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The Structure of 2,4,6,8-Tetrachloro-2,4,6,8-tetramethylcyclohexylaminotetraphosphazine, $P_4N_4Cl_4(CH_3NC_6H_{11})_4$

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Pmr studies, including double resonance, of 2,4,6,8-tetrachloro-2,4,6,8-tetramethylcyclohexylaminotetraphosphazine, the product of the high-yield reaction between a hindered amine, N-methylcyclohexylamine, and $[PNCl_2]_4$, as well as two derivatives, $PH(NHCH_3)(CH_3NC_6H_{11})_4$ and $P_4N_4(NHCH_3)_3(CH_3NC_6H_{11})_4(CH_3NC(O)NHC_6H_5)$, indicate a *β-trans* structure. Evidence is presented that tetrameric phosphonitrilic chlorides react sequentially with pairs of amines at the 2,6 and 4,8 positions, with each substitution taking place *trans* to the previous one.

Tetrasubstituted aminolysis products of $[PNCl_2]_4$ have been reported previously. Of the several possible structures for $P_4N_4Cl_4R_4$ (where R = $N(CH_3)(C_6H_5)$ (I) or NC_5H_{10} (II)) phosphorus-31 nmr spectra indicate that I and II are symmetrically substituted phosphonitriles.[3] Although there are four possible isomers of I and II, as shown in Figure 1, only a single isomer of each was formed in yields of 50% or better.

Steric factors as well as the basicity of the amine are important in determining whether geminal or nongeminal substitution occurs.[4] These factors also are important in determining the mode of nongeminal substitution about the tetrameric ring. We can now demonstrate that the resulting tetrasubstituted product, formed in over 90% yield by reaction with a hindered amine, has the *β-trans* configuration.

By treating $[PNCl_2]_4$ with a large excess of N-methylcyclohexylamine a greater than 90% yield of $P_4N_4Cl_4(N(CH_3)C_6H_{11})_4$ (III) is obtained

$$[PNCl_2]_4 + 8HN(CH_3)C_6H_{11} \xrightarrow{\text{THF}} \underset{\text{III}}{[PNCl(CH_3NC_6H_{11})]_4} + 4HN(CH_3)C_6H_{11}\cdot HCl \quad (1)$$

In order to determine which isomer III is, the following reactions were carried out to yield derivatives $P_4N_4(HNCH_3)_4(CH_3NC_6H_{11})_4$ (IV) and $P_4N_4(HNCH_3)_3(CH_3NC_6H_{11})_4(CH_3NC(O)NHC_6H_5)$ (V)

$$\text{III} + 8CH_3NH_2 \xrightarrow{\text{THF}} \underset{\text{IV}}{[PN(HNCH_3)(CH_3NC_6H_{11})]_4} + 4CH_3NH_2\cdot HCl \quad (2)$$

$$\text{IV} + C_6H_5NCO \longrightarrow \underset{\text{V}}{P_4N_4(HNCH_3)_3(CH_3NC_6H_{11})_4(CH_3NC(O)NHC_6H_5)} \quad (3)$$

Pmr spectral studies of III, IV, and V, utilizing ^{31}P heteronuclear decoupling, allowed a unique isomer assignment to be given to III.

If aminolysis at each phosphorus takes place by the same mechanism, *i.e.*, with inversion or retention, then the mode of substitution does not affect the geometric structure of the products. On this basis, the structure of V would be representative of the structure of III.

The pmr spectrum of III (shown in Figure 2) deviates from the spectrum predicted by a simple first-order treatment (simple doublet for N-methyl protons) due to virtual coupling. The N-methyl absorption peak is approximately a triplet. Harris[5] has shown that this type of spectrum appears in strongly coupled cases where $|J_{PP'}| >> |J_{PH}-J_{P'H}|$ and that *the sharp outer pair of lines will always be present when there is a spin system with two groups of chemically equivalent nuclei of the type* $X_nX'_nX''_n\ldots AA'A''$.

