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The Effects of the First- and Second-Row Substituents on the Structures and Energies of PH_4X Phosphoranes. An ab Initio Study

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Abstract: Pentacoordinated phosphoranes, PH_4X, substituted with a full range of first- and second-row groups have been studied with ab initio computations. The apically and equatorially substituted trigonal-bipyramidal (TB) and apically substituted square-pyramidal (SP) conformations were fully optimized with the 3-21G(*) and 6-31G* basis sets. Frequency calculations were performed at 6-31G* on the optimized structures. Correlation corrections through the MP4 level were carried out on these 6-31G* structures. Energies calculated with zero-point energy corrections, i.e., at MP4SDTQ/6-31G* + ZPE, provide relative energies of various isomers. The apically substituted SP structures for PH_4X (X = Li, Na, BeH, and MgH) are the most stable. The intrinsic apicophilicities of the first- and second-row groups are derived and are compared to available experimental data. The apicophilicities (in kcal mol^{-1}) are OH (0.4) > SH (−0.1) > CH_3 (−0.9) > PH_2 (−3.3) > NH_2 (−7.2) > SiH_3 (−8.6). Due to their high degree of ion pair character, PH_4F and PH_4Cl are unsuitable as models for relative energy comparisons. π interaction energies were evaluated by calculating various PH_4X (X = NH_2, PH_2, OH, SH) conformations. Natural bond orbital (NBO) analysis on these conformers shows that the π interaction is due chiefly to $n_x \rightarrow \sigma_{P-H^*}$. Inductive and π bonding contributions are estimated for the first-row group substituents. The effects of substitution (e.g., relative energies) that are dominated by inductive interactions correlate linearly with group electronegativities.

Introduction

The last two decades have seen a rapid development of the stereochemistry of phosphorus compounds.[1] Pentacoordinated models have been employed to help interpret a wide variety of reaction mechanisms including phosphate ester hydrolysis, the Wittig reaction, and biologically important phosphoryl transfer reactions.[2] Pentacoordinated phosphorus compounds have two basic structures: trigonal-bipyramid (TP) and square-pyramid (SP). Because of the stereochemical nonrigidity, ligand exchange is common in five-coordinated phosphoranes. In 1960, Berry proposed that this stereomutation takes place via a D_{3h}–C_{2v}–C_{4v} (TP–TP–SP) pathway.[3] Although largely inferential, this mechanism has been generally accepted and is employed to account for rearrangements in pentacoordinated phosphoranes. C_{2v} pathways or C_{4v} transition states have been demonstrated to be general. An alternative "turnstile" mechanism has also been proposed to explain intramolecular rearrangements.[4-6] The topological equivalence of these two processes in some systems has been pointed out.[7]

Many studies of the bonding, geometries, and relative energies of various isomers of the two basic structures have been published. Theoretical investigations have employed the directed valence approach,[8] the valence electron-pair repulsion model,[9] a three-center four-electron bonding scheme,[10] EHT analysis, and, more recently, additional semiempirical and ab initio calculations.[12-20] Dieters and Holmes have recently contributed an extensive series of substituted phosphoranes, but the computations were constrained to idealized TP and SP structures.[20]

Generally, the relative energies of apical vs equatorial isomers are believed to be controlled by the substituent electronegativities,[21] π-bonding,[11] steric interactions, and ring strain.[22] By using experimental data based on temperature-dependent NMR spectroscopy, Holmes has developed an empirical apicophilicity scale.[23] Some monosubstituted model phosphoranes have also been examined by computation.[24] However, as pointed out by Magnusson,[25] the relative energies of singly substituted phosphoranes vary considerably with different basis sets. The use of basis sets at least as large as 6-31G supplemented with d functions (6-31G*) is essential to obtain reliable relative energies.

