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Phenylphosphonitriles. III. Structural Identification of Geometric Isomers of Tetrameric Phenylphosphonitrilic Chloride

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Of the four possible geometric isomers of tetrachlorotetraphenyltetraphosphonitrile, *cis*, *α-trans*, and *β-trans* compounds have been identified. The *cis* and *α-trans* tetrachloro isomers melt at 225.5–226° and 155–156°, respectively. The *β-trans* isomer melts at 260–263°. Proton n.m.r. analysis of the derived tetrakisdimethylamides readily distinguished the *α-trans* compound. The *cis* configuration was assigned to the isomer melting at 225.5–226° by comparing dielectric constants of equimolar benzene solutions of tetrachloro compounds and derivatives. In every case dielectric constants measured for solutions of the tetrachloro isomer melting at 225.5–226° and its derivatives were higher than those of the other isomers. The *β-trans* isomer was characterized by proton n.m.r. spectra of derivatives, $(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)P(C_6H_5)_2]$ and $(C_6H_5)_4P_4N_4(NHCH_3)_3N(CONHC_6H_5)$. By comparing the n.m.r. spectra of these derivatives with spectra obtained for the analogous *cis* derivatives, the *β-trans* structure was readily determined.

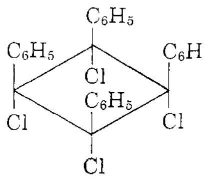
Introduction

From the reaction of tetrachlorophenylphosphorane with ammonium chloride it is possible to prepare cyclic chlorophenylphosphonitriles. This reaction, when first

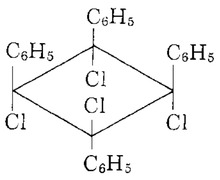
$$xC_6H_5PCl_4 + xNH_4Cl \longrightarrow [C_6H_5PNCl]_x + 4xHCl \quad x = 3, 4, 5, \text{etc.} \quad (1)$$

attempted by Bode and Bach,[1] did not yield the desired cyclic products. Shaw and Stratton[2] and Humiec and Bezman[3] both obtained the desired chlorophenylphosphonitrilic trimer and tetramer from reaction 1. More recently,[4] we have reported an improved synthesis of $[C_6H_5PNCl]_3$ by reaction 1 as well as a full characterization of the two trimeric geometric isomers which are possible.

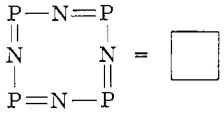
For the tetrameric product of reaction 1 four geometric isomers are possible.

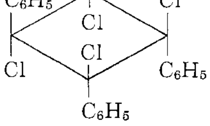


cis

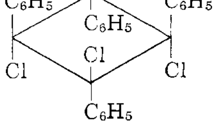


α-trans





β-trans



γ-trans

Three tetrameric products were reported by Shaw and co-workers[2b] to melt at 148° (I), 202° (II), and 248° (III); however, no structural assignments were made. Recently, we reported that the lowest melting isomer has the *α-trans* configuration.[5] This assignment was confirmed subsequently by Smalley, *et al.*[6] They also assigned the *γ-trans* structure to II and believed that III may be the *cis* isomer, but did not rule out the possibility that III may have the *β-trans* configuration. On the other hand, we have found that II, as reported by Smalley, *et al.*, and by Shaw, is an impure *cis* isomer and that III is the *β-trans* isomer. Our assignments are based on proton n.m.r. spectra of derivatives and dielectric constant measurements.

Discussion

Isolation of Tetramers.—Reaction of $C_6H_5PCl_4$ with ammonium chloride in chlorobenzene[4] or in the melt[7] results in the formation of cyclic trimers and tetramers of (C_6H_5PNCl). From the reaction in chlorobenzene three tetrameric materials were isolated by successive extractions of the crude product with *n*-hexane and then benzene. Initially, extraction of the crude product with *n*-hexane gave a mixture of trimers and tetramers I and II. We were able to effect a separation of trimers from tetramers by recrystallizing the extracted solids. Subsequently, extraction of the remaining crude product with benzene gave only tetramer III. The tetrameric products melted at 155–156° (I), 225.5–226° (II), and 260–263° (III). They were identified as tetramers by their characteristic absorptions at 1280 cm.$^{-1}$ and by molecular weight determinations. The ratio in which they are usually isolated is 1.5:1:20.

Compound I, when isolated, melted at 148–150.5°; however, by slowly recrystallizing I from a mixture of benzene–pentane the melting point was raised to 152–154°, and an analytical sample was crystallized to melt at 155–156°. The melting point did not change upon solidification and remelting.

