

and τ_C^{-1} are summations of the various rate processes (other than equilibration) which deplete M^* and MQ^* , respectively.

Table I gives kinetic data for four exciplexes, two reactive (quantum yields for photoaddition, ϕ_R , are given in Table I) and two unreactive.^{2,9} Complete discussion must await the full paper but several points appear clearly. (1) The radiative rates (k_F^C) for all four exciplexes are ca. $5 \times 10^6 \text{ s}^{-1}$. Based on these and other published data,^{4,10} a radiative rate of ca. $1-5 \times 10^6 \text{ s}^{-1}$ appears to be a useful rule of thumb both for excimers and for exciplexes possessing high charge-transfer stabilization, irrespective of their capability for forming stable photoproducts. (2) The reaction rates ($k_R^C = \phi_R \tau_C^{-1}$) vary by a factor of at least a thousand while the rates of radiationless decay ($k_D^C + k_{IS}^C$) vary far less. It seems likely that the weakness or absence of exciplex emission in many reactive systems is a consequence of high reaction rates. (3) We have measured K_{eq} as a function of temperature for 9CNP...p-BA and find $\Delta H^\circ = -7.4 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -13.1 \text{ cal mol}^{-1} \text{ deg}^{-1}$, comparable with expectations based on Weller's finding² for arene-amine exciplexes. *Thermodynamic behavior thus appears to differ little between reactive and unreactive exciplexes.* Factors leading to formation of stable exciplexes are not necessarily those which cause exciplex collapse to stable products. It is possible that the failure to observe product formation in many systems where exciplexes can be observed reflects the instability with respect to starting materials of other metastable intermediates (e.g., biradicals) derived from exciplexes.¹¹ (4) Assumption of $\Delta S^\circ \approx -15 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for those exciplexes where K_{eq} was not measured as a function of temperature leads to values of E_R , the repulsion energy¹² between unexcited M and Q at the equilibrium exciplex configuration, of 7.5–11.5 kcal mol⁻¹, again within the range of arene-amine exciplexes.

In summary, a combination of mode I and mode II experiments with steady-state quantum yield data provides virtually a complete kinetic analysis. Excited-state thermodynamic and kinetic parameters for reactive systems where reversion (k_{MC}) neither dominates nor is negligible seem accessible only with difficulty by the steady-state method owing to the possible temperature dependence¹³ of k_R^C .

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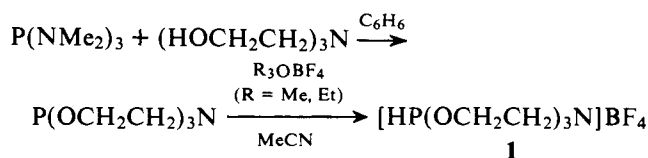
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Characterization and Molecular Structure of [HP(OCH₂CH₂)₃N]BF₄. Pentacoordination of Phosphorus

Sir:

While five-coordination in pentavalent phosphorus systems is profusely documented in the literature,¹ phosphonium cations have been found to be consistently four-coordinate. Here we report the characterization and molecular structure of **1** in which the presence of an N→P coordinate bond confers a trigonal bipyramidal geometry on the phosphorus atom. The second step of the reaction below invariably gives the expected alkyl phosphonium cation $RP(OR)_3^+$ with acyclic



phosphite esters² or bicyclic phosphites such as $P(OCH_2)_3CMe$.³ The abstraction of a proton which occurs with the present system⁴ is highly suggestive of basicity enhancement of the phosphorus via nitrogen lone pair coordination.

In acetonitrile solution the presence of a $^1J_{PH}$ coupling of 791 Hz appearing in both the 1H (δ , 6.03 d) and ^{31}P (δ , 20.2 d of mults⁵) NMR spectra of **1** is unusually low compared to those for $HP(OMe)_3^+$ (826.2 Hz)⁶ and $HP(OCH_2)_3CMe^+$ (899.2 Hz)^{6c,7} which can only be observed in strongly acidic media. This contrast indicates a comparatively low degree of s character in the P-H link of **1** consistent with a tricyclic structure in which the proton is located on the axis of a trigonal bipyramid.

To test this structural hypothesis, a crystal and molecular structure determination of **1** was undertaken by x-ray diffraction techniques. Preliminary examination of **1** showed that the crystals belong to the orthorhombic crystal class with $a = 12.784$ (6), $b = 9.320$ (4), and $c = 8.988$ (3) Å and four units of composition $HP(OCH_2CH_2)_3N \cdot BF_4$ per unit cell. Assignment of a space group was not unambiguous since the systematic extinctions ($0kl$ absent if $k + l = 2n + 1$, $h0l$ absent if $h = 2n + 1$) were consistent with both $Pna2_1$ and $Pnam$. In the latter space group the molecule would have to have a molecular mirror plane in the absence of disorder.