Nitrogen, oxygen, and halogen ligands are commonly used for substituent studies. Phosphoranes substituted by electropositive

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Table I. Geometries and Relative Energies of PH_5 Isomers[a]

	TP(D_{3h})		SP(C_{4v})				
	P–H_e	P–H_a	P–H_b	P–H_a	H_ePH_a	E_1[b]	E_2[c]
3-21G	1.425	1.541	1.489	1.402	99.53	−2.2	81.1
3-21G*	1.405	1.465	1.440	1.387	100.22	−2.6	46.1
6-31G	1.431	1.541	1.440	1.407	100.00	−2.6	82.1
6-31G*	1.407	1.464	1.440	1.388	100.50	−2.8	47.1
6-31G**//6-31G*						−2.9	
6-31G(2d,p)//6-31G*						−2.8	
6-31G(2df,p)//6-31G*						−3.0	
MP2/6-31G*//6-31G*						−2.0	49.2
MP3/6-31G*//6-31G*						−1.8	50.6
MP4/6-31G*//6-31G*						−1.6	51.9
MP4/6-31G*//6-31G*+ZPE[d]						−1.1	58.0
full CI[e]						−1.9	
CI[f]						−1.2	

[a] Bond lengths in Å, bond angles in deg, and relative energies in kcal mol^{-1}. [b] E_1 = E(TP) − E(SP). [c] E_2 = E(TP) − E($PH_3 + H_2$). The dissociation barrier of PH_5 to give $PH_3 + H_2$ is 36.0 kcal mol^{-1} at CI level.[6b] [d] Zero-point energies were calculated at 6-31G* and scaled by 0.89. [e] Reference 6b. [f] Reference 6a.

Table II. Energies[a] of the First-Row Element-Substituted Phosphoranes

X	no.	sym	3-21G(*) //3-31G(*)	6-31G* //6-31G*	MP2/6-31G* //6-31G*	MP3/6-31G* //6-31G*	MP4/6-31G* //6-31G*	ZPE[b]	n[c]
H	**1a**	D_{3h}	341.863 42	343.499 88	343.617 16	343.640 16	343.645 86	29.10	0
	1s	C_{4v}	341.859 28	343.495 36	343.614 01	343.637 34	343.643 24	28.59	1
Li	**3a**	C_{3v}	348.632 11	350.317 05	350.449 63	350.474 04	350.480 81	20.17	2
	3e[d]	C_{2v}	348.678 82	350.364 12	350.489 87	350.512 26	350.520 32	21.04	1
	3s	C_{4c}	348.686 40	350.379 42	350.497 99	350.520 57	350.528 57	21.69	0
BeH	**4a**	C_{3v}	356.366 42	358.091 57	358.240 81	358.269 54	358.279 67	26.42	0
	4e[d]	C_{2v}	356.403 05	358.126 83	358.274 92	358.302 99	358.312 58	27.56	1
	4s	C_{4v}	356.408 34	358.131 05	358.280 32	358.308 52	358.318 16	27.95	0
BH_2	**5a**$_{\perp}$	C_s	366.939 56	368.724 79	368.911 96	368.945 37	368.956 86	35.38	0
	5e$_{\parallel}$	C_{2v}	366.965 79	368.749 19	368.934 78	368.967 57	368.978 82	36.26	1
	5s	C_{2v}	366.960 17	368.742 42	368.926 99	368.962 18	368.973 47	36.37	1
	5a$_{\parallel}$	C_s	366.939 33	368.724 81	369.911 96	368.945 35	368.956 83	34.40	1
	5e$_{\perp}$	C_{2v}	366.953 87	368.737 97	368.923 79	368.956 93	368.968 15	36.81	1
CH_3	**6a**	C_{3v}	380.697 05	382.544 49	382.794 31	382.826 37	382.839 76	48.66	0
	6e	C_s	380.699 80	382.547 21	382.796 25	382.828 34	382.841 60	48.95	0
	6s	C_s	380.693 59	382.540 13	382.788 44	382.821 09	382.834 25	48.36	2
NH_2	7a′	C_s	396.622 90	398.555 47	398.837 47	398.863 54	398.876 27	42.27	0
	7e$_{\perp}$	C_{2v}	396.643 75	398.567 62	398.851 08	398.876 02	398.889 08	43.04	0
	7s	C_{2v}	396.605 77	*e*					
	7a$_{\parallel}$	C_s	396.623 32	398.552 72	398.834 38	398.860 22	398.872 66	41.31	2
	7e$_{\parallel}$	C_{2v}	396.601 14	398.528 39	398.807 70	398.834 23	398.846 35	40.67	2
	7e′	C_s	396.602 08	398.537 27	398.818 65	398.845 17	398.858 06	41.79	1
OH	**8a**	C_s	416.363 70	418.407 14	418.704 48	418.723 95	418.736 73	34.56	0
	8e$_{\perp}$	C_s	416.367 47	418.404 50	418.704 89	418.723 04	418.737 21	35.24	0
	8s	C_s	416.332 82	418.369 75	418.662 51	418.682 77	418.695 70	33.59	1
	8e$_{\parallel}$	C_s	416.347 38	418.385 94	418.683 57	418.702 71	418.716 08	33.30	2
F	**9a**	C_{3v}	440.268 12	442.430 20	442.718 44	442.733 97	442.747 38	27.17	0
	9e	C_{2v}	440.255 99	442.412 64	442.704 41	442.718 56	442.733 74	26.66	1
	9s	C_{4v}	440.224 59	442.377 44	442.662 52	442.678 15	442.692 52	26.19	1