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

(2) (a) R. A. Shaw and C. Stratton, *Chem. Ind.* (London), 52 (1959); (b) *J. Chem. Soc.*, 5004 (1962).

(3) F. S. Humiec and I. I. Bezman, *J. Am. Chem. Soc.*, **83**, 2210 (1961).

(4) B. Grushkin, M. G. Sanchez, and R. G. Rice, *Inorg. Chem.*, **3**, 623 (1964).

(5) B. Grushkin, J. L. McClanahan, and R. G. Rice, *J. Am. Chem. Soc.*, **86**, 4204 (1964).

(6) J. H. Smalley, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 1783 (1964).

(7) I. I. Bezman and J. H. Smalley, German Patent 1,171,915 (June 11, 1965).

Isomer II, when first isolated, melted at 198–202°, but after several slow recrystallizations from a mixture of benzene and pentane, it melted, was solidified, and remelted at 225.5–226°. The major impurity in II was I.

When recrystallized very slowly from chloroform, the melting range of III could be raised from 248–254° to 255–260°. This could be raised further to 260–263° by recrystallization from ethyl acetate. Melting point behavior of III differed sharply from that of II and I. Repeated melting point determinations of III were lower and broader. Initially, the capillary melting point was 260–263°; however, upon solidification and reheating the melting point was lowered to 255–261° and then to 230–248°.

Identification of Isomers.—Tetrakisdimethylamide derivatives of I, II, and III were prepared by allowing the tetrachloro compounds to react with excess dimethylamine in benzene at room temperature. In every case the reaction was essentially quantitative, as indicated by the yield of dimethylamine hydrochloride recovered. An 85% yield, after purification, of tetrakisdimethylamide, m.p. 136–138° (IV), was obtained from the reaction of I with dimethylamine. From II a 91% yield of tetrakisdimethylamide (VI) was recovered. Compound VI could be crystallized to melt at 152–153° or 139–140° depending on the rate of crystallization. The lower melting material, upon resolidification and reheating, melted at 152–153°. This is the first example of dimorphism observed for these tetrameric compounds.

In an earlier communication,[5] we reported that dimethylamination of III resulted in the formation of two different tetrakisdimethylamides melting at 136–138° (IV) and 176–178° (V). The reaction was carried out in benzene at room temperature; however, in order to remove excess amine from the mixture it was brought to reflux before filtering. On the other hand, Smalley, *et al.*, reported the quantitative formation of V by dimethylamination of III with aqueous amine in tetrahydrofuran at room temperature.[8] We have confirmed their work and have also carried out this reaction in tetrahydrofuran under anhydrous conditions. In both cases only one product, compound V, is obtained.

It was believed initially that isomerization of V to IV may take place during the refluxing of the benzene solution while in the presence of amine hydrochloride. Recently, Keat and Shaw[9] have shown that, in a solvent such as chloroform, refluxing an amine hydrochloride with the aminochlorophosphonitrile can result in isomerization. On this basis, we carried out the following series of experiments: (1) refluxed V with $(CH_3)_2NH_2 \cdot HCl$ 4 hr. in benzene; (2) refluxed, IV with $(CH_3)_2NH_2 \cdot HCl$ 4 hr. in benzene; (3) refluxed IV with $(CH_3)_2NH_2 \cdot HCl$ 4 hr. in tetrahydrofuran; and (4) refluxed V with $(CH_3)_2NH_2 \cdot HCl$ 4 hr. in tetrahydrofuran. After removal of the amine hydrochloride and then the solvent, the residues were examined by proton n.m.r. spectroscopy. In no case was there any evidence of isomerization. At present we cannot explain this anomalous behavior of III; *i.e.*, aminolysis in benzene results in the formation of two products whereas aminolysis in tetrahydrofuran results in only one product. The situation is further complicated by the fact that aminolysis of both I and II in benzene gives excellent yields of single products. The results of further work in this area will be reported at a later date.

Proton n.m.r. spectra for these tetrakisdimethylamides have been reported previously.[5,6] The n.m.r. spectrum of IV showed three methyl doublet absorptions which occur in an area ratio of 1:2:1, whereas the spectra of V and VI each showed a single doublet. Each doublet in the spectrum represents a $-N(CH_3)_2$ group in a specific electronic environment. Only one methyl doublet should be observed for two or more $-N(CH_3)_2$ groups that are in equivalent environments. Therefore, for IV, two $-N(CH_3)_2$ groups are in different environments and the third and fourth $-N(CH_3)_2$ groups are in the same environment. These methyl environments exist only in the *α-trans* compound.