The observed spectrum indicates that III is a phosphonitrilic tetramer, nongeminally substituted (by which is meant, here and below, that each phosphorus atom has bonded a methylamide and a chlorine atom as the other substituent), and has either the *β-trans*, *γ-trans*, or *cis* structure.

The fractional intensity of the sharp outer lines corresponds to the tetramer shown by Allen, *et al.*,[6] where the fraction is $^1/_4$. Furthermore, the sharp outer pair of lines is indicative of a spin system of two groups of chemically equivalent nuclei,[5] *e.g.*, a nongeminally substituted compound, not a geminally substituted compound, or the nongeminally substituted *α-trans* isomer.

Smalley, Dickson, and Bezman[7] have shown that decoupling ^{31}P nuclei from ^1H nuclei in phosphonitrilic cyclic amides can be used to advantage in simplifying pmr spectra. Heteronuclear decoupling of phosphorus, while observing the proton spectrum of III, shows a sharp singlet for the methyl groups. Only the *β-trans*, *γ-trans*, or *cis* structures are compatible with this.

Supporting evidence on the nongeminal substitution of III is found in the separation of the sharp outer lines of the proton spectrum, observed to be 16 Hz. The separation of these lines is given by $J_{PH} + J_{P'H} + J_{P''H} + \ldots$[5] Phosphorus–proton coupling constants in nongeminally substituted phosphonitrilic dimethyl-

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[3] K. John, T. Moeller, and L. F. Audrieth, *J. Am. Chem. Soc.*, **83**, 2608 (1961).

[4] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).

[5] R. K. Harris, *Inorg. Chem.*, **5**, 701 (1966).

[6] G. Allen, D. J. Oldfield, N. L. Paddock, F. Rallo, J. Serregi, and S. M. Todd, *Chem. Ind.* (London), 1032 (1965).

[7] J. H. Smalley, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 1780 (1964).

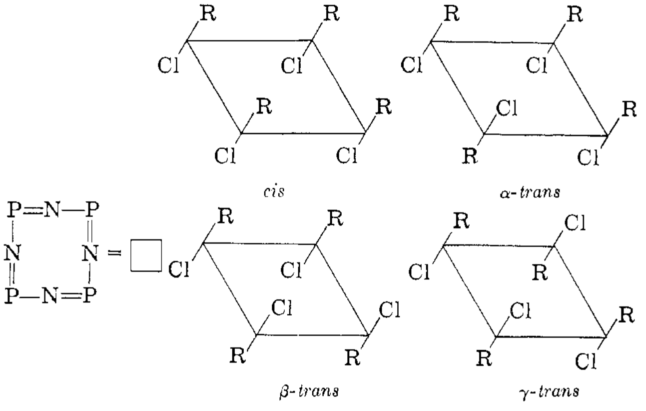

Figure 1.

amides are generally found to be about 17 Hz,[8,9] whereas in geminally substituted dimethylamides J_{PH} is 11–13 Hz.[6,8,9] This is true in cases where virtual coupling is observed and the separation of the sharp outer lines is measured as well as where it is not, indicating that $J_{P'H}$ and $J_{P''H}$ are both quite small with respect to J_{PH}. The variation of J_{PH} with respect to geminal and nongeminal substitution of monomethylamides is similar to that observed in the dimethylamides.[10]

The pmr spectrum of IV, consistent with the assigned structure, is shown in Figure 3. The N-methyl protons consist of two overlapping peaks which show virtual coupling. In the heteronuclear decoupled spectrum these peaks have collapsed to two sharp singlets of equal intensity. This result does not yet allow us to distinguish among the *β-trans*, *γ-trans*, and *cis* structures. The separation between the sharp outer lines (observed on the D_2O-exchanged sample which is not shown) is now about 13 Hz, the expected result for geminal amide substitution.