A total of 873 unique reflection intensities with $2\theta \leq 114^\circ$ were measured using a computer controlled four-circle diffractometer and Cu K_α radiation (1.5418 Å). Of these, 615 were judged observed after correction for Lorentz, polarization, and background effects ($F_o \leq 3\sigma(F_o)$). Intensity statistics were not particularly helpful in deciding the space

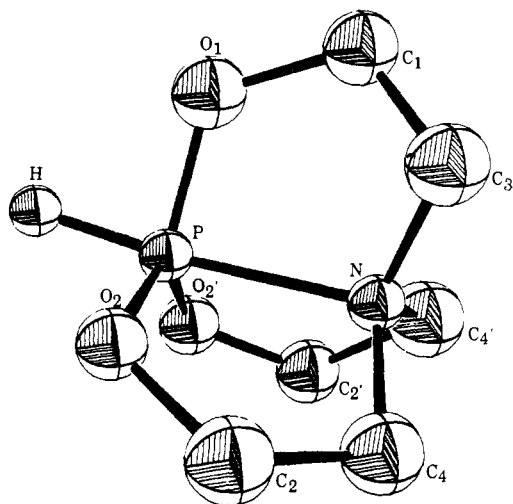


Figure 1. Computer drawing of the 1-hydro-2,8,9-trioxa-1-phospha-5-aza-tricyclo[3.3.3.0]undecane cation of **1**. Only the P-H hydrogen and one of the disordered conformations is shown.

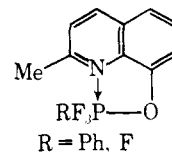
group ambiguity since they were intermediate between centrosymmetric ($Pnam$) and noncentrosymmetric ($Pna2_1$) in value and the presence of a heavy atom could easily give spurious results.

Solution of the crystal structure was begun by routine application of direct methods via a multiple solution weighted tangent formula⁸ scheme in the noncentrosymmetric space group $Pna2_1$. All of the nonhydrogen atoms were easily located in the first phased E synthesis and all hydrogens located in subsequent difference F syntheses.⁹ Full-matrix least-squares refinements proceeded uneventfully to a final crystallographic residual (R) of 6.2% for the 615 observed reflections and 183 variables. The geometry of this model was very poorly behaved with chemically identical bonds differing by five standard deviations. The molecular constitution was essentially that shown in Figure 1.

Refinement was then attempted in space group $Pnam$ (alternate setting of $Pnma$). It became rapidly apparent that a model in which the molecule sat on a mirror plane would not refine and models in which C(3) and C(4) were disordered were tried. These refined satisfactorily to an R of 6.5% for the 135 variables used. Fractional coordinates, bond distances, bond angles, and observed and calculated structure factors for this model are given in the supplemental material to be found in the microfilm edition; see paragraph at end of paper regarding supplementary material. A drawing of this model is given in Figure 1.

The well-defined P←N dative bond in **1** (1.986 Å) is undoubtedly responsible for the unusual proton abstracting property of the bicyclic precursor. The phosphorus atom is clearly trigonal bipyramidal with O-P-O angles of 120°, O-P-N angles of 87°, and a H-P-N angle of 172°. This near trigonal bipyramidal symmetry of the five electron pairs around the phosphorus atom in **1** contrasts the relative instability of this electron pair configuration in: $PX_3←NR_3$ adducts¹⁰ and intermediates involved in certain reactions of trivalent phosphorus compounds.¹¹ The P-H bond distance in **1** (1.35 Å) is about 0.1 Å shorter than the 1.41 to 1.45 Å realized in several phosphines and PH_4^+ ¹² and is also somewhat shorter than the sum of the covalent radii (1.38 Å). It is interesting that although trigonal bipyramidal phosphoranes tend to orient the more electronegative substituents on the apices, molecular constraint appears to preclude this possibility in **1**. The similarity of the structure of phosphatrane **1** to that of silatranes ($RSi(OCH_2CH_2)_3N$)¹³ with which it is isoelectronic is noteworthy.

The P-N bond distance found in **1** is quite comparable to those found in the six-coordinate systems below (1.91–1.98 Å) wherein the electronegative fluorines on the five-coordinate phosphorane moiety are effective in attracting the nitrogen lone pair to the acidic phosphorus.¹⁴



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Supplementary Material Available: fractional coordinates, bond distances, bond angles, and structure factors (6 pages). Ordering information is given on any current masthead page.

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Directive Effects in the Electrophilic Substitution of Deltahedral Boranes and Heteroboranes. Halogenation of 1-SB₉H₉. Unusually Long ¹¹B Spin-Lattice Relaxation Times

Sir:

There has been considerable interest in the stereochemistry of electrophilic substitution of closo(deltahedral) boranes¹ and heteroboranes, at least in part because many members of this class of molecules can be termed aromatic. For deltahedral heteroboranes like 1,2- and 1,7-C₂B₁₀H₁₂ and 2,4-C₂B₅H₇, ground-state charge distributions correlate nicely with the results of electrophilic halogenation.^{2,3}