

is therefore about 30. We now report that substitution of a methyl group for a methoxyl in II (to give the phosphonate III) causes a remarkable change in the product distribution. The reaction is still first order in hydroxide ion and in ester in the pH range 8.5–9.4 (0.07 *M* potassium perchlorate; 25°), but analysis of the products^{10,11} shows that reaction by path a now accounts for about 95% of the total. This is not caused by a large increase in the rate of path a¹² but by a greater than 200-fold *decrease* in that of path b. The ratio of the relative rates (b:a) for the phosphate to that for the phosphonate is about 600. We suggest here a possible mechanism¹⁴ for this reaction which does not appear to be inconsistent with any experimental facts at present available and which, if correct, would imply that for these compounds case 3 (see above) is more nearly correct than case 1 or 2.

If case 1 applied, then pseudo-rotation of the first formed intermediate about R as a pivot² would allow rapid reaction by path b even when R = CH₃. Case 2 can also be excluded since it would predict no reaction

by path a for either compound.¹⁵ Thus, if this mechanism is correct,¹⁴ case 3 appears to apply, and path b is suppressed for the phosphonate since a pseudo-rotation about any pivot other than the methyl group would place the latter in an axial position.^{2,5} An interesting prediction from this mechanism is that base-catalyzed migration of an intact dialkylphosphoryl group to a neighboring hydroxyl may occur; this has been excluded only for a monoalkylphosphoryl group¹⁶ or the unsubstituted phosphoryl group¹⁷ itself. We are currently extending this work to include some phosphinate esters and other neighboring groups.

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(15) It could be claimed that path a need not involve an intermediate and may instead take place by a direct displacement. However, the known² base-catalyzed hydrolysis of phenyl ethylene phosphate to give ethylene phosphate also argues against case 2.

(16) D. M. Brown, D. I. Magrath, A. H. Neilson, and A. R. Todd, *Nature*, 177, 1124 (1956); D. M. Brown and D. A. Usher, *J. Chem. Soc.*, 6547 (1965).

(17) D. M. Brown, *Advan. Org. Chem.*, 75 (1963).

(11) The acetoin methylphosphonate was identified by nmr and infrared spectroscopy and by elemental analysis of the barium salt. *Anal.* Calcd for C₈H₁₀BaO₃O₄P: C, 25.69; H, 4.31; P, 13.25. Found: C, 25.46; H, 4.31; P, 13.20. The phosphonate III was identified by nmr and infrared spectroscopy. *Anal.* Calcd for C₆H₁₃O₄P: C, 40.00; H, 7.27; P, 17.19. Found: C, 40.13; H, 7.40; P, 16.98.

(12) The rate of reaction by path a for the phosphonate (27 activity⁻¹ sec⁻¹) is about three times that for the phosphate. Similar small rate increases can be found¹³ in other phosphonate-phosphate comparisons. However, phosphonate III and phosphate II^{7c} hydrolyze many orders of magnitude faster than dimethyl methylphosphonate and trimethyl phosphate, respectively.

(13) J. R. Cox, Jr., and O. B. Ramsay, *Chem. Rev.*, 64, 317 (1964); R. F. Hudson and L. Keay, *J. Chem. Soc.*, 2463 (1956); but see A. Eberhard, Ph.D. Thesis, Harvard University, 1964, pp 6–8.

(14) For some of the other experimental facts that must be taken into account see ref 7–9. For simplicity, only one of the possible pseudo-rotations is shown here.

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A New Conformation for an Isolated Six-Membered Ring System¹

Sir:

The reaction of monophenylphosphonitric fluoride trimer, P₃N₃F₅(C₆H₅), with benzene in the presence of

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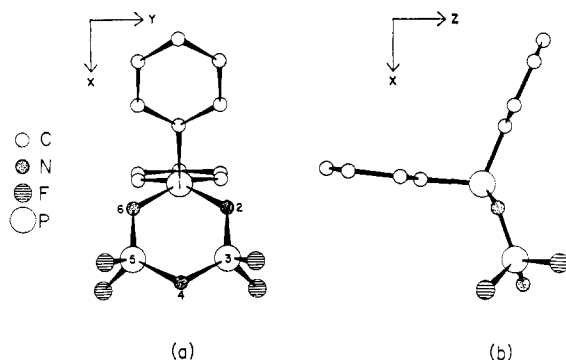


Figure 1. Views of one of the $1,1\text{-P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)_2$ molecules looking down (a) the c axis and (b) the b axis. In a there is a crystallographic mirror plane through atoms P(1) and N(4) and bisecting the two phenyl rings. In b the molecule is viewed along the normal to the mirror plane, and only half of the molecule is shown.

aluminum chloride and triethylamine yields a diphenylphosphonitrilic fluoride trimer, $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)_2$ (I).² By analogy with the Friedel-Crafts reaction with the phosphonitrilic chloride trimer³ and from phosphorus-31 and fluorine-19 nuclear magnetic resonance evidence, a geminally substituted structure was proposed for I.²

The crystal structure of the corresponding chloro derivative, $\text{P}_3\text{N}_3\text{Cl}_4(\text{C}_6\text{H}_5)_2$, has been determined and found to have a "slight" chair conformation.⁴ In view of the often dramatic structural differences between fluorine-⁵ and chlorine-⁶-substituted phosphonitrilic halides, we have investigated the crystal structure of I.