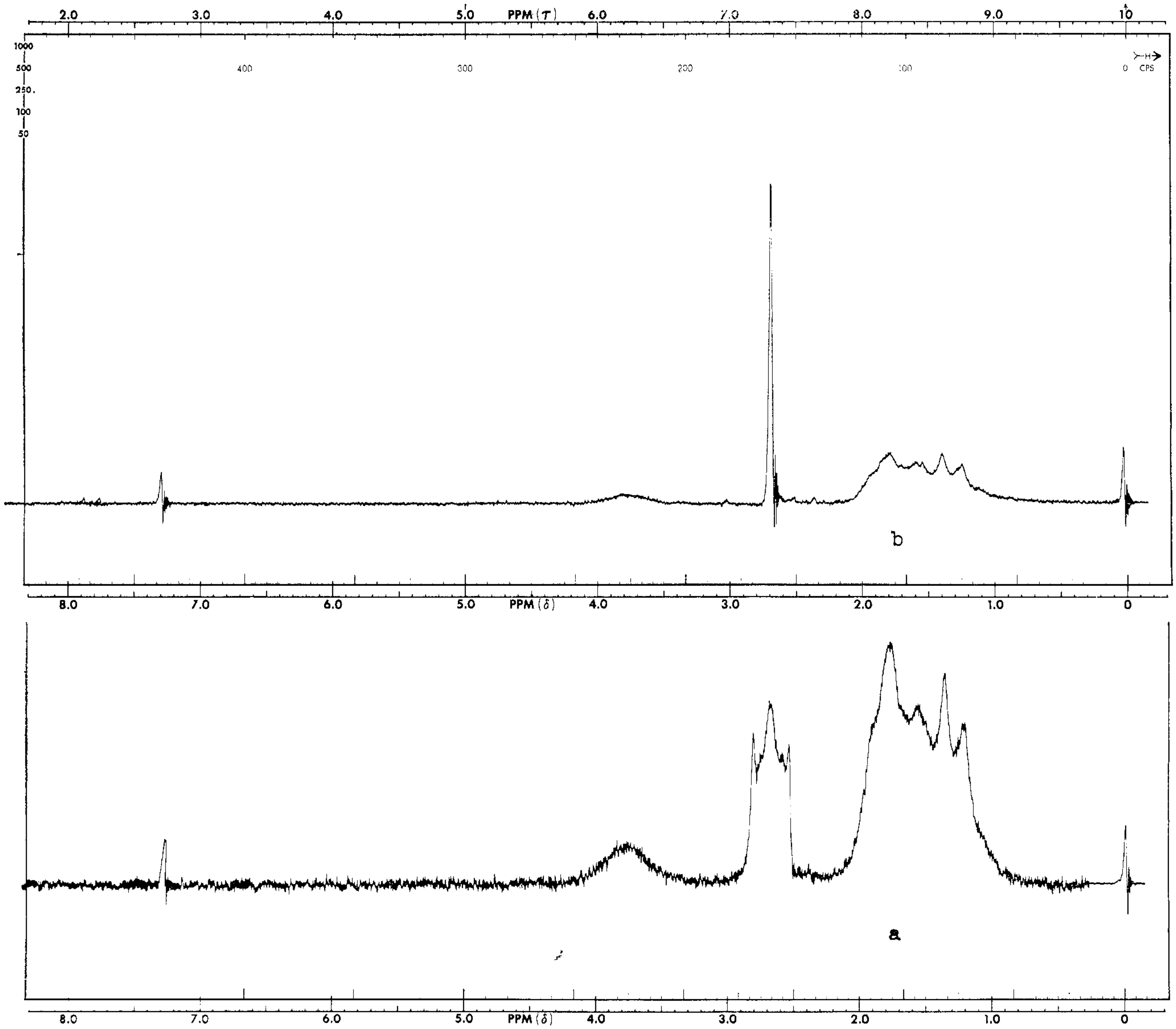

Figure 2.—Pmr spectra of $P_4N_4Cl_4(CH_3NC_6H_{11})_4$: (a) in chloroform; (b) decoupled.