[a] Absolute energies in −au. [b] Zero point energies (kcal mol^{-1}) were calculated at 6-31G*. [c] Number of imaginary frequencies. [d] Partially optimized; see text. [e] Converted to 7e$_{\perp}$.

groups are difficult to investigate experimentally. The entire set of first- and second-row substituents can only be studied in a systematic way by computations.[26] Moreover, there are few theoretical results on SP structures. The calculational results in this paper provide insight into the nature of substitution effects of first- and second-row groups on phosphoranes in both TP and SP conformations. In addition, we provide a large body of fundamental structure and energy data to facilitate further theoretical and experimental investigations.

Methods

Standard single-determinant spin-restricted Hartree–Fock calculations were performed with the GAUSSIAN 80[27] and GAUSSIAN 82[28] programs. Optimizations with Schlegel's gradient technique[29] were carried out under the constraints of the point group specified; further constraints were imposed in some cases. All calculations were carried out with standard 3-21G(*)[30] and 6-31G*[31] basis sets. Harmonic vibrational frequencies were calculated at 6-31G*, and zero-point energies (ZPE) were scaled by 0.89.[32] Full fourth-order Møller–Plesset (MP4)[33] correlation cor-

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Table III. Energies[a] of the Second-Row Element-Substituted Phosphoranes

