated in the C=C stretch-

(13) E. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 20.

(14) Fundamental modes divide as follows:  $4A_{1g} + 2A_{2u} + 4B_{1g} + 4B_2 + 3E_g + 7E_u$  where classes  $A_{1g}$ ,  $B_{1g}$ ,  $B_2g$  and  $E_g$  are Raman active only and  $A_{1u}$  and  $E_u$  are infrared active only.

(15) 895 cm.<sup>-1</sup> Raman line is considered accidentally coincident as are 725, 620 and 590 cm.<sup>-1</sup>.

(16) E. Lippincott, R. Lord and R. McDonald, *THIS JOURNAL*, **73**, 3370 (1951).

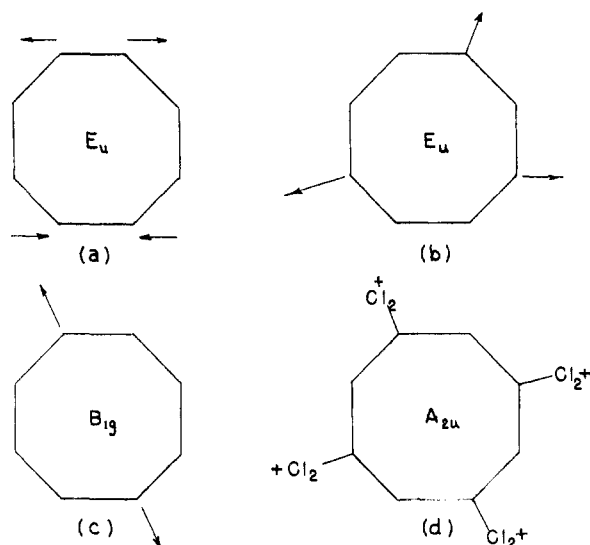


Fig. 4.—Approximate motion of  $(\text{PNCl}_2)_4$  in certain of its fundamental modes.

ing motion. This is a class  $B_1$  vibration for  $D_4$  symmetry and has been assigned in cyclooctatetraene to a frequency of  $1601 \text{ cm.}^{-1}$ . The form of the vibration must be something like (c) in Fig. 4 which is actually more comparable to what has been called a ring elongation vibration and which in III has been assigned to the infrared band at  $885 \text{ cm.}^{-1}$ . Therefore in IV, where this vibration is now in the

Raman active class  $B_{1g}$ , it has been assigned to the  $895 \text{ cm.}^{-1}$  Raman line.

One further assignment might be made and that is the infrared active-Raman inactive band at  $790 \text{ cm.}^{-1}$ . In III there was believed to be an overlapping of  $A_1'$  and  $A_2''$  modes at about this frequency. The  $A_2''$  mode was assigned to a  $\text{PCl}_2$  wagging, in phase vibration. This same type of motion in IV does come in class  $A_{2u}$  which matches the selection rules of the observed band at  $790 \text{ cm.}^{-1}$ .

Other than to say that the three vibrations of class  $E_g$  probably occur among the six observed Raman lines below  $260 \text{ cm.}^{-1}$ , nothing further in the way of assignment has been made. There are still  $3B_{1g} + 4B_{2g} + 1A_{2u} + 3E_u$  whose range cannot be given, much less proposals for assignment to observed frequencies.

### Conclusions

The selection rules for  $D_{3h}$  symmetry in the molecule  $(\text{PNCl}_2)_3$  are shown to account for the observed infrared and Raman data. Selection rules for neither  $D_{4h}$  or  $D_{2d}$  fully account for the observed data on  $(\text{PNCl}_2)_3$  and yet the molecule is believed to have one of these two symmetries. The data at present favor the  $D_{4h}$  structure. Vibrational assignments, as yet incomplete, are given for both molecules.

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## A Rate Study of the Silanol Condensation Reaction at $25^\circ$ in Alcoholic Solvents<sup>1</sup>

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A method is described for measuring the rates of silanol condensation reactions. The method consists of a titration of samples of the reacting solution with Kari Fischer reagent. This titration measures the total content of  $\text{SiOH}$  groups plus  $\text{H}_2\text{O}$  in the solution. Complete condensation of a silanol solution results in a reduction of the apparent water concentration to one-half of its initial value. Using this method of analysis, a detailed study has been made of the condensation of trimethylsilanol in the solvent methanol with the following results. The condensation of trimethylsilanol is found to be incomplete in this system. Incomplete condensation is caused by the rapid reaction  $(\text{CH}_3)_3\text{SiOH} + \text{CH}_3\text{OH} \rightleftharpoons (\text{CH}_3)_3\text{SiOCH}_3 + \text{H}_2\text{O}$ , which removes silanol from the system, while the following condensation equilibrium is established slowly.  $(\text{CH}_3)_3\text{SiOH} + (\text{CH}_3)_3\text{SiOCH}_3 \rightleftharpoons (\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3 + \text{CH}_3\text{OH}$ . The formula for the condensation equilibrium constant is  $K = [(\text{CH}_3)_3\text{SiOCH}_3]^2[\text{H}_2\text{O}] / [(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3]$ . This form for the equilibrium constant reveals that essentially no free trimethylsilanol is present at equilibrium. The equilibrium constant has the same value when different concentrations of both acidic and basic catalysts are employed, and the same equilibrium is attained by starting from a mixture of hexamethyldisiloxane and water, thus demonstrating that this is a true thermodynamic equilibrium. It is found by studying the rate of attainment of the condensation equilibrium that the rate determining reaction in condensation is  $(\text{CH}_3)_3\text{SiOCH}_3 + (\text{CH}_3)_3\text{SiOH} \rightarrow (\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3 + \text{CH}_3\text{OH}$ . A rate law deduced from this reaction agrees with the experimental results. The rate law is found to be the same for both acidic and basic catalysts although  $\text{HCl}$  is about 500 times as active as  $\text{KOH}$  in promoting condensation. Silanols containing bulkier substituents react much more slowly. Triethylsilanol and triphenylsilanol react, respectively,  $1/600$  and  $<2 \times 10^{-6}$  as fast as trimethylsilanol under the same conditions. The

proposed mechanisms for the silanol condensation reaction in methanol are: in acidic catalysis,  $-\text{SiO}- \xrightarrow{\text{H}^+} -\text{SiOCH}_3^+ \rightleftharpoons -\text{SiOSi}- + \text{CH}_3\text{OH} + \text{H}^+$ ; and in basic catalysis,  $-\text{SiO}^- \rightarrow -\text{SiOCH}_3 \rightleftharpoons -\text{SiOSi}- + \text{CH}_3\text{O}^-$ . These mechanisms account for the observed rate law, the linear relation between rate of condensation and catalyst concentration, and the large effect of steric factors upon the rate of condensation. No evidence for the formation of  $\text{R}_3\text{Si}^+$  has been found.

### Introduction

Rate studies in organosilicon chemistry have been

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confined chiefly to hydrolysis or cleavage reactions of atoms or groups attached to silicon, *e.g.*,  $\text{Si-H}$ ,<sup>2a</sup>

(2) (a) F. P. Price, *THIS JOURNAL*, **69**, 2600 (1947); (b) C. G. Swain, R. M. Esteve and R. H. Jones, *ibid.*, **71**, 965 (1949).