Ab Initio Calculations on Phosphorus Compounds. II. Effects of Disubstitution on Ligand Apicophilicity in Phosphoranes

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Geometry optimizations at the HF/3-21G(*) and HF/6-31G* levels of *ab initio* theory have been carried out for various isomers of model disubstituted phosphoranes PH_3XY(*X*, *Y*=OH, CH_3, NH_2, and SH). Reasonable agreement was obtained between the optimized geometries and available crystal structure data for analogous compounds. The isomers were further characterized by frequency calculations. The MP2/6-31G*//6-31G* + ZPE energy data reveal that the interactions between the ligands are relatively small (0–4 kcal mol^{-1}) for the most stable conformations of the isomers. Hence, for these conformations the apicophilicities (based upon monosubstituted phosphoranes) are approximately additive. The less stable PH_3XY conformations are in general transition states or higher-order saddle points, and their interligand interactions are larger in magnitude (up to 10 kcal mol^{-1}); the results with these conformations suggest that apicophilicities may not be as additive for some highly substituted phosphoranes.

INTRODUCTION

To help understand the structures and energies of pentacoordinated phosphorus compounds, we extended our theoretical calculations of monosubstituted phosphoranes[1] to some disubstituted derivatives. The intermediates in the Wittig reaction and in substitution reactions of tetravalent phosphorus compounds are closely related to acyclic and cyclic pentacoordinated phosphoranes multiply substituted by RO, R, NR_2, and RS groups.[2] Many effects have been invoked to explain the relative stabilities of isomeric-substituted phosphoranes including ligand electronegativity,[3] π-effects,[4] ring strain, and steric interactions.[5] Interpretations are in general based upon a trigonal bipyramidal model in which the preference of a group for the apical rather than equatorial position is referred to as its "apicophilicity." In various systems that have been studied, quantitative estimates of apicophilicity vary over a wide range.[6] *Ab initio* calculations provide an important means to study these various factors in more detail. In our first article,[1] a series of phosphoranes with first- and second-row substituents were calculated with full geometry optimizations at the HF/6-31G* *ab initio* level for various structures. For a number of substituents, such as OH, SH, CH_3, etc., apical and equatorial conformations of approximate trigonal bipyramids are minima on the potential energy surface and were used to define an intrinsic apicophilicity. For the highly electropositive substituents Li, Na, BeH, and MgH, the apical structures are minima but the equatorial conformations are transition states; the global minima for these cases are square pyramids. Thus, apicophilicities cannot be rigorously defined for these substituents. Similarly, the strongly electronegative substituents F and Cl are so highly ionic that only the apical phosphoranes are minima; these substituents also do not lend themselves to a definition of apicophilicity based upon monosubstituted phosphoranes.

Recently, Deiters et al.[7] calculated a set of phosphoranes comprised of all combinations of the ligand atoms hydrogen, chlorine, and fluorine using partially optimized geometries. They found the apicophilicities of fluorine and chlorine to be dependent upon the other substituents. We have previously shown that several polyfluorophosphoranes have well-defined minima and established pseudorotation paths between them.[8] In the present work, we have chosen the "normal" ligands, OH, CH_3, NH_2, and SH, and performed computations on various isomers and conformers of acyclic phosphoranes disubstituted by combinations of these ligands. The results help delineate the effects of disubstitution in phosphoranes.

METHODS

Single-determinant restricted Hartree–Fock calculations were performed with the Gaussian 82[9] and Gaussian 86[10] programs on VAX 11/780 and CONVEX C1 computers. Optimizations with Schlegel's gradient technique[11] and Baker's eigenvector-following algorithm[12] were carried out within the symmetry

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groups specified; further constraints were imposed in some cases. The standard basis set 6-31G*[13] was used for the optimizations. The 3-21G(*)[14] was used for many of the structures, and as found in other systems[15] this basis set gives geometries close to that of 6-31G*. Harmonic vibrational frequencies were obtained from analytic second derivatives at 6-31G* and zero-point energies were scaled by 0.89.[16] Møller–Plesset (MP2) perturbation theory[17] was employed for the electron correlation corrections. The MP2(FC)/6-31G*//6-31G* + ZPE (abbreviated as MP2) level should be reasonably reliable for energy comparisons. In our previous study,[1] this level gave relative energies close (in general $<\pm 1$ kcal mol^{-1}) to the MP4/6-31G*//6-31G* + ZPE results.

RESULTS AND DISCUSSION

In addition to general interest in the structures of disubstituted phosphoranes, a major concern in this study was the additivity of apicophilicities—the extent of their dependence upon other substituents. In preliminary studies involving disubstituted model phosphoranes including at least one fluorine or chlorine ligand, PH_3XY(X = F, Cl; Y = F, Cl, CN, OLi, BH_2),[18] the effective apicophilicities of fluorine and chlorine were found to be influenced substantially by the other substituents. This is in accord with the results of Dieters et al.,[7] but our first article showed F and Cl to be ill-suited for such investigations. For this reason, we focus our attention here on the other common ligands, OH, CH_3, NH_2, and SH. Apicophilicities of the monosubstituted phosphoranes are summarized in Table I. This table compares the apicophilicities at the highest-level MP4/6-31G*//6-31G* + ZPE in our first article with the MP2(FC)/6-31G*//6-31G + ZPE (MP2) calculations corresponding to the highest levels in the present article. The table shows the agreement between the two levels. It also summarizes that OH and SH have small preferences for the apical position, CH_3 has a slightly larger equatorial preference, and NH_2 has a large preference for an equatorial orientation.