Since the n.m.r. spectra of V and VI each show a single methyl doublet, but at different chemical shifts, it can be assumed that V and VI are single compounds. The fact that excellent yields of single compounds are obtained by dimethylamination of I, II, and III eliminates the possibility that either I, II, or III is a solid solution of two or more isomers. Furthermore, it can be concluded that in the process of dimethylamination, each chlorine is replaced by the amine *via* the same mechanism, *i.e.*, with or without inversion about each phosphorus atom of the phosphonitrile tetramer ring.

The *β-trans* isomer was identified by means of proton n.m.r. spectra of derivatives of the type $(C_6H_5)_4P_4N_4X_3Y$, where $X = NHCH_3$ and $Y = (C_6H_5)PNCH_3$ or $CH_3NCONHC_6H_5$. Compounds of this type were prepared by first allowing III to react with an excess of monomethylamine. The result, as in the case of dimethylamination in benzene, was the isolation of two tetrakismonomethylamides melting at 151–152° (VII) and 119–122° (VIII). Reaction of III with monomethylamine in tetrahydrofuran, however, produced only VII. Compound VII also could be crystallized to melt at 129–130°. Compounds melting at 151–152° and 129–130° showed the same proton n.m.r. spectrum, thus providing a second example of dimorphism. Compound VIII also was prepared from I, therefore establishing that it is a derivative of the *α-trans* isomer and that VII must be a derivative of III.

Compound VII was allowed to react with 1 equiv. of $(C_6H_5)_2PCl$ in the presence of triethylamine. The monosubstituted product of this reaction was $(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)P(C_6H_5)_2]$ (IX), m.p. 220–222°. Compound VII also was allowed to react with 1 equiv. of phenyl isocyanate to yield $(C_6H_5)_4P_4N_4(NHCH_3)_3(CH_3NCONHC_5H_4)$ (X), m.p. 165–167°. The sequence

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[8] I. I. Bezman, private communication.

[9] R. Keat and R. A. Shaw, *Chem. Ind.* (London), 1232 (1964).

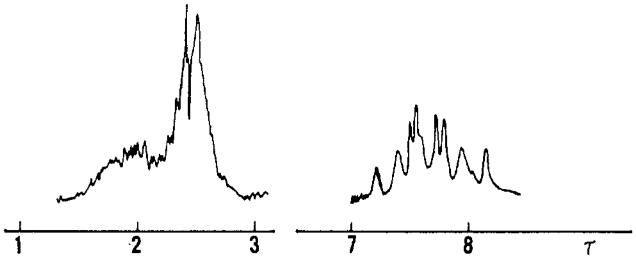


Figure 1.—Proton n.m.r. spectrum of β-*trans*-$(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)P(C_6H_5)_2]$ after deuterium exchange of amido protons.

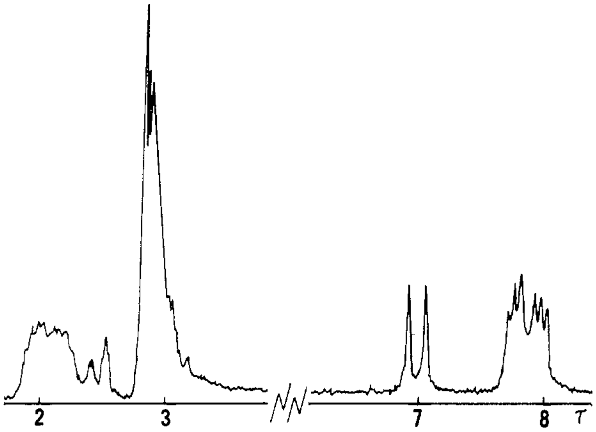


Figure 2.—Proton n.m.r. spectrum of β-*trans*-$(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)CONHC_6H_5]$ after deuterium exchange of amido protons.

of reactions leading to IX and X are illustrated by the equations

$$\underset{\text{III}}{[C_6H_5PNCl]_4} \xrightarrow[\text{THF}]{4NH_2CH_3} \underset{\text{VII}}{[C_6H_5PN(NHCH_3)]_4} \qquad (2)$$

$$\mathrm{VII}\begin{cases} \xrightarrow[\text{N}(C_2H_5)_3]{(C_6H_5)_2PCl} \underset{\text{IX}}{(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)P(C_6H_5)_2]} \\ \xrightarrow{C_6H_5NCO} \underset{\text{X}}{(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)CONHC_5H_5]} \end{cases} \qquad (3)$$

Proton n.m.r. spectra for IX and X after deuterium exchange of amido protons are shown in Figures 1 and 2, respectively. For each compound the spectrum shows four doublets, indicating that the methylamido groups are in four different environments. The only configuration that satisfies this requirement for IX and X is β-*trans*. Thus, compounds IX and X have β-*trans* configurations and the compounds from which they were derived, VII and III, also have β-*trans* configurations.