Whereas for III the methyl groups are in a single

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(8) H. Koopman, F. J. Spruit, F. VanDeursen, and J. Bakker, *Rec. Trav. Chim.*, 341 (1965).

(9) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **6**, 1594 (1967).

(10) A. J. Berlin, B. Grushkin, and R. Rice, unpublished data.

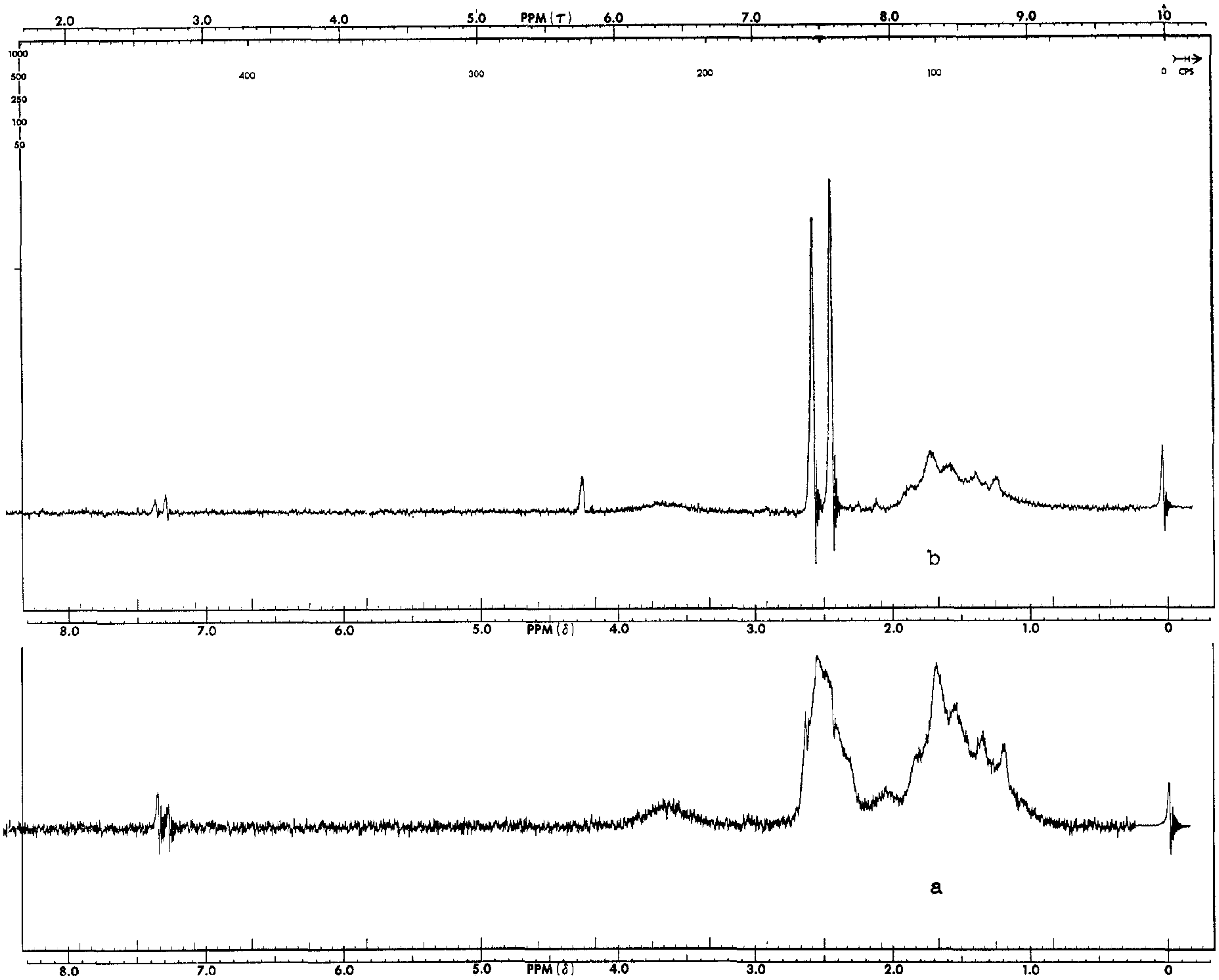


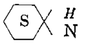
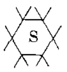
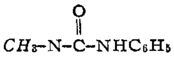
Figure 3.—Proton nmr spectra of $P_4N_4(HNCH_3)_4(CH_3NC_6H_{11})_4$: (a) in chloroform; (b) after D_2O exchange and ^{31}P decoupling.

environment, as a result of reactions 2 and 3 methyl groups of V would all be chemically nonequivalent for a *β-trans* structure. The decoupled spectrum of this compound would be expected to consist of eight methyl singlets, or less if some of the peaks accidentally had similar magnetic environments. The *γ-trans* or *cis* structures have six methyl environments in a ratio of 2:2:1:1:1:1. The decoupled spectra of these would be expected to exhibit at most six methyl peaks, less if a fortuitous magnetic similarity existed among some of them.

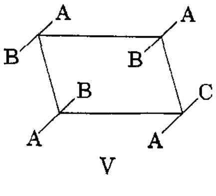