To study the effect of disubstitution on apicophilicity, only trigonal bipyramidal (TP) configurations were calcualted. The energies of the disubstituted phosphoranes are given at several theoretical levels in Table II. These results are used to derive the relative energies (REs). Because of the importance of cyclic phosphoranes in which the rings are apical-equatorial (a-e), the energies are also given relative to the most stable a-e structure and are summarized for the various levels in Table III. It has been well established that ~90° apical-equatorial ligand–ligand interactions are in general more significant than ~120° diequatorial ligand–ligand interactions.[19] In several cases, however, the diequatorial isomers are the global minima.

These REs may be compared to the corresponding sums of the apicophilicities of the two substituents, e.g., at MP2. These apicophilicity summation energies (ASEs) also are summarized in Table III. The difference between the RE and relative ASE values is a measure of the mutual interaction or effect of the two substituents. The energies of the disubstituted phosphoranes may also be compared with monosubstituted analogs by means of the isodesmic equation, eq. (1).

$$PH_3XY + PH_5 = PH_4X + PH_4Y \qquad (1)$$

In evaluating this equation, the appropriate monosubstituted phosphorane PH_4X and PH_4Y conformers are chosen in which the substituents have the same conformations (apical or equatorial) as in PH_3XY. The data for PH_4X, PH_4Y, and PH_5 come from our previous study.[1] Equation (1) gives the bond summation energies (BSEs), which also are summarized in Table III. Note that most BSE values are negative, that is, the disubstituted phosphoranes are in general *less* stable than their monosubstituted analogs relative to hydrogen. The BSE values indicate the net mutual interactions among ligands in PH_3XY based upon the monosubstituted phosphoranes, PH_4X and PH_4Y. These interactions include all five ligands (i.e., the hydrogens as well), but the main effect presumably is that involving the two substituents (X and Y). The ASEs and BSEs are both based upon the monosubstituted phosphoranes and hence are interrelated. The BSE difference between two isomers is equal to the difference between REs and ASEs [i.e., $BSE_1 - BSE_2 = RE_{(1,2)} - (ASE_2 - ASE_1)$].

The structures calculated are shown in Figures 1–5. The numbers chosen for the structures in these

Table I. Apicophilicities based upon monosubstituted phosphoranes: PH_4X.

Subst.	MP2/6-31G*//6-31G* + ZPE	MP4/6-31G*//6-31G* + ZPE
OH	0.5	0.4
SH	0.3	−0.1
CH_3	−0.9	−0.9
NH_2[a]	−7.7	−7.2
PH_2	−3.2	−3.3
SiH_3	−9.1	−8.6

From ref. 1. Apicophilicities, $-(E_{apical} - E_{equatorial})$, are in kcal mol^{-1}.

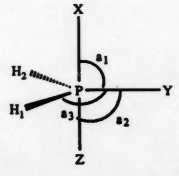
[a]The apicophilicity of NH_2 with a planar NH_2 group at an apical position is −8.6 kcal mol^{-1} at MP2/6-31G*//6-31G* + ZPE; this value was used for the ASE calculations in Table III for those apical NH_2 groups constrained to be planar.

Table II. Energies of disubsituted phosphoranes.

Cpd[a]	Ap.	Eq.	Sym.	3-21G(*)//3-21G(*)	6-31G*//6-31G*	MP2/6-31G*//6-31G*	ZPE[b]	n[c]
1_eon		OH,NH_2	C_1		473.46985	473.93435	48.44	0
2on*	OH	NH_2	C_s	471.14178	473.47009	473.93147	47.67	0
[2on[d]	OH	NH_2			473.44296	473.90378	46.80	1]
3_aon	OH,NH_2		C_s		473.45898	473.92160	47.41	0
[3_aon*	OH,NH_2		C_s	471.12115	473.45561	473.91775	46.45	2]
4no	NH_2	OH	C_s		473.45566	473.91998	47.99	0
[4no*	NH_2	OH	C_s	471.12491	473.45201	473.91440	46.79	2]
5no*	NH_2	OH	C_1	471.10538	473.43427	473.89512	45.45	3
1oc	OH	CH_3	C_s	455.19968	457.45292	457.88280	54.02	0
2_aoc	OH,CH_3		C_s	455.19760	457.45024	457.88112	53.88	0
3co	CH_3	OH	C_s	455.20118	457.44784	457.88095	54.50	0
4oc	OH	CH_3	C_s	455.19523	457.44845	457.87840	53.75	1
5co	CH_3	OH	C_s	455.19121	457.42778	457.87116	54.35	1
1_ecn		CH_3,NH_2	C_s		437.61453	438.03043	62.46	0
2cn	CH_3	NH_2	C_s	435.47392	437.60831	438.02467	62.32	0
3cn	CH_3	NH_2	C_s	435.46753	437.60218	438.01891	62.25	1
4nc*	NH_2	CH_3	C_s	435.45441	437.59533	438.00984	60.98	2
5nc*	NH_2	CH_3	C_s	435.45422	437.59474	438.00862	60.81	2
1_eoo		OH,OH	C_2		493.30667	493.78749	40.75	0
2_eoo		OH,OH	C_s		493.30581	493.78659	40.69	0
3oo	OH	OH	C_s	490.86868	493.30728	493.78490	39.98	0
4_aoo	OH,OH		C_{2v}	490.85919	493.30710	493.78412	39.84	0
5_aoo	OH,OH		C_s	490.85756	493.30555	493.78251	39.06	1
6oo	OH	OH	C_s	490.85611	493.29861	493.77533	39.76	0
7oo	OH	OH	C_s	490.85795	493.29640	493.77440	39.38	1
1_eos		OH,SH	C_1		815.94408	816.36275	37.09	0
2_aos	OH,SH		C_s	812.06120	815.94748	816.36012	35.82	0
3os	OH	SH	C_s	812.05840	815.94157	816.35886	36.25	0
4os	OH	SH	C_s	812.05734	815.93952	816.35658	36.13	0
5os	SH	OH	C_s	812.06015	815.93767	816.35451	36.37	0