The reaction sequence when carried out with II gave the product $(C_6H_5)_4P_4N_4(NHCH_3)_3(CH_3NCONHC_6H_5)$ (XII), m.p. 125–129°. The crystalline product of reaction 4 recovered from a solution of cyclohexane–pentane melted at 78–80.5°. Elemental analysis of the product corresponds to $(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)CONHC_6H_5]\cdot C_6H_{12}$ (XIII). The presence of cyclohexane as a 1:1 adduct was also established by a proton n.m.r. spectrum of XIII. The spectrum of XIII, after deuterium exchange of amido protons, is shown in Figure 3. Three well-defined methyl doublets are apparent, with an area ratio of 1:2:1. Based on this spectrum, the only geometrical configurations possible for XIII are *cis* and γ-*trans*. For these two geometric structures three different methyl environments are present.

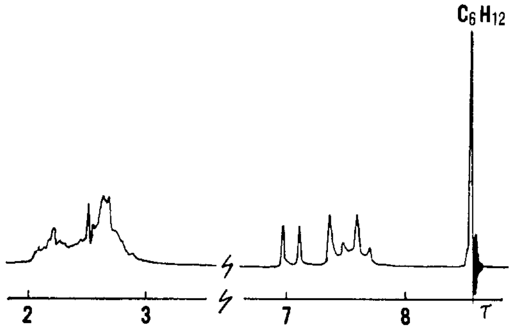
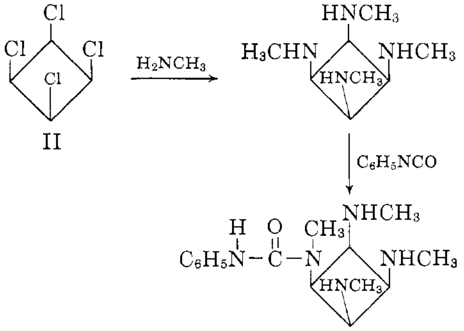
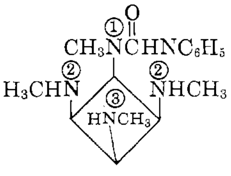


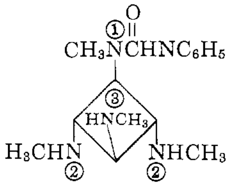
Figure 3.—Proton n.m.r. spectrum of *cis*-$(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)CONHC_6H_5]$ after deuterium exchange of amido protons.



XII (4)



cis



γ–*trans*

Dielectric constant measurements of benzene solutions of I and II and their derivatives establish the configuration of II. The dipole moment of the *cis* isomer should be greater than that of the α-*trans* isomer, and the dipole moments of both the β-*trans* and γ-*trans* isomers should be smaller than that of either the *cis* or α-*trans* isomer. Dielectric constants calculated from capacitance measurements of equimolar benzene solutions of I and II gave values of ϵ_{soln} for solutions of II which were higher than those obtained for I. Also, capacitance measurements were made of solutions of tetrakismonomethylamides of I and II with the same result. The capacitance of benzene solutions of tetrakisdimethylamides of I and III also were measured. A plot of ϵ_{soln} *vs.* concentration is illustrated in Figure 4.

The slopes of the curves for II and its tetrakisdimethylamide in each case are greater than those obtained for the corresponding α-*trans* compounds. If it is assumed that atomic and electron polarizations are

