x-, y-, and z-axes, respectively. In Ib–d, the only structure observable was in the z-absorption below 1000 gauss. Here a triplet of lines was observed with Ib, a single line with Ic, and a doublet with Id. The splittings in Ib and Id were 10–12 gauss. The hyperfine structure in Ia may then be assigned to the protons attached to C-2 and C-6. The magnitude and signs of the anisotropic components (the deviations along the three axes from the isotropic value of 8.63 gauss) are compatible with this assignment and with the choice of axes given above with the formulas.[9] The anisotropic components indicate that the sign of the isotropic coupling is positive. We expect that the interaction of the unpaired σ-electron will dominate this isotropic coupling as $\rho_{meta} \approx 0.08$ for a phenoxyl radical.[6,7] The sign should be that for the *cis* proton of the vinyl radical, which Adrian and Karplus predict to be positive.[10]

The observed magnitude of the *cis*-hydrogen in the vinyl splitting (34 gauss[11]) may be compared with $2 \times 8.63 = 17.3$ gauss for Ia.[12] Since there are differences in the two systems in the σ- and π-systems as well as in the carbon–carbon bond lengths, the variation in the hyperfine coupling by a factor of two may not be unreasonable. The 17.3 gauss is, however, quite close to an 18 ± 2 gauss splitting obtained by Tolkachev, Chkheidze, and Buben[13] on photolysis of phenyl iodide adsorbed on silica gel and ascribed to the phenyl radical. Unfortunately, the relatively poor resolution of their spectrum and the possibility of anistropic effects leaves uncertain the assignment to an isotropic hyperfine interaction with the adjacent protons. The computations of Ingalls and Kivelson gave 21 gauss for the splitting in a phenyl radical with an sp^2 unpaired electron.[14]

Acknowledgments.—We wish to thank Mr. W. A. Yager and Mr. R. M. R. Cramer for their aid in obtaining the e.s.r. spectra.

(9) A simple dipolar approximation was used in which the spin density in each orbital lobe was approximated by a point dipole approximately at the center of the lobe.

(10) F. J. Adrian and M. Karplus, *J. Chem. Phys.*, **41**, 56 (1964).

(11) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964); R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

(12) The $\Delta m = 1$ transitions of the triplets which we are observing involve one state ($m_s = 0$) in which there is no hyperfine interaction. The corresponding transitions for doublet species have hyperfine interactions in both levels. For comparison we must double the observed values in the triplet.

(13) V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben, *Zh. Strukt. Khim.*, **3**, 709 (1962). We thank Dr. R. W. Fessenden for bringing this reference to our attention.

(14) R. B. Ingalls and D. Kivelson, *J. Chem. Phys.*, **38**, 1907 (1963).

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Structural Identification of a Geometric Isomer of Tetrameric Phenylphosphonitrilic Chloride

Sir:

In the chemistry of trimeric phenylphosphonitrilic halides, two geometrical isomers have been isolated and identified for the bromides[1] and also for the chlorides.[2] However, with tetrameric phenylphosphonitrilic chloride four geometrical isomers may exist. Shaw and his co-workers[3] have discussed this isomer-

(1) (a) T. Moeller and P. Nannelli, *Inorg. Chem.*, **2**, 896 (1963); (b) *ibid.*, **2**, 659 (1963); (c) *ibid.*, **1**, 721 (1962).

(2) B. Grushkin, M. G. Sanchez, and R. G. Rice, *ibid.*, **3**, 623 (1964).

(3) (a) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 251 (1962); (b) R. A. Shaw and C. Stratton, *Chem. Ind.* (London), **52** (1959).

ism and reported three isomers of $(C_6H_5PNCl)_4$, melting at 148, 202, and 248°, respectively, but could not assign any geometric configuration.

We have recrystallized a mixture of tetrameric phenylphosphonitrilic chlorides, m.p. 240–254°[2] to a melting range of 248–254°. This mixture then was dissolved in benzene, anhydrous ferric chloride was added, and the mixture was refluxed for 1 hr. We have shown earlier[4] that under these conditions no phenylation of *trans*-$(C_6H_5PNCl)_3$ takes place, but that some *cis*-$(C_6H_5PNCl)_3$ is formed by isomerization.

Decomposition of the mixture with water–HCl and extraction with benzene gave a solution from which was crystallized an isomer of $(C_6H_5PNCl)_4$, m.p. 202–205°. Careful recrystallization raised the melting point to 225–226°. Solidification and remelting gave the same value.