Energies are in $-$a.u.
[a]Asterisk denotes NH_2 groups constrained to be planar.
[b]Zero-point energies in kcal mol^{-1} were calculated at 6-31G*.
[c]Numbers of imaginary frequencies.
[d]Pyramidal NH_2 group perpendicular, staggered, and anti to PO.

figures are in the order of increasing energy. Lowercase letters designate the substituents: o, n, c, and s refer to OH, NH_2, CH_3, and SH, respectively. For a-e structures, the letter for the apical substituent is given first. Diapical and diequatorial isomers are indicated by the appropriate subscript 1 or 3 after the number. For each set of substituents, the number in parentheses is the energy (in kcal mol^{-1}) relative to the most stable isomer at the highest level. For convenience, the number of imaginary frequencies is given by a subscript. Geometry data are summarized in Table IV. The parameters are defined in scheme 1; the positions of the substituents in Figures 1–5 correspond to this scheme.



Scheme 1. General structure of a-e and diapical disubstituted phosphoranes defining the structural parameters in Table IV.

$PH_3(OH)(NH_2)$

Several acyclic $PH_3(OH)(NH_2)$ isomers were optimized at the 6-31G* level and several were compared at the 3-21G(*) level (Fig. 1). The resulting geometries for the two basis sets are almost the same. For monosubstituted phosphoranes, the most stable structures are those with an apical OH group and an equatorial NH_2 with a planar amino group perpendicular to the equatorial plane. The corresponding disubstituted derivative with a planar amino group is a stable structure, **2on**, and is a local minimum with all frequencies real. A similar structure with a pyramidal amino group was found to be a transition state of higher energy (Table II). The global minimum at MP2, however, is **1_eon** with OH and planar NH_2 groups both equatorial but it is only 1.0 kcal mol^{-1} more stable than **2on**. In **1_eon**, the NH and OH bonds essentially eclipse the apical PH bonds. At the SCF level, this structure is slightly less stable than **2on** (by 0.15 kcal mol^{-1}). Conformations with apical amino groups, **3no** and **4no**, are much higher in energy as expected given the strong equatorial preference for NH_2. With pyramidal amino groups, these compounds are local minima; corresponding structures with constrained planar amino groups have

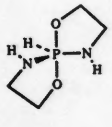
Table III. REs, ASEs, and BSEs of disubstituted phosphoranes.

Cpd	Ap.	Eq.	Sym.	6-31G*/6-31G* RE	MP2/6-31G*//6-31G* + zPE[a] RE	ASE	BSE
1$_e$on		OH,NH_2	C_1	0.15	−1.0	0.5	−2.1
2on	OH	NH_2	C_s	0.0	0.0	0.0	−3.6
3$_a$on	OH,NH_2		C_s	7.0	5.9	7.7	−1.8
4no	NH_2	OH	C_s	9.1	7.5	8.2	−2.9
5no	NH_2	OH	C_1	22.5	20.6	20.6	−3.6
1oc	OH	CH_3	C_s	0.0	0.0	0.0	−0.1
2$_a$oc	OH,CH_3		C_s	1.7	0.9	0.9	−0.1
3co	CH_3	OH	C_s	3.2	1.6	1.4	−0.3
4oc	OH	CH_3	C_s	2.8	2.6	0.0	−2.7
5co	CH_3	OH	C_s	15.8	7.6	1.4	−6.3
1$_e$cn		CH_3,NH_2	C_s	−3.9	−3.5	0.0	0.6
1cn	CH_3	NH_2	C_s	0.0	0.0	0.9	−2.0
2cn	CH_3	NH_2	C_s	3.8	3.5	0.9	−5.5
3nc	NH_2	CH_3	C_s	8.1	8.1	7.7	−3.3
4nc	NH_2	CH_3	C_s	8.5	8.8	7.7	−4.0
1$_e$oo		OH,OH	C_2	0.4	−0.9	1.0	−3.5
2$_e$oo		OH,OH	C_s	0.9	−0.4	1.0	−4.0
3oo	OH	OH	C_s	0.0	0.0	0.5	−3.9
4$_a$oo	OH,OH		C_{2v}	0.1	0.4	0.0	−4.8
5$_a$oo	OH,OH		C_s	1.1	0.7	0.0	−5.1
6oo	OH	OH	C_s	5.4	5.8	0.5	−9.7
7oo	OH	OH	C_s	6.8	6.1	0.5	−10.0
1$_e$os		OH,SH	C_1	−1.6	−1.6	0.8	−2.3
2$_a$os	OH,SH		C_s	−3.7	−1.2	0.0	−3.5
3os	OH	SH	C_s	0.0	0.0	0.3	−4.4
4os	OH	SH	C_s	1.7	1.3	0.3	−5.7
5so	SH	OH	C_s	2.5	2.8	0.5	−7.0