The pmr spectrum of V is illustrated in Figure 4. Assignments of the chemical shifts for V are given in Table I. Seven methyl peaks (after decoupling and D_2O exchange) are observed. Three singlets are assigned to methyl groups of $DNCH_3$ on the basis of the appearance of the spectrum before and after D_2O exchange. Another singlet at τ 6.94 is assigned to the methyl group of $N(CH_3)C(O)NDC_6H_5$. Three methyl peaks remain but one of them has twice the intensity of each of the other six. Therefore, V has eight nonequivalent methyl groups with two methyl groups having a similar chemical shift.

TABLE I

CHEMICAL SHIFT OF VARIOUS PROTONS IN *β-trans*-$P_4N_4(NHCH_3)_3(NCH_3C_6H_{11})_4(NCH_3CONHC_6H_5)$

Proton count	Chemical shift, τ	Multiplicity under decoupling	Type of proton
5	2.3–3.1	Extremely complex	Aromatic
1	−1.7	Singlet, med broad	NH–C_6H_5
4	6.4	Broad, featureless	
9	7.53, 7.56, 7.58	3 singlets 1:1:1	D–N–CH_3
12	7.42, 7.45, 7.47 (2)	3 singlets 1:1:2	CH_3–N–C_6H_{11}
3	8.0	Broad singlet, disappears after D_2O exchange	CH_3–N–H
40	8.0–9.2	Broad, complex	 all non methine cyclohexyl
3	6.97	Singlet	 $CH_3\text{–N–}\overset{\overset{\large O}{\|}}{C}\text{–NHC}_6H_5$