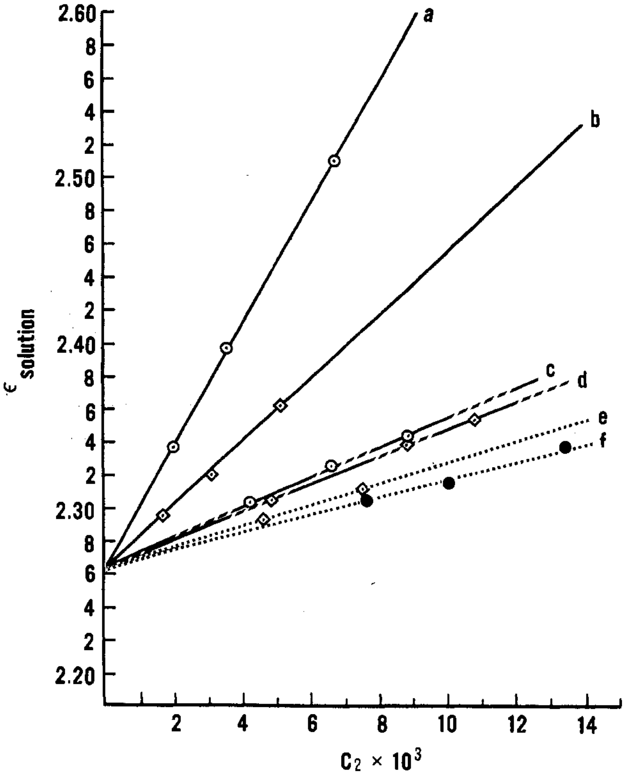


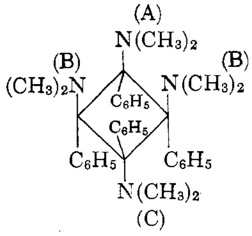
Figure 4.—Dielectric constants of benzene solutions at 30.0°: (a) *cis*-$[PNC_6H_5Cl]_4$; (b) *α-trans*-$[PNC_6H_5Cl]_4$; (c) *cis*-$[PNC_6H_5$-$NHCH_3]_4$; (d) *α-trans*-$[PNC_6H_5NHCH_3]_4$; (e) *α-trans*-$[PN_5$-$C_6H_5N(CH_3)_2]_4$; (f) *β-trans*-$[PNC_6H_5N(CH_3)_2]_4$.

essentially the same for both tetrachloro isomers and both tetrakisdimethylamides, then differences in dielectric constants must result mainly from differences in their permanent dipoles. Thus, it may be concluded that isomer II has a greater dipole than I. Since it has been established that I has the *α-trans* configuration, isomer II must therefore have the more polar *cis* configuration.

This interpretation of our dielectric constant data is consistent with the recently published results of Koopman, *et al.*[10] They elucidated the structures of nongeminal *cis*- and *trans*-$P_3N_3[N(CH_3)_2]_2Cl_4$ by means of dipole moment measurements. Their results show that the two isomers have nearly the same refractive indices, indicating that electron polarizations are essentially the same for the two isomers. Also, a plot of ϵ_{soln} *vs.* concentration for both trimeric isomers is similar to that shown in Figure 4 for *cis*- and *α-trans*-tetrachlorotetraphenyl isomers in that dielectric constants of equimolar benzene solutions are greater for the *cis* isomers.

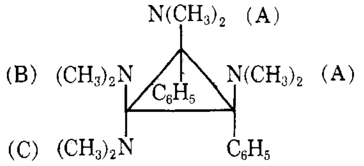
Our assignment of *cis* and *β-trans* configurations do not agree with those proposed by Smalley, *et al.*[6] They assigned to isomer II the *γ-trans* structure and to III the *cis* configuration, although on the basis of their data the *β-trans* configuration was not excluded. Because their assignments were based on small displacements (0.3–1.3%) of chemical shifts in the proton n.m.r. spectra of tetrakisdimethylamides when deuteriobenzene was added to chloroform solutions, they did not regard these as definitive assignments. They correlated the magnitude of displacements of the chemical shifts for *α-trans*-$[C_6H_5PNN(CH_3)_2]_4$, which has methyl groups in three different environments, with the displacement of the chemical shifts observed for the tetrakisdimethylamides of the other isomers.

The chemical shifts observed by Smalley, *et al.*, and in our laboratories for the *α-trans* tetrakisdimethylamide are τ 7.834, 7.500, and 7.414; area ratios were 1:2:1, respectively. All subsequent structural assignments of Smalley, *et al.*, are based on the assumption that these shifts can be assigned to the four $-N(CH_3)_2$ groups of the *α-trans* compounds. Their assignments are as follows.



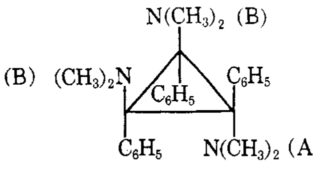
(A) τ 7.834
(B) τ 7.500
(C) τ 7.414

There is no question of the assignment of τ 7.500 to group (B) since the doublet has twice the area of the others. However, we believe that the assignments made to groups (A) and (C) are incorrect. Smalley, *et al.*, state, "$-N(CH_3)_2$ groups assumed to be neighbored by phenyls were found to appear at much lower fields than the corresponding $-N(CH_3)_2$ flanked only by other $-N(CH_3)_2$ groups." In support of this statement they cite that the proton n.m.r. spectrum of trimeric $(C_6H_5)_2P_3N_3[N(CH_3)_2]_4$[11] shows three methyl doublets in a 1:2:1 area ratio; consequently there exist three dimethylamido environments. This would indicate the structure



Here, as with the *α-trans* tetramer, one of the doublets, (A), can be assigned without any difficulty. However, as with the *α-trans* tetramer, there is a choice for assigning the remaining two doublets. Smalley, *et al.*, assume that the doublet which is farthest downfield arises from the $-N(CH_3)_2$ (C) group flanked by two phenyl groups.

