relatively close limits provided the charge per monomer unit is known. In most cases involving monodisperse chelate systems, the value of the charge may be determined from potentiometric titration data, although some ambiguity exists if there is the possibility of complexing by chloride or other negative ions. Since the calculation of N is often rather insensitive to changes in the value of the assumed charge per monomer unit, z', it is difficult to determine the charge with any degree of certainty from ultracentrifugation data. Conversely it is possible to obtain a good approximation to the molecular weight of a species even though its charge is unknown provided that the charge is of small magnitude, *i.e.*, approximately 2.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Some Disubstituted Aminolysis Products of Tetrameric Phosphonitrilic Chloride

BY KARL JOHN, THERALD MOELLER AND L. F. AUDRIETH

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The interaction of tetrameric phosphonitrilic chloride with aliphatic, aromatic or heterocyclic amines in mole ratio 1:2 or 1:4 yields the corresponding disubstituted aminolysis products. Nuclear magnetic resonance spectra suggest that the two substituents are in *trans* ring positions. The properties of these compounds are described.

Although a variety of partially substituted amine derivatives of trimeric phosphonitrilic chloride have been described,[1–7] considerably less is known about those of tetrameric phosphonitrilic chloride. Most of the derivatives of the tetramer have been obtained by using the corresponding partially substituted reactants in the initial synthesis reaction rather than by direct substitution.[8–12] Tetrameric phosphonitrilic chloride itself has been used directly only in the synthesis of completely substituted derivatives with aniline,[13] dimethylamine,[6] ethyleneimine,[14] methoxyl[15] and isothiocyanate[16] and of partially substituted derivatives with ammonia.[17] It is probable that both the reduced availability of the tetrameric chloride and its somewhat enhanced reactivity have limited studies of this type.

It has been found possible, however, to obtain disubstituted aminolysis products by using

1. Mixed solvents, *e.g.*, ether–water or benzene–water, and (a) treating the phosphonitrilic chloride dissolved in the organic liquid with standardized aqueous solutions of the amine hydrochloride and potassium hydroxide

$$(PNCl_2)_4 + 2R_2NH_2Cl + 4KOH \longrightarrow P_4N_4Cl_6(NR_2)_2 + 4KCl + 4H_2O$$

or (b) treating the phosphonitrilic chloride with the free amine in the mole ratio 1:4 and employing the water to remove the amine hydrochloride formed

$$(PNCl_2)_4 + 4R_2NH \longrightarrow P_4N_4Cl_6(NR_2)_2 + 2R_2NH_2Cl$$

2. Anhydrous media, *e.g.*, ether, benzene or acetonitrile, and adding to a well-stirred, refluxing solution of the amine a diluted solution of tetrameric phosphonitrilic chloride in the mole ratio 4:1

$$(PNCl_2)_4 + 4R_2NH \longrightarrow P_4N_4Cl_6(NR_2)_2 + 2R_2NH_2Cl$$

In the first procedure, removal of by-products and hydrolysis products is facilitated by their water

TABLE I

INFRARED DATA FOR TETRAMERIC PHOSPHONITRILES

Compound	Solvent	Frequency, cm.$^{-1}$	Interpretation	Ref.
$P_4N_4Cl_8$	CS_2	1315	P = N stretch	18
$P_4N_4Cl_6(NHCH_3)_2$	Nujol mull	1310	P = N stretch	
$P_4N_4Cl_6[N(CH_3)_2]_2$	$CHCl_3$	1310	P = N stretch	
$P_4N_4Cl_6(NHC_2H_5)_2$	CS_2	1310	P = N stretch	
$P_4N_4Cl_6[NHC(CH_3)_3]_2$	CS_2	1312	P = N stretch	
$P_4N_4Cl_6(NHC_6H_5)_2$	Nujol mull	1225 1287		
$P_4N_4Cl_6[N(CH_3)(C_6H_5)]_2$	CS_2	1308	P = N stretch	
$P_4N_4Cl_6(o\text{-}NHC_6H_4CH_3)_2$	Nujol mull	1232 1258		
$P_4N_4Cl_6(m\text{-}NHC_6H_4CH_3)_2$	Nujol mull	1275		
$P_4N_4Cl_6(p\text{-}NHC_6H_4CH_3)_2$	CH_3CN	1220 1275		
$P_4N_4Cl_6[N(CH_2CH_2)_2O]_2$	$CHCl_3$	1315	P = N stretch	
$P_4N_4Cl_6(NC_5H_{10})_2$	Nujol mull	1310	P = N stretch	
$P_4N_4(NHC_6H_5)_8$	Nujol mull	1214 1260		[a]
$P_4N_4[N(CH_3)_2]_8$	?	1209 1265		15

[a] Prepared according to ref. 13.