Energies are in kcal mol^{1-}.
[a]Zero-point energies were calculated at 6-31G* and scaled by 0.89.

two imaginary frequencies (Table II). In **5no**, the OH group was constrained to lie in the equatorial plane. This structure has three imaginary frequencies and a high relative energy. The comparable monosubstituted phosphorane also is unfavorable.[1]

The optimized bond lengths in these $PH_3(OH)(NH_2)$ isomers are in reasonable agreement with available crystal structure data. For example, the equatorial P—N bond lengths are 1.640 Å and **6**,[20] as well as 1.698 and 1.681 Å in **7**.[21] In **2on**, the optimized P—N bond length is 1.656 Å. The apical P—O bond length, 1.710 Å in **6** and 1.697 Å in **7**, may be compared with 1.702 Å in **2on**.



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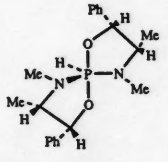

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From simple electrostatic considerations, electron-withdrawing substituents *X* in disubstituted phosphoranes, PH_3XY, should result in shorter P—Y bonds whereas electron-donating *X* groups should lengthen the P—Y bond. The calculated geometries agree with this generalization. In PH_4NH_2, the apical P—N bond length is 1.757 Å and the equatorial value is 1.675 Å at 6-31G*. In $PH_3(OH)(NH_2)$, the length of the P—N bond is reduced in all of the isomers because of the presence of the OH group but the changes are small. These shortenings are −0.006 Å (**1$_e$on**), −0.019 Å (**2on**), −0.007 Å (**3$_a$on**), −0.038 Å (**4no**), and −0.012 Å (**5no**). The OH group in the equatorial position (**4no**) shortens the apical P—N bond more than an OH group in the apical position (**2on**). The π electron-donating NH_2 group lengthens the P—O bond in diapically substituted **3$_a$on** by

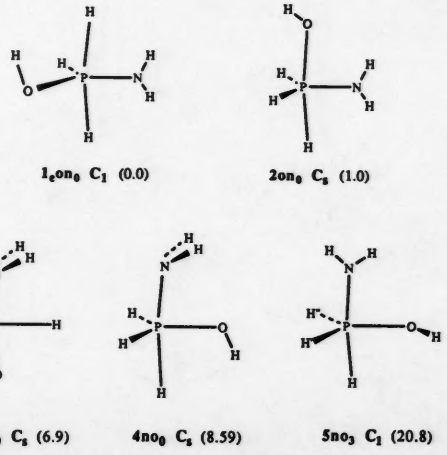


Figure 1. Relative energies of several conformations of $PH_3(OH)(NH_2)$.

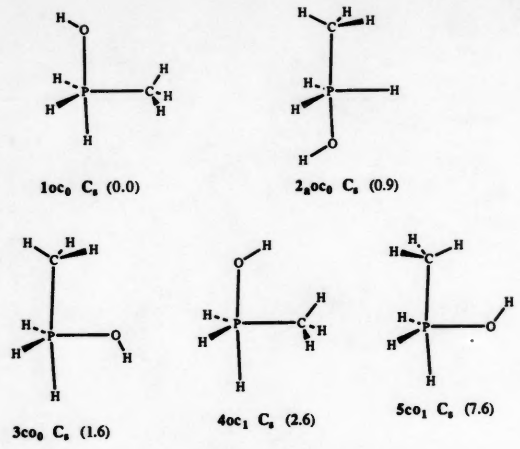


Figure 2. Relative energies of several conformations of $PH_3(OH)(CH_3)$.

0.011 Å; but, in the apical-equatorial isomers the P—O length hardly changes. For disubstituted phosphoranes, the *XPY* angle is the most significant. In $PH_3(OH)(NH_2)$, this angle is around 87–88°, close to that in an ideal trigonal bipyramid.

The BSE for the global minimum structure **1$_e$on** has a relatively low magnitude. Because of the high preference for the amino group to be equatorial, its ASE relative to **2on** is also small. For the other isomers, the ASE values are comparable to the relative energies and the BSE values are all comparable. All these results indicate that the mutual effects of the OH and NH_2 substituents are relatively small.