We have obtained proton n.m.r. data for trimeric nongeminal *trans*-$(C_6H_5)_3P_3N_3[N(CH_3)_2]_3$. For this



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[10] H. Koopman, F. J. Spruit, F. Van Deursen, and J. Bakker, *Rec. trav. chim.*, **84**, 341 (1965).

[11] I. I. Bezman and C. T. Ford, *Chem. Ind.* (London), 163 (1963).

Table I

Analysis of Compounds

Compound	M.p., °C.	C, %		H, %		N, %		P, %		Cl, %		Mol. wt.	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
I	152–154	46.05	45.75	3.54	3.19	8.84	8.90	15.19	19.65	22.84	22.50	638	630
II	225.5–256	46.24	45.75	3.59	3.19	12.49	8.90	18.28	19.65	22.33	22.50	640	630
III	260–263	45.28	45.75	3.40	3.19	8.83	8.90	20.05	19.65	22.36	22.50	635	630
IV	136–138	57.17	57.80	6.57	6.68	16.57	16.86	18.08	18.63			670	664
V	176–178	57.65	57.80	7.03	6.68	16.52	16.86	15.42	18.63			683	664
VII	151–152	55.35	55.25	5.93	5.96	18.52	18.41	19.54	20.34			609	608.5
VIII	78–80.5	60.93	60.65	6.50	6.58	15.39	15.50	15.05	15.22				
IX	220–222	59.54	60.70	5.68	5.72	13.88	14.14					810	792.7
X	165–167	57.99	57.85	5.70	5.68	16.01	17.35	16.26	17.02			708	727.7

compound, τ 7.53 and 7.74, and these methyl doublets occur in an area ratio of 2:1, respectively. It is readily seen that, for this compound, both assignments are unequivocal. The value τ 7.53 must be assigned to groupings (B), and τ 7.74 belongs to grouping (A). Contrary to the assumptions of Smalley, *et al.*, the absorption of the $-N(CH_3)_2$ group flanked by two phenyl groups is at a higher field than absorption of $-N(CH_3)_2$ groups flanked by a $-N(CH_3)_2$ and a phenyl group. If this statement is also valid for symmetrically substituted cyclic tetramers, then the premise upon which Smalley, *et al.*, have made their assignments is incorrect.

The presence of a fourth tetrachloro isomer has never been observed as one of the products of the reaction of $C_6H_5PCl_4$ with ammonium chloride. We are attempting to prepare this isomer, which we believe will prove to have the γ-*trans* configuration, by a rearrangement reaction. This work will be reported at a later date.

Experimental Section

Synthesis of $[C_6H_5PNCl]_4$.—A mixture of 6 moles of dry NH_4Cl in 9 l. of chlorobenzene, in a 12-l. flask, was brought to reflux in a nitrogen atmosphere. Three moles of $C_6H_5PCl_4$ (prepared by bubbling Cl_2 into a $C_6H_5PCl_2$ solution) in 1 l. of chlorobenzene was added rapidly to the reaction flask. The solution was kept at reflux until no more HCl evolved. The solution then was filtered hot to remove the unreacted NH_4Cl, and the filtrate was evaporated to dryness, leaving 425 g. of solid. The reaction was repeated and 405 g. of solid product was recovered. Both solids were combined and extracted with *n*-hexane. Initial extraction of the product for 3 days removed approximately 235 g. of trimer. Subsequent extractions of the crude product with *n*-hexane gave approximately 20 g. of tetramer, m.p. 152–154° (I), and 15 g. of tetramer, m.p. 225.5–226° (II). Extraction of the remaining crude product with benzene gave, after recrystallization, 300 g. of tetramer melting from 248 to 254° (III). Elemental analyses for these products are given in Table I.