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	Chemical shift, p.p.m. (reference H_3PO_4)	Solvent	RF frequency, Mc.
$P_4N_4Cl_6(NHC_6H_5)_2$	+2.4, +4.6, +7.1; +11.0, +13.5, +16.4	$(C_2H_5)_2O$	16.2
$P_4N_4Cl(n\text{-}NHC_6H_4CH_3)_2$	+3.3, +5.6, +7.9; +11.2, +13.5, +14.9	$(C_2H_5)_2O$	16.2
$P_4H_4Cl_6(o\text{-}NHC_6H_4CH_3)_2$	+4.4, +5.9, +7.5; +9.7, +11.6, +12.3	$(C_2H_5)_2O$	16.2

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(1) H. Bode and H. Bach, *Ber.*, **75**, 215 (1942).

(2) H. Bode, K. Bütow and G. Lienau, *ibid.*, **81**, 547 (1948).

(3) R. J. A. Otto and L. F. Audrieth, THIS JOURNAL, **80**, 5894 (1958).

(4) R. J. A. Otto and L. F. Audrieth, *ibid.*, **80**, 3575 (1958).

(5) M. Becke-Goehring and Karl John, *Angew. Chem.*, **70**, 657 (1958).

(6) S. K. Ray and R. A. Shaw, *Chem. and Ind.* (*London*), 53 (1959).

(7) M. Becke-Goehring, K. John and E. Fluck, *Z. anorg. allgem. Chem.*, **302**, 103 (1959).

(8) H. Bode and R. Thamer, *Ber.*, **76**, 121 (1943).

(9) R. G. Rice, L. W. Daasch, J. R. Holden and E. J. Kohn, *J. Inorg. Nuclear Chem.*, **5**, 190 (1958).

(10) C. P. Haber, D. L. Herring and E. A. Lawton, THIS JOURNAL, **80**, 2116 (1958).

(11) R. A. Shaw and C. Stratton, *Chem. and Ind.* (*London*), 52 (1959).

(12) H. T. Searle, *Proc. Chem. Soc.*, 7 (1959).

(13) A. W. Hofmann, *Ber.*, **17**, 1909 (1884).

(14) R. F. W. Rätz and C. J. Grundmann, U. S. 2,858,306, October 28, 1958.

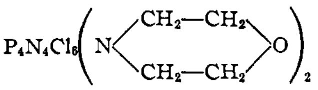
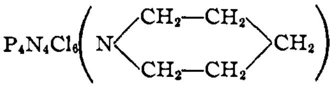
(15) R. A. Shaw, *Chem. and Ind.* (*London*), 54 (1959).

(16) G. Tesi, R. J. A. Otto, F. G. Sherif and L. F. Audrieth, THIS JOURNAL, **82**, 528 (1960).

(17) A. M. de Fiquelmont, *Ann. chim.*, (11), **12**, 214 (1939).

TABLE III

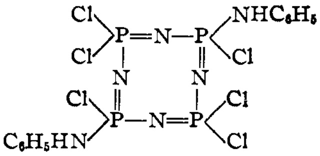
CHARACTERISTICS OF DISUBSTITUTED AMINOLYSIS PRODUCTS

Compound	Method	Yield, %	M.p., °C.		Analysis C	H	N	P	Cl
$P_4N_4Cl_6(NHCH_3)_2$	1a	27	143	Calcd.	5.30	1.78	18.56	27.37	46.99
				Found	5.66	1.62	18.42	27.78	47.16
$P_4N_4Cl_6[N(CH_3)_2]_2$	1a	28	171	Calcd.	9.99	2.51	17.48	25.77	44.25
			(subl.)	Found	9.93	2.45	17.37	26.52	44.27
$P_4N_4Cl_6(NHC_2H_5)_2$	1a	30	113	Calcd.	9.99	2.51	17.48	25.77	44.25
			(subl.)	Found	9.90	2.56	17.25	26.40	44.40
$P_4N_4Cl_6[NHC(CH_3)_3]_2$	2	25	124	Calcd.	17.89	3.76	15.65	23.08	39.62
				Found	18.07	3.79	15.50	23.06	39.32
$P_4N_4Cl_6(NHC_6H_5)_2$	1a, 1b	18	166	Calcd.	24.98	2.09	14.57	21.48	36.88
	2	26		Found	24.85	2.17	14.58	21.51	36.75
$P_4N_4Cl_6[N(CH_3)(C_6H_5)]_2$	1a or 2	32	146	Calcd.	27.79	2.67	13.89	20.48	35.17
				Found	28.00	2.95	13.88	20.32	34.87
$P_4N_4Cl_6(o\text{-}NHC_6H_4CH_3)_2$	2	32	172	Calcd.	27.79	2.67	13.89	20.48	35.17
				Found	28.05	2.76	13.64	20.44	34.87
$P_4N_4Cl_6(m\text{-}NHC_6H_4CH_3)_2$	2	24	204	Calcd.	27.79	2.67	13.89	20.48	35.17
				Found	28.19	2.63	13.83	20.67	34.57
$P_4N_4Cl_6(p\text{-}NHC_6H_4CH_3)_2$	2	26	196	Calcd.	27.79	2.67	13.89	20.48	35.17
				Found	28.15	2.72	13.84	20.53	34.96
	2	34	205	Calcd.	17.01	2.85	14.88	21.94	37.66
				Found	17.30	3.12	14.78	22.05	37.50
	2	34	194	Calcd.	21.41	3.60	14.98	22.09	37.92
				Found	21.60	3.68	14.84	22.32	37.81