$PH_e(OH)(CH_3)$

The combination of alkoxy and alkyl ligands is also important in pentacoordinated phosphoranes. One example is the oxaphosphetane intermediate in Wittig reactions.[22] The two pseudorotational forms of Wittig intermediates have similar energies.[23]

In monosubstituted phosporanes, the methyl group has a small preference for the equatorial position (apicophilicity, −0.9), slightly greater than the apical preference for the OH group (apicophilicity, 0.5). The global minimum found for the disubstituted compound has the OH apical and the methyl equatorial (**1oc**). The five acyclic $PH_3(OH)(CH_3)$ isomers optimized in C_s symmetry all have nearly ideal trigonal bipyramidal structures. The OH—CH_3 interactions in the three most stable isomers (Fig. 2) are

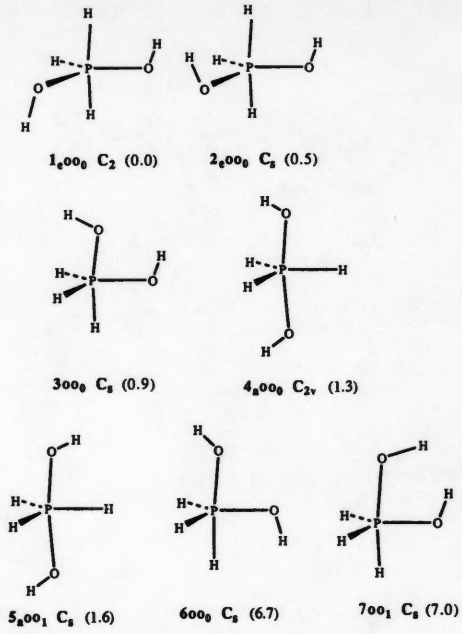


Figure 4. Relative energies of several conformations of $PH_3(OH)_2$.

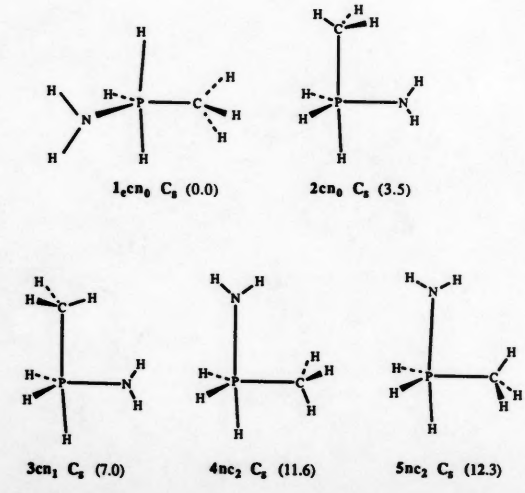


Figure 3. Relative energies of several conformations of $PH_3(NH_2)(CH_3)$.

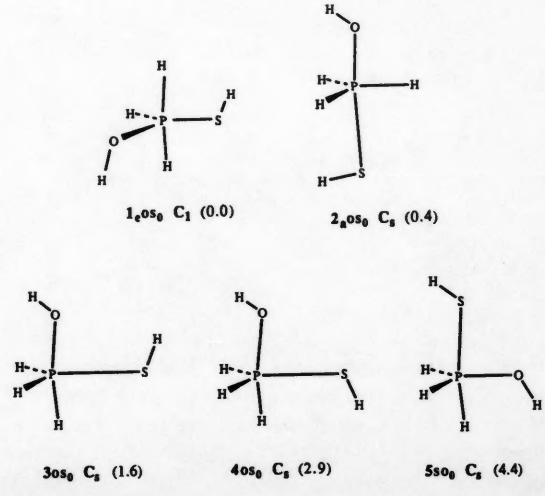


Figure 5. Relative energies of several conformations of $PH_3(OH)(SH)$.

Table IV. Selected optimized geometry parameters of disubstituted phosphoranes.

Cpd	P—*X*	P—*Y*	P—*Z*	P—H_e	a_1	a_2	a_3	d[a]
1_eon	1.443[b]	1.669[c]	1.419	1.401	88.38	89.74	117.13	
2on	1.702	1.656	1.440	1.397	87.24	88.79	125.27	90.68
3_aon*	1.750	1.384	1.715	1.388	87.40	84.43	124.34	92.22
4no*	1.719	1.640	1.454	1.396	86.68	87.29	126.43	86.49
5no*	1.745	1.656	1.432	1.400′	87.43	88.57	128.55′	90.00
				1.396″			122.55″	
1oc	1.716	1.830	1.456	1.396	90.51	89.92	121.74	92.86
2oc	1.895	1.390	1.714	1.395	91.27	85.02	121.95	89.41
3co	1.869	1.649	1.451	1.405	87.94	87.01	126.68	92.03
4oc	1.720	1.843	1.456	1.389	95.84	87.85	121.13	93.54
5co	1.931	1.646	1.425	1.403	92.43	84.04	126.70	92.02
1_ecn	1.454	1.840[d]	1.454	1.405	92.22	92.22	108.35	
2cn	1.898	1.679	1.453	1.407	91.27	86.45	126.24	92.46
3cn	1.926	1.679	1.454	1.404	92.09	86.13	126.39	93.32
4nc*	1.769	1.844	1.471	1.396	92.94	87.19	123.18	94.73
5nc*	1.778	1.848	1.466	1.396	89.98	90.74	123.13	92.23
1_eoo	1.417	1.635	1.417	1.397	90.58[e]	86.24	114.18	
2_eoo	1.439[f]	1.635	1.400	1.396	89.18[g]	87.49	112.77	
3oo	1.709	1.615	1.420	1.395	86.90	87.48	124.67	89.91
4_aoo	1.699	1.375	1.699	1.388	86.43	86.43	123.07	90.00
5_aoo	1.703	1.383	1.702	1.382	90.99	84.94	122.56	90.39
6oo	1.670	1.618	1.446	1.395	86.42	89.22	124.50	91.34
7oo	1.711	1.632	1.420	1.387	93.09	86.59	123.79	90.74
1_eos	1.422[h]	1.641[i]	1.406[j]	1.391	89.91[k]	86.21	112.88	
2_aos	1.674	1.376	2.295	1.380	88.67	83.87	122.16	92.27
3os	1.698	2.099	1.434	1.394	89.50	85.21	123.86	92.88
4os	1.692	2.108	1.433	1.394	84.64	89.87	124.22	89.98
5os	2.229	1.622	1.437	1.389	84.44	89.60	125.46	88.31

Bond lengths are in Å and bond angles are in degrees. The geometries were optimized at 6-31G*. Primes and double primes refer to nonequivalent hydrogens as indicated in Fig. 1.

