Hyperconjugation versus Apicophilicity in Trigonal-Bipyramidal Phosphorus Species[†]

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It is generally accepted that more electronegative substituents prefer to occupy axial positions in trigonal bipyramids (TBPs) in the absence of steric constraints.[1] Another commonly accepted notion is that stereochemical permutation of substituents in TBPs occurs via Berry pseudorotation.[2] This well-known process involves the simultaneous inward and outward bendings of both axial and any two equatorial ligands to reach a square-pyramidal (SP) transition state (TS). From this TS, continued motion generates a new TBP in which the axial and equatorial pairs of substituents have exchanged positions. However, the new TBP may fail to be a local minimum on the potential energy hypersurface if the original axial ligands have been replaced with others less apicophilic: the SP structure becomes nonstationary, and it is the new TBP which is a TS.[3,4]

As an example, tetrasubstituted phosphoranyl radicals[4,5] adopt trigonal-bipyramidal geometries in which the unpaired electron may be thought of as a fifth ligand, and it is typically viewed as being strongly *apicophobic*—indeed, TBP structures with the unpaired electron assigned to be axial (TBP$_a$) have appeared only rarely[6] and generated significant controversy.[4e,7] Based on experimental evidence for selected phosphoranes,[8] Wasada and Hirao[3i] have proposed that pseudorotation will not occur for phosphoranes bearing exactly two or three electronegative (apicophilic) substituents, since such a substitution pattern will inevitably decrease the total number of apicophilic groups found axial after pseudorotation from the preferred, diaxially-substituted minimum. We report here, however, that hyperconjugation
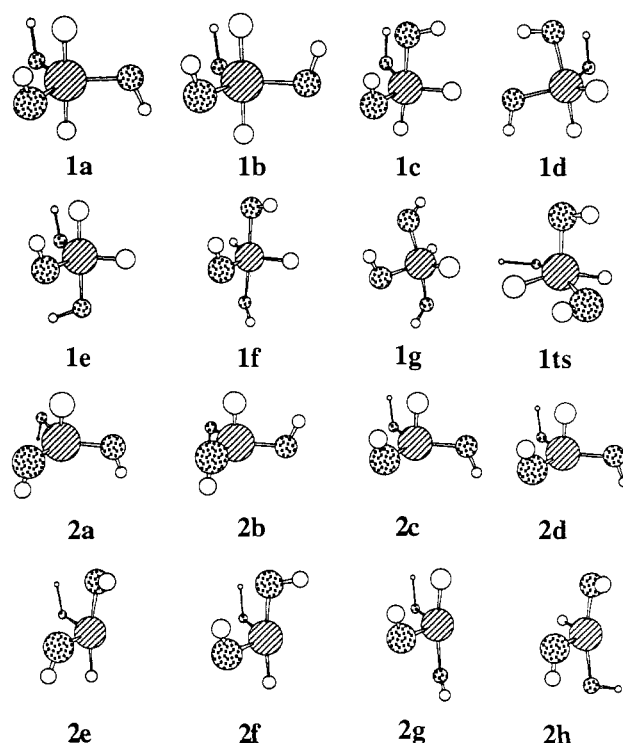

Figure 1. Trihydroxyphosphorane and -phosphoranyl stationary points. Geometrical data are provided as supplementary material.

involving equatorial ligands can dramatically reverse the expected stabilities of TBP stereoisomers, *even to the point of conferring stability upon TBP$_a$ phosphoranyl radicals.*

We have performed large basis set[9] correlated[10] ab initio calculations[11] on trihydroxyphosphorane (**1**) and trihydroxyphosphoranyl (**2**).[12] Structural representations may be found in Figure 1 and energies in Table I; geometric details are provided as supplementary material. All stationary points were characterized as local minima or TSs by analytic frequency calculations at the HF level. Geometries were then optimized at the MP2 level; frequencies were recomputed for structures incorporating symmetry elements to verify that they remained minima.