solubility. Nevertheless, the second approach is usually preferable since troublesome hydrolysis of tetrameric phosphonitrilic chloride and of its substitution products is eliminated, and yields are correspondingly improved. Complete purification is rendered difficult in both cases, however, by conversion of considerable quantities of the tetramer into an uncharacterized oily resinous material. It is remarkable that use of the tetrameric chloride and amine in a 1:2 mole ratio yielded only disubstituted products, plus unreacted tetramer, and no monosubstituted derivative.

The infrared spectra (Table I) of most of the compounds prepared exhibit bands between 1305 and 1315 cm.$^{-1}$, the region assigned by Daasch[18,19] to the P_4N_4 ring system. Certain compounds, however, have bands in the *ca.* 1220–1290 cm.$^{-1}$ region, a region also reported for the octasubstituted dimethylamine derivative.[15] There is no indication in these data of change in ring size or of ring opening.

Further structural evidence has been obtained from nuclear magnetic resonance spectra. The spectra for compounds containing aliphatic and heterocyclic substituents could not be resolved and suggested only a single type of phosphorus environment. These observations are consistent with the view that substitution of an alkyl or saturated heterocyclic nitrogen for chlorine does not measurably affect the shielding of the phosphorus atom involved. Compounds with aromatic amine substituents, except for *m*-toluidine and N-methylaniline where no signals could be observed, show two triplets of equal intensity, however, as indicated for the dianilino derivative in Fig. 1. This six-line pattern is characteristic only of *trans* ring substitution, since here each phosphorus atom is affected by two unlike phosphorus atoms. For *cis* substitution, a pair of doublets of equal intensity would be expected. The third possible structure, with both amine groups bonded to the same phosphorus atom, is ruled out by intensity considerations since for it the presence of three times as much phosphorus in one environment as in the other would lead to unequal areas covered by the maxima.



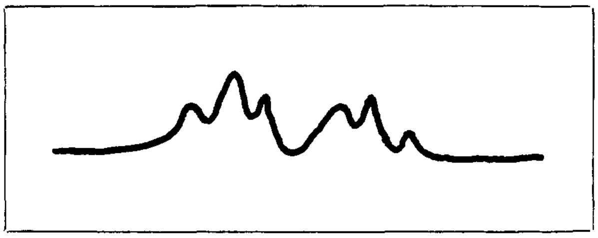


Fig. 1.—Phosphorus-31 nuclear magnetic resonance spectrum of $P_4N_4Cl_6(NHC_6H_5)_2$.

Chemical shifts for three compounds that show this six-line pattern are summarized in Table II. There is some indication of the development of this type of pattern among alkyl derivatives as the bulk of the alkyl group increases, but it is not completely definitive. However, it is reasonable to conclude that these amine disubstituted derivatives of the tetrameric chloride have the *trans* ring configuration.

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[18] L. W. Daasch, THIS JOURNAL, 76, 3403 (1954).

[19] L. W. Daasch and D. C. Smith, *Anal. Chem.*, 23, 853 (1951).

Experimental

Only typical syntheses are described to illustrate the general methods employed. Yield, melting point and analytical data for all the compounds prepared are summarized in Table III.

Method 1a—Two Solvent Phases. Bis-(methylamino)-hexachloro-tetraphosphonitrile.—11.59 g. (0.025 mole) of tetrameric phosphonitrilic chloride[20] was dissolved in 400 ml. of diethyl ether in a flask fitted with a stirrer and two burets. One buret contained a solution of 3.38 g. (0.05 mole) of monomethylamine hydrochloride in 100 ml. of water: the other contained a solution of 5.61 g. (0.1 mole) of potassium hydroxide in 100 ml. of water. A few drops of brom thymol blue were added to the ether solution, and the two aqueous solutions then were added to the vigorously stirred ether solution in such fashion that the reaction medium remained at the neutral point. Addition of the reagents was complete in 1 hr. The aqueous phase containing potassium chloride and hydrolysis products was removed. The ether layer was decolorized with activated charcoal, dried over calcium chloride and evaporated. The oily residue remaining was extracted with boiling petroleum ether and the crude bis-(methylamino)-hexachlorotetraphosphonitrile remaining was purified by repeated recrystallization from petroleum ether.