Of the three possible structures for V, only the β-



A = $-N(CH_3)C_6H_{11}$
B = $-NHCH_3$
C = $-N(CH_3)C(O)NHC_6H_5$

V

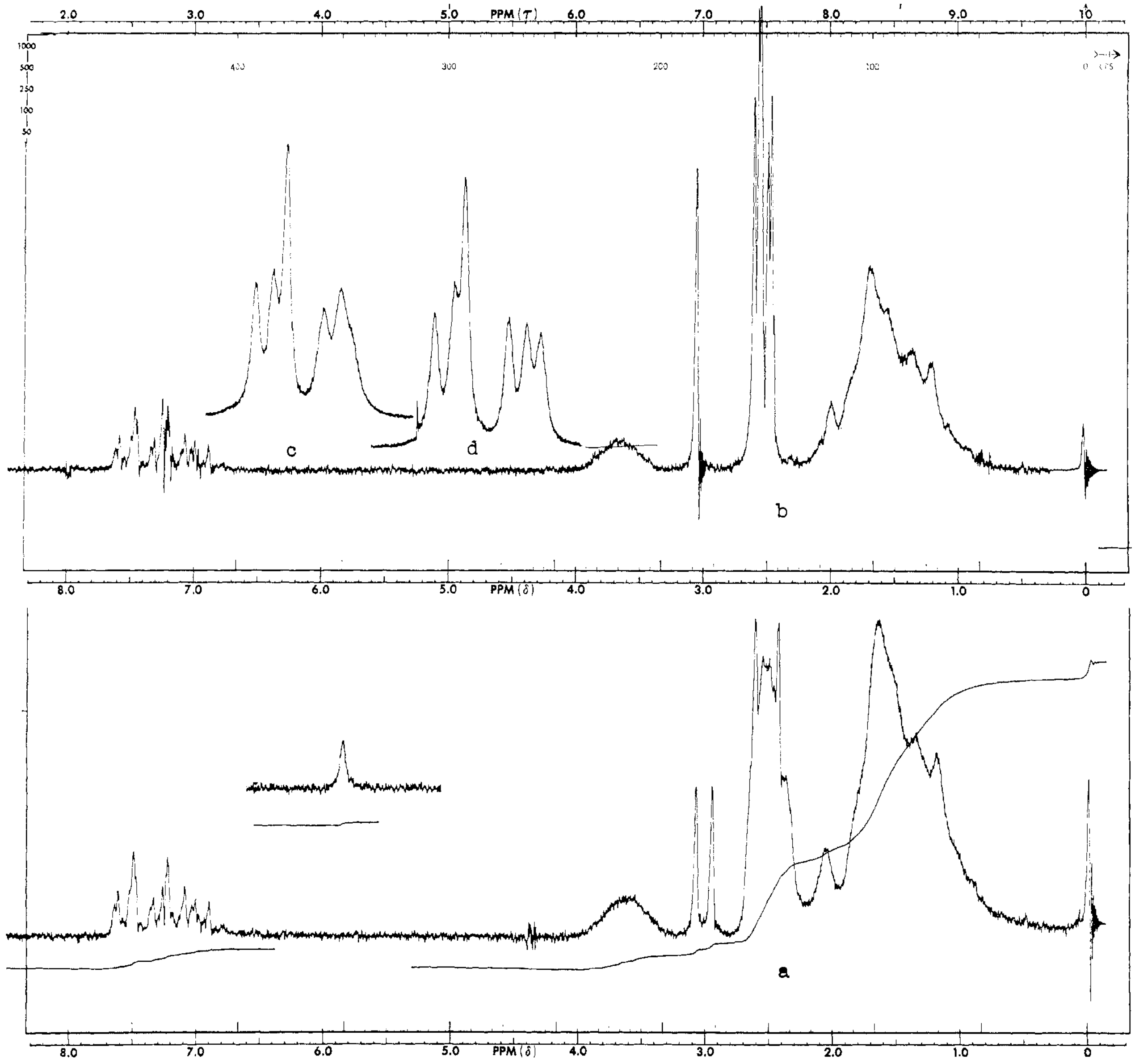
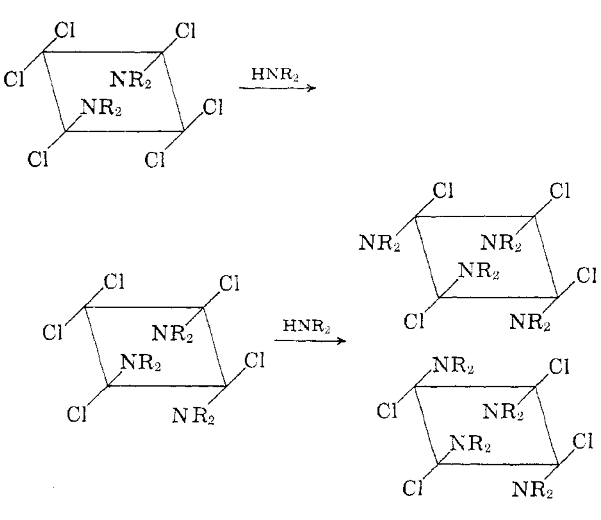