From the mother liquors we have isolated a second isomer of $(C_6H_5PNCl)_4$, m.p. 148–150.5° (same value on solidification and remelting) which we believe corresponds to the 148° isomer of Shaw. *Anal.* Calcd. for $C_{24}H_{20}Cl_4N_4P_4$: C, 45.75; H, 3.19; Cl, 22.50; N 8.90. Found: C, 46.05; H, 3.54; Cl, 22.84; N, 8.84. The infrared spectra of all reported compounds exhibited very strong absorption at about 1300 cm.$^{-1}$, indicative of the tetrameric phosphonitrilic ring.

Both of these chloro isomers were treated with excess dimethylamine in refluxing benzene producing, from the chloro tetramer melting at 225–226°, a 91% yield of a tetrakisdimethylamide (A), m.p. 153–155°, and from the chloro tetramer melting at 148–150.5°, an 85% yield of a tetrakisdimethylamide (B), m.p. 136–138°. *Anal.* Calcd. for $C_{32}H_{44}N_8P_4$: C, 57.80; H, 6.68; N, 16.86; P, 18.63. Found: C, 57.17; H, 6.57; N, 16.57; P, 18.08. Compounds A and B were examined by proton magnetic resonance spectroscopy. Based on the arguments given below, the n.m.r. spectra strongly indicate that both compound B and the tetrachloro isomer melting at 148–150.5° are α-*trans* isomers having three phenyl groups on one side of the tetrameric PN ring, and one on the other side.

If the puckered tetrameric phosphonitrilic ring is represented for simplicity by a rectangle, then the four possible geometric isomers of $(C_6H_5PNCl)_4$ can be represented as
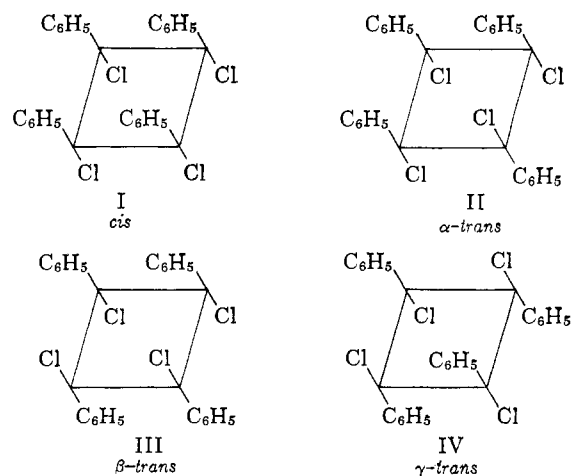
(4) B. Grushkin, M. G. Sanchez, and R. G. Rice, presented before the Symposium on Inorganic Polymers, University of London, Ontario, Canada, Sept., 1963; to be submitted to *Inorg. Chem.*

Substitution of all chlorine atoms by dimethylamino groups is essentially quantitative, and assuming that this substitution at each phosphorus atom proceeds by the same mechanism, the configurations of the derived dimethylamides will be the same as those of the chloro compounds, regardless of whether the amination takes place with or without inversion.

It can be seen that each dimethylamino group in the derivatives of isomers I, III, and IV is in a single magnetic environment, although the environment is different for each of the three isomers. Consequently, the proton n.m.r. spectrum of each of these three dimethylamides would be expected to show a single methyl absorption.

On the other hand, in the dimethylamide of isomer II, there are three distinctly different magnetic environments for the dimethylamino groups. Two of these dimethylamino groups are in the same environment, while the other two are in second and third environments. Thus the proton n.m.r. spectrum of this dimethylamide would be expected to show three methyl absorptions having an area ratio of 2:1:1.

It is well known that the tetrameric phosphonitrilic ring in the solid state is not planar, but rather is puckered. $(PNCl_2)_4$ exists in the boat form,[5] and $(PNF_2)_4$ in the .chair form.[6] On the other hand, in solution $(PNCl_2)_4$ is planar.[7]

If discrete chair or boat forms of the tetrameric phenylphosphonitrilic chlorides exist in solution, then the proton n.m.r. spectra of the derived tetrakisdimethylamides would be expected to show a multiplicity of absorptions, and the more simple arguments given above would not be valid.