Method 1b—Two Solvent Phases. Bis-(anilino)-hexachloro-tetraphosphonitrile.—A solution of 46.36 g. (0.1 mole) of tetrameric phosphonitrilic chloride in 400 ml. of diethyl ether, to which *ca.* 400 ml. of water had been added, was stirred vigorously, and a solution of 37.25 g. (0.4 mole) of aniline in 100 ml. of ether was added over a period of 1 hr. Stirring then was continued for an additional hour. The ether layer next was separated and treated as outlined above. The product was purified by repeated recrystallization from *n*-heptane.

Method 2—Anhydrous Media. Bis-(N-methylanilino)-hexachloro-tetraphosphonitrile.—46.36 g. (0.1 mole) of tetrameric phosphonitrilic chloride was dissolved in 1200 ml. of anhydrous benzene. The solution was refluxed gently while 44.26 g. (0.4 mole) of N-methylaniline, diluted to double its volume with benzene, was added over a period of 3 to 4 hr. Refluxing was continued for an additional 10 hr. Precipitated amine hydrochloride was removed by filtration in the absence of moisture, and the slightly colored filtrate was evaporated to dryness without regard for separating hydrochloride. The desired product was removed by extraction with petroleum ether and purified by recrystallization from a 1:3 mixture of benzene and petroleum ether.

Instrumental Studies.—Infrared spectra were measured with a Perkin–Elmer spectrometer, Model 21, using a sodium chloride prism. The nuclear magnetic resonance spectra of phosphorus-31 were measured with a Varian Model V-4300B instrument, employing a Varian magnet Model V-4012-HR, with a 16.2 mc. radiofrequency oscillator and a field of 9395 gauss. Microanalyses for phosphorus and chlorine were made by the Clark Microanalytical Laboratory, Urbana, Illinois.

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[20] Obtained from Albright and Wilson Mfg. Ltd., Oldbury, Birmingham, England, and purified by repeated distillation in vacuum (12 mm. (188°)); m.p. 124°.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

The Boron Trifluoride Addition Compounds of Dimethyl Ether and Diethyl Ether[1,2]

BY DONALD E. MCLAUGHLIN[3] AND MILTON TAMRES

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An apparatus is described which permits convenient, rapid, and constant temperature control over a wide range of temperature in manometric studies. This is achieved by placing the reaction vessel in the vapor of a pure, boiling liquid whose boiling point can be changed rapidly to a desired temperature by varying the pressure on the liquid. As a check on the apparatus, the boron trifluoride addition compounds of dimethyl ether and diethyl ether were studied and the results are compared with those reported by Brown and Adams.[4] The agreement between the two studies is good. Somewhat closer agreement is obtained by modifying an assumption made by Brown and Adams in their investigation.

Introduction

The manometric investigation of interacting gaseous species is a method which is widely used to determine thermodynamic data for the formation of molecular addition compounds. The usual practice in such an investigation is to surround the manometric unit with a liquid bath, such as mineral oil, in order to control the temperature of the system. Since this method of temperature control is slow and somewhat inconvenient, a thermostat and manostat unit was designed which used the vapor of a pure boiling liquid for temperature regulation. With this unit a range of temperatures could be obtained by controlling the pressure upon the boiling liquid.

The addition compounds of boron trifluoride with dimethyl ether and diethyl ether were chosen to check the correct functioning of the apparatus, since thermodynamic data for the gas phase dissociation of these two addition compounds had been reported in the literature.[4,5]

An added reason for the choice of dimethyl ether:boron trifluoride for study was to attempt to clarify a somewhat controversial point regarding its stability. Analysis of electron diffraction data[6] for this addition compound, which was based on a relatively large extent of dissociation,[5] was ques-

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 133rd Meeting of the American Chemical Society, San Francisco, California, April, 1958.

[2] Taken in part from the Ph.D. thesis of Donald E. McLaughlin, University of Michigan, June, 1959.

[3] Department of Chemistry, Augustana College, Rock Island, Illinois.

[4] H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

[5] A. W. Laubengayer and G. R. Findlay, *ibid.*, **65**, 884 (1943).

[6] S. H. Bauer, G. R. Findlay and A. W. Laubengayer, *ibid.*, **65**, 889 (1943).