Figure 4.—(a) Pmr spectrum of $P_4N_4(NHCH_3)_3(CH_3NC_6H_{11})_4(CH_3NCONHC_6H_5)$; (b) after D_2O exchange and ^{31}P decoupling; (c) expanded spectrum of $(NHCH_3)_3$ and $(CH_3NC_6H_{11})_4$; (d) same as (c) except that amide protons have been exchanged with D_2O.

trans configuration is consistent with the observed spectrum. Compound III also can be assigned the *β-trans* structure if our earlier assumption that the geometry is not affected by reactions 2 and 3 is correct.

In addition to preparing tetrasubstituted phosphonitriles I and II, John, *et al.*,[11] also prepared disubstituted tetrameric phosphonitriles, $P_4N_4Cl_6(NR_2)_2$. A *trans*-2,6 structure was proposed for these compounds on the basis of their ^{31}P nmr spectra. If it is assumed that the disubstituted precursor of III also has a *trans*-2,6 configuration, then further substitution could result in only *α-trans*- and *β-trans*-tetrasubstituted products. This is illustrated by the reaction following sequence



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[11] K. John, T. Moeller, and L. F. Audrieth, *J. Am. Chem. Soc.*, **82**, 5616 (1960).

Conversely, if the precursor of III is *cis*-2,6 disubstituted, further substitution could not lead to a β-*trans*-tetrasubstituted product. Therefoure our results indirectly substantiate those of John, *et al.* We can conclude that *for phosphonitrilic tetramers pairs of amines react sequentially at the 2,6 and 4,8 positions with each substitution taking place trans to the previous one.*

The stereospecificity of reaction 1 can be attributed primarily to the bulkiness of the amine. However, an explanation for the formation of a single nongeminal isomer is not yet clear. Complicating the mechanistic picture is the fact that the tetrameric ring is not planar but puckered.[12,13] Consequently, through-space interactions of the amine ligand and the leaving group may contribute to the over-all mechanism.

Experimental Section

$P_4N_4Cl_4(N(CH_3)(C_6H_{11}))_4$ (III).—To a solution of freshly distilled N-methylcyclohexylamine (91.7 g, 0.81 mole) in 500 ml of dry tetrahydrofuran cooled in an ice–salt bath was added dropwise with stirring a solution of $(PNCl_2)_4$ (46.4 g, 0.1 mole) in 200 ml of dry tetrahydrofuran. The temperature of the reaction mixture was maintained at −5 to 0° throughout the addition of the phosphonitrilic chloride solution. When addition was complete, the cooling bath was removed and the mixture was stirred at room temperature for 24 hr. At the end of this time, the N-methylcyclohexylamine hydrochloride which had separated was collected by filtration; yield, 59.9 g, 99%. The combined filtrate and washings were concentrated *in vacuo*, and the oily residue was triturated with acetonitrile. From the mixture was separated 69.1 g (90% yield) of solid, mp 118–121°, which upon recrystallization from a 4:1 solution of acetonitrile–benzene had a melting point of 126.5–128°.

Anal. Calcd for $C_{28}H_{56}Cl_4N_8P_4$: C, 43.64; H, 7.33; N, 14.54; Cl, 18.40; P, 16.09. Found: C, 43.48; H, 7.64; N, 14.31; Cl, 18.54; P, 17.17.