Seven distinct local minima exist for **1**. The two lowest energy isomers, **1a** and **1b**, place all three hydroxyl groups equatorial. There are additionally three diequatorial minima and two diaxial minima. For **2**, we have located eight remarkably similar minima, including four TBP$_a$ structures where all three hydroxyls are in equatorial positions. No TBP$_a$ minima with axial hydroxyls were found. In every case, the OH bonds of equatorial hydroxyl groups in **1** and **2** eclipse the axial TBP bonds/orbitals. The hyper-

† Dedicated to the memory of Regents' Professor Paul G. Gassman, 1935–1993.

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Table I. Relative Energies (kcal/mol) for Stereoisomers of **1** and **2**[a,b,c]

isomer	HF	MP2	highest level[d]	ZPVE[e]
1a	0.2	0.0	0.0	1.1
1b	1.7	1.5		1.0
1c	1.2	2.4	3.5	0.4
1d	1.1	2.9		0.6
1e	4.3	6.4		0.5
1f	0.5	4.2	4.6	0.0
1g	0.0	4.2		0.0
1ts	5.9	7.2	7.0	0.1
2a	4.7	0.9	3.4	1.2
2b	5.4	2.3		1.0
2c	8.5	6.0		0.7
2d	13.4	11.6		0.4
2e	1.4	2.2		0.0
2f	0.0	0.0	0.0	0.0
2g	8.5	8.2		0.1
2h	2.3	2.0		0.2

[a] Absolute energies may be found in supplementary material. [b] Calculations for **1** and **2** based on RHF/cc-pVDZ and UHF/6-31G* methods respectively. $\langle S^2 \rangle$ for the latter did not exceed 0.76 in any instance. [c] HF and MP2 energies are for fully optimized structures. [d] CCSD/cc-pVTZ//MP2/cc-pVDZ; perturbative triples (T) were included for **1**. [e] Calculated from HF/6-31G* frequencies scaled by 0.89.

conjugative origin of this effect (i.e., oxygen lone pair delocalization into appropriately oriented unfilled orbitals) has been discussed for both monohydroxyphosphorane[3g] and -phosphoranyl.[4e]

For the lowest energy isomers from each distinct class, additional calculations were performed with the triple-ζ cc-pVTZ basis taking further account of correlation. It is apparent that in every case *correlation favors equatorial hydroxyl groups*, and our best relative energies appear to be converged in this respect.

Since the hydroxyl group is known to be moderately

apicophilic,[3g,4e] it is evident that equatorial–equatorial ligand interactions stabilize the corresponding TBPs.[3f,h,4f] This is more than sufficient to make phosphorane **1a** the global mimimum. Moreover, in spite of the pronounced apicophobicity of the unpaired electron, phosphoranyl **2a** is not only a minimum but is also close in energy to the global minimum **2f** (which itself has only *one* axial hydroxyl group). Early theoretical results suggest that alkyl and/or alkoxyl substitution give rise to systems which *do* have the TBP$_a$ geometry as their global minimum,[13] and we continue to explore these experimentally accessible compounds.

Finally, we have verified that pseudorotation in the Berry sense is an available, low-energy pathway for stereopermutation in these systems. Thus, SP isomer **1ts** lies roughly 6 kcal/mol above **1a**. We have verified it as a pseudorotation TS by following the minimum energy path[14] downwards to isomers **1a** and **1f**, i.e., two hydroxyl groups exchange positions with two hydrogen atoms. These results have interesting implications for the hydrolysis of phosphate and phosphonate derivatives, which are often postulated to proceed through phosphorane intermediates.[15] These will be reported in due course.

Supplementary Material Available: Gaussian 92 archive information and energies at several other levels of calculation for all isomers of **1** and **2** and a pictorial representation of the MEP down from **1ts** (18 pages). Ordering information is given on any current masthead page.

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