X	no.	sym	3-21G(*) //3-31G(*)	6-31G* //6-31G*	MP2/6-31G* //6-31G*	MP3/6-31G* //6-31G*	MP4/6-31G* //6-31G*	ZPE[b]	n[c]
Na	**11a**	C_{3v}	502.098 79	504.718 37	504.850 68	504.875 72	504.886 39	21.30	0
	11e[d]	C_{2v}	502.141 15	504.760 67	504.887 17	504.909 12	504.917 55	20.54	1
	11s	C_{4v}	502.147 06	504.765 38	504.893 04	504.915 33	504.923 40	21.09	0
MgH	**12a**	C_{3v}	540.304 81	543.047 69	543.194 75	543.223 40	543.234 08	25.14	0
	12e[d]	C_{2v}	540.344 10	543.085 45	543.230 55	543.257 94	543.267 73	25.18	1
	12s	C_{4v}	540.350 92	543.090 81	543.237 13	543.264 60	543.274 36	25.60	0
AlH_2	**13a**$_{\parallel}$	C_s	583.043 30	585.947 94	586.114 32	586.147 01	586.158 70	30.35	1
	13e$_{\parallel}$	C_{2v}	583.079 78	585.981 29	586.147 02	586.178 98	586.190 12	31.07	0
	13s	C_{2v}	583.079 53	585.980 98	586.147 22	586.179 23	586.190 40	35.10	1
SiH_3	**14a**	C_{3v}	630.490 89	633.564 24	633.760 50	633.797 21	633.810 24	39.50	0
	14e	C_s	630.509 76	633.581 67	633.776 39	633.812 68	633.825 41	40.38	0
	14s	C_s	630.509 78	633.580 53	633.776 13	633.812 58	633.825 39	39.86	2
PH_2	**15a′**	C_s	681.538 55	684.803 61	685.021 44	685.058 00	685.071 17	36.02	0
	15e″	C_s	681.543 29	684.808 85	685.027 56	685.063 93	685.077 34	36.64	0
	15s	C_{2v}	681.475 76	*e*					
	15a$_{\parallel}$	C_s	681.503 51	684.771 33	684.984 87	685.021 20	685.033 44	35.32	1
	15e$_{\parallel}$	C_{2v}	681.469 69	684.736 96	684.959 84	684.996 74	685.009 95	34.84	3
	15e′	C_s	681.535 27	684.800 79	685.019 86	685.056 76	685.070 31	36.20	1
	15e$_{\perp}$	C_{2v}	681.507 12	684.773 36	684.996 06	685.031 33	685.044 58	36.37	1
SH	**16a**	C_s	737.568 51	741.047 50	741.279 33	741.312 84	741.324 45	31.02	0
	16e$_{\perp}$	C_s	737.563 61	741.042 78	741.279 82	741.313 03	741.325 61	31.72	0
	16s	C_s	737.538 49	741.016 71	741.251 04	741.285 34	741.297 53	30.29	1
	16e$_{\parallel}$	C_s	737.545 43	741.025 16	741.262 69	741.296 64	741.309 14	30.24	2
Cl	**17a**	C_{3a}	798.762 40	802.472 57	802.708 25	802.738 48	802.747 94	25.95	0
	17e	C_{2v}	798.738 52	802.452 48	802.684 54	802.715 41	802.724 79	24.77	1
	17s	C_{4v}	798.705 99	802.415 54	802.658 05	802.688 64	802.699 13	24.99	1

[a] Absolute energies in −au. [b] Zero point energies (kcal mol^{-1}) were calculated at 6-31G*. [c] Number of imaginary frequencies. [d] Partially optimized; see text. [e] Did not converge.