Dimethylaminations.—Three grams (4.76 mmoles) of III was allowed to react with an excess of dimethylamine in 50 ml. of benzene. The amine was added at room temperature; then the mixture was refluxed 30 min. and filtered while hot. The amine hydrochloride was not weighed because of its hygroscopic nature. It was, therefore, dissolved in water and the chloride was precipitated with $AgNO_3$ in the usual manner. Accordingly, 18.92 mmoles of chloride was recovered (expected for complete reaction, 19.04 mmoles). Therefore the reaction is essentially quantitative.

The benzene filtrate was evaporated to an oil which was taken up in benzene–pentane. After several days 0.6 g. of crystalline solid, m.p. 170–175°, was obtained. This solid was recrystallized to melt at 176–178° (V). Elemental analysis data are shown in Table I.

A second solid, 0.9 g., melting from 120 to 135° was also recovered. This was recrystallized three times from pentane to give an analytical sample of IV, m.p. 136–138°. The analysis is shown in Table I.

A 13-g. sample of tetramer, m.p. 248–254°, was dimethylaminated simply by putting the solid into 100 ml. of benzene and adding an excess of dimethylamine. The mixture was stirred overnight, after which it was brought to reflux and filtered hot. The amount of dimethylamine hydrochloride that was recovered corresponded to that expected for complete substitution to give $[C_6H_5PNN(CH_3)_2]_4$. The benzene filtrate was evaporated to dryness, and the residue was taken up in 80 ml. of hot *n*-hexane and allowed to stand for 48 hr., giving 6 g. of crystalline solid, m.p. 170–176°. Recrystallized from *n*-hexane, the solid melts at 176–178°. A second fraction, 2 g., melted from 130 to 160°, and a third fraction of 5 g. melted from 130 to 135°.

To 3 g. of tetramer, m.p. 260–263°, in 50 ml. of tetrahydrofuran was added an excess of dimethylamine. After 24 hr. the solution was filtered to remove amine hydrochloride. The volume of the filtrate was reduced by vacuum distillation and *n*-pentane added to the solution. Upon standing 3.1 g. of V, m.p. 170–178°, crystallized.

In 50 ml. of benzene 3.0 g. of V, m.p. 176–178°, and 5.0 g. of dimethylamine hydrochloride was refluxed for 4 hr., after which the solution was filtered. Upon evaporation of the benzene only V was recovered.

In 50 ml. of tetrahydrofuran 2.0 g. of IV was refluxed with 5.0 g. of dimethylamine hydrochloride for 4 hr. After removing the amine hydrochloride and flash evaporating the filtrate only IV was recovered. This was established by a proton n.m.r. spectrum of the residue.

In a micro reaction flask, 0.0586 g. (0.0930 mmole) of isomer II, m.p. 223–225°, was allowed to react with an excess of dimethylamine in 5 ml. of benzene. The precipitate was filtered and dissolved in water. A chloride determination ($AgNO_3$) gave 0.0536 g. (0.374 mmole) of AgCl (expected 0.372 mmole). Thus, the reaction was quantitative.

The benzene filtrate was evaporated to dryness and the residue taken up in *n*-hexane–pentane. The first crystalline solid, VI, 0.0415 g., melted at 152–153°. A second crystalline solid, 0.0145 g., appearing as large plates, melted at 139–140°. It was solidified and remelted, however, at 153–155°. A mixture melting point of the remelted material and VI showed no depression. The total yield of recovered product was 90.7%. By proton n.m.r. analysis the ratio of aromatic to aliphatic protons was determined to be 1:1.20. For $(C_6H_5)_5P_4N_4[N(CH_3)_2]_4$ this ratio is 1:1.20.

To 0.10 g. (0.159 mmole) of I, m.p. 148–150.5°, was added an excess of dimethylamine in 5 ml. of benzene. The precipitate that formed was filtered and analyzed for chloride by precipitation with $AgNO_3$. The chloride analysis indicated that the reaction was quantitative. The benzene filtrate was evaporated to dryness and the residue taken up in hexane. Upon standing, 0.085 g. of crystalline solid IV was recovered, m.p. 136–138°.

***β-trans*-$[C_6H_5PN(NHCH_3)_4]$.**—This compound was prepared by allowing 20 g. (31.7 mmoles) of tetramer III, melting at 260–

263°, to react with an excess of monomethylamine in benzene at room temperature. After 1 hr. the mixture was brought to reflux and filtered hot. There was separated 8.6 g. (127 mmoles) of monomethylamine hydrochloride. By fractional crystallization of the benzene filtrate 9.1 g. (15 mmoles) of crystalline solid was separated initially. This solid, when crystallized rapidly from hot benzene, gave needles which melted at 129–130°. When crystallized slowly from the same solvent the crystalline solid melted at 151–152° (VII).