$(N(CH_3)(C_6H_{11}))_4P_4N_4(NHCH_3)_4$ (IV).—Tetra-N-methylcyclohexylaminotetrachlorotetraphosphonitrile (III) (41.6 g, 0.054 mole) was dissolved in 500 ml of dry tetrahydrofuran, and gaseous monomethylamine was introduced just over the surface of the stirred solution. When the exothermic reaction had spontaneously reached room temperature, introduction of the monomethylamine was stopped and the resulting mixture was stirred at room temperature for 24 hr. At the end of this time, the solid which had separated was collected by filtration and the filtrate was concentrated using a rotary vacuum evaporator. The residue was combined with the separated solid and the mixture was exhaustively extracted with benzene in a Soxhlet apparatus. The insoluble monomethylamine hydrochloride was collected and weighed; yield, 14 g, 97%. The extracts were evaporated to dryness and the residue (34.4 g, 85% yield, mp 174–176°) was recrystallized from benzene as a crystalline solid, mp 176–177°.

Anal. Calcd for $C_{32}H_{72}N_{12}P_4$: C, 51.32; H, 9.69; N, 22.45; P, 16.54. Found: C, 51.81; H, 9.78; N, 22.45; P, 17.25.

$(N(CH_3)(C_6H_{11}))_4P_4N_4(NHCH_3)_3(N(CH_3)CONHC_6H_5)$ (V).—This compound was prepared from the reaction of 7.5 g (10 moles) of IV with 1.07 g (9 moles) of freshly distilled phenyl isocyanate in 225 ml of benzene under a nitrogen atmosphere. The solution was kept at reflux for 20 hr after which the solvent was removed by distillation *in vacuo*. The oily residue was triturated with *n*-hexane and the solid (0.8 g) which separated was removed by filtration. The filtrate was concentrated to the point of incipient cloudiness and stored at −25°. After 7 days the solid which had formed (1.3 g, 17% yield, mp 130–135°) was separated. After recrystallization from Super Naphtholite,[14] the crystalline solid had a melting point of 134–135°.

Anal. Calcd for $C_{39}H_{77}N_{13}OP_4$: C, 53.96; H, 8.94; N, 20.98; P, 14.27. Found: C, 54.15; H, 9.09; N, 21.05; P, 14.93.

The residue obtained on evaporation to dryness of the hexane filtrate was dissolved in refluxing Super Naphtholite. The white solid which separated from the cooled solution was found to be unreacted IV, mp and mmp 176–177°; yield, 4.5 g, 60% recovery. The infrared spectra of the two compounds were identical.

The solid which first separated on trituration of the reaction mixture with *n*-hexane was recrystallized from Super Naphtholite and identified as the disubstituted derivative, mp 216–217°.

Anal. Calcd for $C_{46}H_{82}N_{14}O_2P_4$: C, 55.96; H, 8.37; N, 19.87; P, 12.55. Found: C, 56.21; H, 8.12; N, 19.77; P, 13.44.

Proton Magnetic Resonance.—Pmr spectra were obtained on a Varian Associates A-60A spectrometer. The probe insert was fitted with a transmitting coil for decoupling experiments by N.M.R. Specialties Co.

Decoupling experiments were carried out by means of an N.M.R. Specialties H.D. 60A Decoupler. This was swept by means of the Hewlett-Packard 200 CDR audio oscillator fitted with a fine-tuning vernier dial constructed by Mr. J. Light of W. R. Grace & Co. (details will be published at a later date). Special care was taken in decoupling V since all ^{31}P nuclei are nonequivalent.

Spectra were calibrated with the above audio oscillator using the Hewlett-Packard 522 B Counter.

Deuteriochloroform was used as the solvent with TMS as an internal standard.

Analyses.—Elemental analyses were performed by the Chemistry Branch of the Materials Division, Propulsion and Vehicle Engineering Laboratory, George C. Marshall Space Flight Center, Huntsville, Ala.

Acknowledgment.—The authors wish to thank Mr. Karel Ensing for his assistance in obtaining the pmr spectra and Professor Barry Shapiro for his valued advice during various aspects of this work.

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[12] M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem' Soc.*, 2424 (1960).

[13] It seems probable that in solution time-averaging, through-ring motions occur giving equivalent methyl groups in these tetrameric rings.

[14] Obtained from Amsco Solvents and Chemicals Co., Cincinnati, Ohio.