Experimentally we have found that the proton n.m.r. spectrum of the tetrakisdimethylamide B, melting at 136–138°, in carbon tetrachloride solution does exhibit three methyl absorptions. Each methyl absorption consists of a doublet having additional structure between the two peaks. Two. of these doublets overlap and have not as yet been separated. The ratio of the area of these three doublets is approximately 2:1:1, and the ratio of the area of the two overlapping doublets to that of the separate doublet is approximately 3:1.

Further, dimethylamination of the mixture of tetrameric phosphonitrilic chlorides, m.p. 248–254°, followed by careful recrystallization of the products, has given compound B, m.p. 136–138°, and still a third tetrakisdimethylamide (C), m.p. 176–178°. *Anal.* Calcd. for $C_{32}H_{44}N_8P_4$: C, 57.80; H, 6.68; N, 16.86. Found: C, 57.65; H, 7.03; N, 16.52. The proton n.m.r. spectra of compounds A and C in carbon tetrachloride solution both show a single methyl absorption, each having a different chemical shift. This indicates that compounds A and C are derivatives of a different one of the isomers I, III, or IV. These n.m.r. data confirm the identity of compound B as *cis*-2,4,6-*trans*-8-tetrakisdimethylamino-*trans*-2,4,6-*cis*-8-tetraphenyl-1,3,5,7,2,4,6,8-tetrazatetraphosphocine. The corresponding chloro isomer, melting at 148–150.5°, thus is identified as *cis*-2,4,6-*trans*-8-tetrachloro-*trans*-2,4,6-*cis*-8-tetraphenyl-1,3,5,7,2,4,6,8-tetrazatetraphosphocine.[8]

(5) J. A. A. Ketelaar and T. A. deVries, *Rec. trav. chim.*, **58**, 1081 (1939).

(6) N. L. Paddock, *Endeavour*, **19**, 137 (1960).

(7) L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954).

(8) A. M. Patterson, L. T. Capell, and D. Walker, "The Ring Index," 2nd Ed., Supplement I, American Chemical Society, Washington, D. C., 1963, p. 8.

In addition, the n.m.r. data are interpreted as evidence that, if chair and boat forms of the tetrameric phenylphosphonitrilic ring do exist in solution, they are rapidly interconverting. The simplest tetrakisdimethylamide chair or boat isomer would be expected to have a proton n.m.r. spectrum exhibiting two methyl doublets, whereas two isomeric tetrakisdimethylamides have been isolated, each having only a single methyl doublet.

Finally, if chair and boat forms of compound B are present and are not rapidly interconverting in solution, the proton n.m.r. spectrum would be expected to be considerably more complex.

Low temperature n.m.r. studies are in progress to investigate the conformation of the ring. Work is also continuing to separate and identify the other isomers of $(C_6H_5PNCl)_4$ and their derivatives. Detailed results will be reported separately.

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The Effect of Viscosity on the Internal Deactivation Modes of the Triplet State[1]

Sir:

In a study concerning the effects of temperature and viscosity on the unimolecular deactivation modes of the triplet state, we have observed an interesting and unique result: the decrease of the rate constant, k_0, of the radiative process with increasing viscosity. Phosphorescence from fluid solution has been previously observed.[2,3] We have measured both lifetimes and relative quantum yields of phosphorescence for palladium(II) mesoporphyrin IX dimethyl ester dissolved in methyl phthalylethylglycolate over the temperature range 0 to −150°. Between 20 and −45°, the solvent, methyl phthalylethylglycolate, undergoes a viscosity change of 10^2 to 10^8 cp.; at $\approx -50°$ a meniscus appears, indicating the formation of a rigid system. Extreme care has been employed to eliminate oxygen (the partial pressure was reduced to less than 10^{-5} mm.) and other quenching impurities from the solutions.

In order to eliminate the effects of concentration quenching, measurements were made at several different concentrations and the data extrapolated to infinite dilution.

Figure 1 shows the variation of the lifetime of the decay of the triplet state with the temperature of the solution at infinite dilution, as well as the variation of the relative quantum yield of phosphorescence with temperature for a 10^{-4} M solution. Measurement of

(1) Taken in part from a dissertation by S. J. Ladner, to be submitted to the faculty of the Department of Chemistry, University of Houston, in partial fulfillment of the requirements for the Ph.D. degree.

(2) R. S. Becker and S. J. Ladner, unpublished work, 1960.

(3) C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **66**, 2506 (1962).