[a] *d* is the dihedral angle between the HP*Y* and P*YX* planes (the HP*YX* dihedral angle).

[b] H syn to H of OH.

[c] *Y*=N; NH, 0.997; NHN, 116.37; PO, 1.637; POH, 112.08; NPO, 129.52.

[d] Y=C; CH (in plane), 1.087; HCP, 108.16; CH(out of plane), 1.084; HCP, 110.95; PN, 1.679; NH, 0.998; PNH, 121.21; NPC, 126.55.

[e] To *syn*-OH; OPO, 131.65; XPZ, 172.23.

[f] *syn* to OH.

[g] OPO, 132.45; HOP, 113.77; *XPZ*, 171.71.

[h] *syn* to OH.

[i] *Y*=O; OH, 0.951; POH, 113.28; PS, 2.151; SH, 1.328; PSH, 99.86.

[j] *syn* to SH.

[k] XPS, 84.51; *Z*PS, 90.44; *XPZ*, 167.20; OPS, 139.08.

all small (less than 0.5 kcal mol^{-1} at MP2 for **1oc**, **2oc**, and **3co**). These three isomers are all confirmed to be energy minima by frequency calculations. Again, the ASE relative energy predictions for these three isomers are accurate within 0.2 kcal mol^{-1}.

The OH and one of the CH_3 hydrogens in the C_s plane of the **4oc** and **5oc** conformations point toward each other. Steric repulsion results in an increase in the OPC angles to 95.8° in **4oc** and to 92.5° in **5oc**. As expected, the ASEs for these two conformations deviate from the REs (Table III) due to these steric effects.

Attempts to find diequatorial isomers gave optimizations back to one of the above structures.

$PH_3(NH_2)(CH_3)$

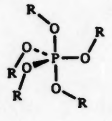
For monosubstituted phosphoranes, both methyl and amino groups prefer the equatorial position. The global minimum for the corresponding disubstituted compound, **1_ecn**, in a C_s structure with both substituents equatorial. The NH_2 group is slightly pyramidal (sum of bond angles about nitrogen is 359.18°) away from methyl. Four a-e isomers of $PH_3(NH_2)(CH_3)$ were calculated (Fig. 3). Both apical and equatorial NH_2 groups were restrained to planarity. Isomer **2cn**, the most stable of these structures, is a local minimum with all frequencies real, indicating that the NH_2 group, as in the monosubstituted equatorial phosphorane, is indeed planar. The isomer **3cn** differs only in the rotation of the methyl group and is the transition state for P—CH_3 rotation with a barrier of 3.5 kcal mol^{-1} at MP2. Isomers **4nc** and **5nc** each have one imaginary frequency, 545i and 541i cm^{-1}, respectively, representing the transformation of planar NH_2 to pyramidal NH_2. They also have a second imaginary frequency of 215i and 266i cm^{-1}, respectively, corresponding

to the pseudorotation of the NH_2 group from apical to equatorial. Indeed, during the optimizations of **4nc** and **5nc** with pyramidal NH_2 groups the N-P-C angles increase to about 120° and the structures transform into diequatorially substituted isomers. Because the interligand interactions are similar for **2cn**, **4nc**, and **5nc**, the relative energies can be derived from the apicophilicities with errors less than 1.1 kcal mol^{-1}. For **3cn**, the ASE and RE deviations are larger.

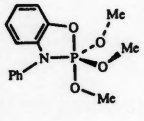
$PH_3(OH)(OH)$

The hydroxy group in PH_4OH is slightly apicophilic but with two hydroxy groups two diequatorial isomers are the most stable, albeit by small amounts. The global minimum, $\mathbf{1_eoo}$, is 0.9 kcal mol^{-1} more stable at MP2 than the lowest a-e isomer, **3oo**. $\mathbf{1_eoo}$ is the *anti*-rotomer; the *syn*-rotomer $\mathbf{2_eoo}$ is higher by 0.5 kcal mol^{-1}. Five acyclic isomers of dihydroxyphosphoranes were optimized at 6-31G* (Fig. 4). Two diapical isomers are only slightly less stable (<1 kcal mol^{-1}) than **3oo**. Accordingly, the P—O bond in the diapical dihydroxyphosphorane $\mathbf{4_aoo}$ is only slightly shortened by 0.005Å compared to the value in monosubstituted apical PH_4OH. In $\mathbf{4_aoo}$, the two OH groups bend toward each other; the OPO angle is 172.9°. The other diapical comformation $\mathbf{5_aoo}$ has a slightly higher energy and is a transition state on the PES of $PH_3(OH)(OH)$.