Proton nuclear magnetic resonance spectra of both solids are the same. The aromatic to aliphatic proton ratio obtained from n.m.r. measurements, before and after deuterium exchange of amido protons, agrees with the formula $[C_6H_5PNNHCH_3]_4$. The elemental analysis for VII is given in Table I.

Nine grams of a second amide, VIII, m.p. 119–121°, was recovered from the benzene solution. Molecular weight and proton n.m.r. analysis confirm that it is *α-trans*-$[C_6H_5PN(NHCH_3)]_4$.

***β-trans*-$(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)P(C_6H_5)_2]$.**—This compound was prepared by allowing 5 g. (8.2 mmoles) of VII to react with 8.2 mmoles of $(C_6H_5)_2PCl$ in 50 ml. of a 2:1 mixture of benzene and pyridine at reflux under a nitrogen atmosphere. From this reaction mixture was separated 0.5 g. of solid IX, which, upon recrystallization from benzene, melted at 220–222°. Elemental analysis of IX is given in Table I.

***β-trans*-$(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)CONHC_6H_5]$.**—This compound was prepared from the reaction of 3.0 g. (4.93 mmoles) of VII with 0.4 ml. (3.68 mmoles) of freshly distilled phenyl isocyanate in benzene under a nitrogen atmosphere. The solution was kept at reflux 20 hr., after which it was flash evaporated to dryness. A sticky residue remained which was taken up in benzene. By a series of fractional precipitations, 1.14 g. of solid, m.p. 160–167°, was recovered. After several recrystallizations from benzene–pentane a crystalline solid, X, melting at 165–176° was obtained. An elemental analysis is given in Table I.

***cis*-$(C_6H_5)_4P_4N_4(NHCH_3)_3[N(CH_3)CONHC_6H_5]$.**—This compound was prepared by first allowing 5 g. of II to react with an excess of monomethylamine in benzene. After filtering the insoluble $CH_3NH_2 \cdot HCl$, the volume of the benzene solution was reduced and pentane was added. Upon standing, 4.5 g. of solid XI, m.p. 129–133°, crystallized from the solution. The ratio of aromatic to aliphatic protons, obtained from the n.m.r. spectrum, indicated that XI was $[C_6H_5PN(NHCH_3)]_4$.

Three grams (4.94 mmoles) of XI then was allowed to react with 0.40 ml. (3.7 mmoles) of phenyl isocyanate in 90 ml. of dry benzene at reflux under a nitrogen atmosphere. After 20 hr., the solvent and any unreacted phenyl isocyanate were removed by distillation *in vacuo* at 25–30°. The residue was taken up in benzene. Several fractions of oils then were separated by addition of cyclohexane and *n*-hexane. These oils could be converted to low-melting solids by washing with a mixture of *n*-hexane and cyclohexane. After standing 8 days, 1.5 g. of solid, m.p. 70–82°, precipitated from the original benzene solution. Upon recrystallization from a mixture of benzene, cyclohexane, and *n*-hexane, crystals (XIII) melting at 78–80.5° were recovered. The elemental analysis is given in Table I.

After heating XIII 1 hr. at 75° at reduced pressure, the melting point was raised to 125–129°.

Dielectric Constants.—For dielectric constant measurements a General Radio Capacitance type 1610-A measuring assembly was used. The cell consisted of four concentric platinum cylinders with a capacity of 49.26 $\mu\mu$f. All measurements were made with the cell in a constant-temperature bath capable of regulating the temperature to ±0.05°. Capacitance measurements were made in benzene. Reagent grade benzene was distilled twice through a column in a dry nitrogen atmosphere and collected and stored over microtraps. Measurements for each concentration were made at a series of temperatures ranging from 28 to 65°. A plot of ϵ_{soln} *vs.* temperature was made for each solution. Dielectric constants at 30.0°, extrapolated from this plot, were then used to plot ϵ_{soln} *vs.* concentration. This plot is illustrated in Figure 4.

Proton N.m.r. Measurements.—Proton n.m.r. spectra were obtained on a Varian DP60 high-resolution instrument. Deuteriochloroform was the solvent for obtaining the spectra at 60 Mc., which were referred to tetramethylsilane (internal).

Molecular Weight Determinations.—Molecular weights were measured of chloroform solutions at 37° using a Mechrolab osmometer. The instrument was calibrated with benzyl. Solutions containing 2–4 wt. % of the sample were used for the measurements.

Analyses.—Elemental analyses were done by Huffman Laboratories, Inc., Wheatridge, Colo. Phosphorus analysis was done by Na_2O_2 fusion.

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