The 1,1-diphenylphosphonitrilic fluoride trimer crystallizes as water-white needles belonging to the orthorhombic system, with $a = 14.74 \pm 0.01$, $b = 12.57 \pm 0.01$, and $c = 16.66 \pm 0.01$ Å as determined on a precession camera (Mo $K\alpha$, λ 0.7107 Å). There are eight molecules of $1,1\text{-P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)_2$ in the unit cell. The systematic absences indicate that the space group is either Pnma or $\text{Pn}2_1a$; the number of molecules per unit cell and various statistical tests suggest the former. A total of 1442 independent nonzero structure amplitudes was obtained by visual estimation of equiinclination Weissenberg photographs (Cu $K\alpha$, λ 1.5418 Å) at 25° . The structure was solved by the symbolic addition procedure.⁷ Full-matrix least-squares refinement incorporating anisotropic temperature factors has given an R factor of 0.10 on the 1442 observed nonzero reflections.

The resulting molecular structure is shown in Figure 1, and it confirms the previous assignment.² The crystal asymmetric unit contains two symmetry-independent molecules, each of which has a crystallographic mirror plane bisecting both the benzene rings and the phosphorus-nitrogen ring, with the result that the molecule is utilizing all its symmetry elements. There are three sets of phosphorus-nitrogen bond

(2) C. W. Allen, Doctoral Dissertation, University of Illinois, 1967.

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

(4) N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **19**, 693 (1965).

(5) H. McD. McGeachin and F. R. Tromans, *J. Chem. Soc.*, 4777 (1961).

(6) R. Hazekamp, T. Migchelsen, and A. Vos, *Acta Cryst.*, **15**, 539 (1962).

(7) See, e.g., J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966). The procedure was carried out with the aid of a series of programs developed by E. B. Fleischer, A. Stone, and R. Dewar at the University of Chicago.

lengths which are slightly shorter than those found in the chloro derivative⁴ but are distributed about the molecule in an analogous manner.

The conformation of the phosphorus-nitrogen ring, however, differs between the two compounds. The 1,1-diphenylphosphonitrilic chloride trimer exists as a "slight" chair, whereas the corresponding fluoride, to good approximation, has the phosphorus atom (P(1)), bearing the phenyl groups, 0.205 Å above the plane of the other five atoms of the ring. The nitrogen atom (N(4)), opposite P(1), is slightly above (0.025 Å) the central plane, although this displacement is only marginally significant.

Although this particular conformation has been observed in fused ring systems in the carbocyclic series (e.g., in 4-bromoestrone)⁸ and proposed in several other fused ring systems on the basis of models and infrared data,⁹ this is the first example in an isolated six-membered ring system.

The factors which lead to a stable conformation in phosphorus-nitrogen ring systems are different from those that apply in carbocyclic and simple heterocyclic systems. In the parent phosphonitrilic halides, the nitrogen lone pair is taken to be donated to energetically favorable phosphorus d orbitals.¹⁰ This is referred to as the π' system. The replacement of a fluorine atom by a phenyl group causes an expansion in the phosphorus d -orbital size, and consequently there is less efficient overlap with the nitrogen σ orbitals. The π' system is, therefore, weakened at the phenyl-substituted phosphorus atoms, thereby giving it greater flexibility to move out of the plane of the ring. The fluorine atoms on the remaining two phosphorus atoms tend to pull nitrogen lone-pair and σ -bonding electrons closer to their respective centers than chlorine atoms do. This is reflected in the slightly shorter bond lengths between N(2)-P(3) and N(4)-P(3) in the fluorine-substituted case than in the chlorine-substituted case.¹¹ Therefore, the remaining five ring atoms remain virtually planar. The deviation of N(4) from the plane is of the order of magnitude of the corresponding deviations in trimeric phosphonitrilic chloride, $\text{P}_3\text{N}_3\text{Cl}_6$.¹²

Acknowledgment. We have benefited from discussions with Mrs. S. M. Johnson concerning the symbolic addition procedure, while Miss Leslie Brooks assisted in the data estimation.

(8) D. A. Norton, G. Kartha, and C. T. Lu, *ibid.*, **16**, 89 (1963); H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, **23**, 439 (1967).

(9) E. M. Philbin and T. S. Wheeler, *Proc. Chem. Soc.*, 167 (1958).

(10) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(11) In $1,1\text{-P}_3\text{N}_3\text{Cl}_6(\text{C}_6\text{H}_5)_2$,⁴ N(2)-P(3) is equal to 1.55 ± 0.005 and N(4)-P(3) is equal to 1.578 ± 0.005 Å, whereas in the $1,1\text{-P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)_2$, N(2)-P(3) is equal to 1.54 ± 0.01 and N(4)-P(3) is equal to 1.56 ± 0.01 Å.

(12) A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960).

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The Crystal and Molecular Structure of $\text{Zn}[\text{Co}(\text{CO})_4]_2$

Sir:

Although transition metal derivatives of group II metals have been known for over 30 years,¹ it is only

(1) M. P. Shubert, *J. Am. Chem. Soc.*, **55**, 4563 (1933).