Three acyclic a-e dihydroxyphosphoranes were investigated in C_s symmetry, **3oo**, **6oo**, and **7oo**. The most stable of these forms is **3oo**, with two OH groups bent in the same direction around the central phosphorus. This propeller-like conformation is also found in many crystal structures of multialkoxy-substituted phosphoranes such as **8** and **9**.[24]



8



9

In **3oo**, the distance between the oxygen in the apical hydroxy group and the hydrogen in the equatorial hydroxy group is 2.0 Å, close to the limit for H—O hydrogen bonding. The electrostatic interactions certainly are favorable in this conformation. The BSE value for **3oo** is close to that of $\mathbf{4_aoo}$; hence, ASE is similar to the calculated relative energy.

The ligand interactions in the other two a-e conformations are larger: −9.7 and −10.0 kcal mol^{-1} for **6oo** and **7oo**, respectively. This effect is also reflected in the higher relative energies of **6oo** and **7oo**. These higher energies can be attributed to the unfavorable electrostatic interactions between the two OH groups. Conformations of **6oo** and **7oo** (or distorted forms) exist commonly in TP spirobicyclic phosphorane compounds.[2] The nonadditivity of these conformations points to an additional source of strain in the cyclic phosphoranes. In particular, comparison of **6oo** with **3oo** confirms the effect noted in our first article[1]: Cyclic dioxophosphoranes that resemble **6oo** contain an instability associated with the orientation of substituents about the oxygen in addition to any ring strain effects.

$PH_3(OH)(SH)$

From variable-temperature nuclear magnetic resonance (NMR) studies, Trippett et al. has shown that oxy-, thio- and selenogroups have comparable apicophilicities in pentacoordinated phosphoranes. For example, ethoxy- and ethylthio groups have similar preferences for an apical position,[25] and phenoxy-, phenylthio-, and phenylseleno groups possess comparable apicophilicities.[26] These results were also confirmed in our model PH_4XH (X = O, S) calculations,[1] which gave OH and SH apicophilicities of 0.5 and 0.3 kcal mol^{-1}, respectively. The disubstituted phosphoranes $PH_3(OH)(SH)$ calculated here are analogous to the $PH_3(OH)_2$ system. Although both OH and SH groups are modestly apicophilic, the global minimum, $\mathbf{1_eos}$, for the disubstituted phosphorane is diequatorial but by only a small amount (0.4 kcal mol^{-1}) compared to the diapical isomer, $\mathbf{2_aos}$. Both are more stable than the lowest a-e conformer. All five structures found are local energy minima and their geometries are close to the ideal trigonal bipyramid. The diapical isomer, $\mathbf{2_aos}$, and the lowest-energy a-e conformation, **3os**, have BSEs similar to the corresponding $PH_3(OH)(NH_2)$ and $PH_3(OH)_2$ structures. The higher-energy a-e conformations **4os** and **5os** have higher BSEs. The unfavorable electrostatic interactions in **4os** and **5so** raise the relative energies. Hence, deviations from apicophilicity additivity are significant for these less stable local minima.

CONCLUSIONS

This work has demonstrated that the intrinsic ligand apicophilicities of OH, CH_3, NH_2, and SH obtained from monosubstituted PH_4X phosphorane models can be transferred to many of the disubstituted phosphorane combinations. This is especially true for the most stable conformations that are free from strong steric interactions. The summation of the apicophilicities of each ligand gives an estimate in general better than 2 kcal mol^{-1} for the relative energies of corresponding disubstituted isomers. This also provides a theoretical basis for the empirical experimental approach in which apicophilicities of ligands are deduced from multiply substituted phosphoranes.[6a] Hence, the theoretically derived apicophilicities may also be applicable to mutisubstituted phosphoranes. Nevertheless, even these small en-

ergy differences can have significant conformational effects. For example, OH and SH groups that are apicophilic in monosubstituted phosphoranes prefer the diequatorial conformation in disubstituted phosphoranes although this preference is slight. Deviations of several kcal mol^{-1} do occur for less stable isomers. These high-energy structures are frequently not minima on the potential energy surface but they do also suggest that more highly substituted phosphoranes may show significant deviations from additivity.

Electronegative groups attached to the same central atom often interact strongly. This "generalized anomeric effect" involves p interaction with an antibonding σ^* orbital, optimum for an angle about 100°.[27] The effects on tricoordinate phosphorus compounds have been analyzed in detail.[27] Pentacoordinated phosphorus compounds can be expected to behave similarly provided suitable conformations are present. But, this is not generally the case for the stable isomers considered here. Thus, both **4_aoo** and **2_aoo** are diapical, for which $p \rightarrow \sigma^*$ anomeric interaction is negligible. Both **1oc** and **2cn** involve a methyl group, a relatively poor π donor. In **3_aon**, the N lone pair of the NH_2 group is oriented 90° with regard to the P—O bond, precluding $\pi(p(N) \rightarrow \sigma^*(P—O))$ interaction. These are all examples in which RE and ASE differ by less than 1 kcal mol^{-1}.

Finally, in all these examples the a-e conformations so important in cyclic phosphoranes are of relatively low energy and easily accessible even when not the lowest-energy structures.

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References

1. P. Wang, Y. Zhang, R. Glaser, A.E. Reed, A. Streitwieser, and P.v.R. Schleyer, *J. Am. Chem. Soc.*, **113,** 55 (1991). See this article for general information.
2. Review on experimental and theoretical work on pentavalent phosphorus: R.R. Holmes, *Pentacoordinated Phosphorus*, Vol.s I and II. ACS Monographs Nos. 175 and 176. American Chemical Society, Washington, DC, 1980.
3. E.L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2,** 613 (1963).
4. R. Hoffmann, J.M. Howell, and E.L. Muetterties, *J. Am. Chem. Soc.*, **94,** 3047 (1972).
5. F.H. Westheimer, *Acc. Chem. Res.*, **1,** 70 (1968).
6. (a) R.R. Holmes, *J. Am. Chem. Soc.*, **100,** 433 (1978); (b) G.O. Moreland, L.B. Doak, N.S. Littlefield, L.W. Walker, R.W. Brown, and A.H. Cowley, *J. Am. Chem. Soc.*, **101,** 2161 (1979).
7. J.A. Deiters, R.R. Holmes, and J.M. Holmes, *J. Am. Chem. Soc.*, **110,** 7672 (1988).
8. P. Wang, D.K. Agrafiotis, A. Streitwieser, and P.v.R. Schleyer, *J. Chem. Soc. Chem. Comm.*, 201 (1990).
9. J.S. Binkley, M.J. Frisch, D.J. DeFrees, R. Krishnan, R.A. Whiteside, H.B. Schlegel, E.M. Fluder, and J.A. Pople, Gaussian 82. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1985.
10. M.J. Frisch, J.S. Binkley, H.B. Schlegel, K. Raghavachari, C.F. Melius, R.L. Martin, J.J.P. Stewart, F.W. Bobrowicz, C.M. Rohlfing, L.R. Kahn, D.J. DeFrees, R.A. Seeger, R.A. Whiteside, D.J. Fox, E.M. Fleuder, and J.A. Pople, Gaussian 86. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1989.
11. H.B. Schlegel, *J. Comp. Chem.*, **3,** 214 (1982).
12. J. Baker, *J. Comp. Chem.*, **7,** 385 (1986).
13. (a) W.J. Hehre, R. Ditchfield, and J.A. Pople, *J. Chem. Phys.*, **56,** 2257 (1972); (b) P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, **28,** 213 (1973); (c) J.S. Binkley, M.S. Gordon, D.J. DeFrees, and J.A. Pople, *J. Chem. Phys.*, **77,** 3654 (1982); (d) W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory.* Wiley, New York, 1986, sect. 4.3.
14. (a) J.S. Binkley, J.A. Pople, and W.J. Hehre, *J. Am. Chem. Soc.*, **102,** 939 (1980); (b) M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro, and W.J. Hehre, *J. Chem. Soc.*, **104,** 2197 (1982); (c) M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, and J.A. Pople, *J. Chem. Phys.*, **104,** 5039 (1982).
15. E. Magnusson, *J. Comp. Chem.*, **5,** 612 (1984).
16. J.A. Pople, J.S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp.*, **10,** 1 (1976); J.S. Binkley and J.A. Pople, *Int. J. Quantum Chem. Symp.*, **9,** 229 (1975), and references therein.
17. (a) J.A. Pople, H.B. Schlegel, R. Krishnan, D.J. DeFrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, R.F. Hout Jr., and W.J. Hehre, *Int. J. Quantum Chem. Symp.*, **15,** 269 (1981); (b) D.J. DeFrees and A.D. McLean, *J. Chem. Phys.*, **82,** 333 (1985) (c) A. Komornicki, F. Pauzat, and Y. Ellinger, *J. Phys. Chem.*, **87,** 3847 (1983).
18. R. Glaser, dissertation, University of California, Berkeley, CA, 1987.
19. R. Sarma, F. Ramirez, B. McKeever, J. Marecek, and S. Lee, *J. Am. Chem. Soc.*, **98,** 581 (1976).
20. P. Meunier, R.O. Day, J.R. Devillers, and R.R. Holmes, *Inorg. Chem.*, **17,** 3270 (1978).
21. N.G. Newton, J.E. Collier, and R. Wolf, *J. Am. Chem. Soc.*, **96,** 6888 (1974).
22. P.J. Murphy, J. Chandrasekhar, W.G. Downey, and P.v.R. Schleyer, *J. Chem. Soc. Chem. Comm.*, 978 (1980).
23. R.S. McDowell and A. Streitwieser, *J. Mol. Struct. (THEOCHEM)*, **138,** 89 (1986).
24. J.I.G. Gadogan, R.O. Gould, S.E.B. Gould, P.A. Sadler, S.J. Sweir, and B.S. Tait, *J. Chem. Soc. Perkin Trans. I*, 2392 (1975).
25. J. Brierley, S. Trippett, and M.W. White, *J. Chem. Soc. Perkin Trans. I*, 273 (1977).
26. (a) M.P. Johnson and S. Trippett, *J. Chem. Soc. Perkin Trans. I*, 3074 (1981); (b) S.A. Bone, S. Trippett, and P.J. Whittle, *J. Chem. Soc. Perkin Trans. I*, 2125 (1974).
27. A.E. Reed and P.v.R. Schleyer, *Inorg. Chem.*, **27,** 3969 (1988).