Table IV. Relative Energies[a] of the First-Row Element-Substituted Phosphoranes

X	no.	sym	3-21G(*) //3-31G(*)	6-31G* //6-31G*	MP2/6-31G* //6-31G*	MP3/6-31G* //6-31G*	MP4/6-31G* //6-31G*	MP4/6-31G* //6-31G*+ZPE[b]
Li	**3a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	3e	C_{2v}	−29.3	−29.5	−25.2	−24.0	−24.8	−24.7
	3s	C_{4v}	−34.1	−33.5	−30.3	−29.2	−30.0	−28.4
BeH	**4a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	4e	C_{2v}	−23.0	−22.1	−21.4	−21.0	−20.6	−19.8
	4s	C_{4v}	−26.3	−24.8	−24.8	−24.5	−24.2	−22.8
BH_2	**5a**$_{\perp}$	C_s	0.0	0.0	0.0	0.0	0.0	0.0
	5e$_{\parallel}$	C_s	−16.4	−15.3	−14.3	−13.9	−13.8	−13.0
	5s	C_{2v}	−13.1	−11.0	−9.4	−10.5	−10.4	−9.5
	5a$_{\parallel}$	C_s	0.1	−0.0	0.0	0.0	0.0	−0.9
	5e$_{\perp}$	C_{2v}	−9.0	−8.3	−7.4	−7.2	−7.1	−5.8
CH_3	**6a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	6e	C_s	−1.7	−1.7	−1.2	−1.2	−1.2	−0.9
	6s	C_s	2.2	2.7	3.7	3.3	3.4	3.2
NH_2	7a′	C_s	0.0	0.0	0.0	0.0	0.0	0.0
	7e$_{\perp}$	C_{2v}	−13.1	−7.6	−8.5	−7.8	−8.0	−7.2
	7s	C_{2v}	10.7					
	7a$_{\parallel}$	C_s	−0.3	1.7	1.9	2.1	2.3	1.3
	7e$_{\parallel}$	C_{2v}	13.6	17.0	18.7	18.4	18.8	17.4
	7e′	C_s	13.1	11.4	11.8	11.5	11.4	10.9
OH	**8a**	C_s	0.0	0.0	0.0	0.0	0.0	0.0
	8e$_{\perp}$	C_s	−2.2	1.7	−0.2	0.6	−0.3	0.4
	8s	C_s	19.3	23.5	26.3	25.8	25.7	24.8
	8e$_{\parallel}$	C_s	10.2	13.3	13.1	13.3	12.7	11.6
F	**9a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	9e	C_{2v}	7.6	11.0	8.8	9.7	8.6	8.0
	9s	C_{4v}	27.3	33.1	35.1	35.0	34.4	33.5

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

rections were computed on the 6-31G* geometries. Combined with the ZPE, our highest level is MP4SDTQ/6-31G*//6-31G*+ZPE. These energies will be used in the following discussions. Tables II and III list the absolute energies at various basis sets for the first- and second-row groups; Tables IV and V list the corresponding relative energies. Geometries around phosphorus are summarized in Tables VII, VIII, and IX. Further details are available from the senior authors.

Natural bond orbital (NBO) analysis, a method for representing ab initio wave functions in terms of localized Lewis structures, has been employed, inter alia, to study hypervalence and hyperconjugation.[34] This method provides a quantitative analytical framework for the interpretation of MO interactions. Thus, hyperconjugation can be equated with the electron delocalization from bond or lone pair NBOs into antibond NBOs (e.g., n → σ^*, n → π^*).[35] The magnitude of the energy associated with such delocalization can be evaluated by deleting the antibonding orbitals from the Fock matrix and recalculating the total energy to determine the associated variational energy change. The total energy is decomposed into covalent $E_{\sigma\sigma}$ and noncovalent $E_{\sigma\sigma^*}$ contributions. $E_{\sigma\sigma^*}$

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(34) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
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Table V. Relative Energies[a] of the Second-Row Element-Substituted Phosphoranes

X	no.	sym	3-21G(*) //3-31G(*)	6-31G* //6-31G*	MP2/6-31G* //6-31G*	MP3/6-31G* //6-31G*	MP4/6-31G* //6-31G*	MP4/6-31G* //6-31G*+ZPE[b]
Na	**11a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	11e	C_{2v}	−26.6	−26.5	−22.9	−21.0	−19.6	−20.4
	11s	C_{4v}	−30.3	−29.5	−26.6	−24.9	−23.2	−23.4
MgH	**12a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	12e	C_{2v}	−24.6	−23.7	−22.5	−21.7	−21.1	−21.1
	12s	C_{4v}	−28.9	−27.1	−26.6	−25.9	−25.3	−24.8
AlH_2	**13a**$_{\parallel}$	C_s	0.0	0.0	0.0	0.0	0.0	0.0
	13e$_{\parallel}$	C_s	−22.9	−20.9	−20.5	−20.1	−19.7	−19.0
	13s	C_{2v}	−22.7	−20.7	−20.6	−20.2	−19.9	−15.7
SiH_3	**14a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	14e	C_s	−11.7	−10.9	−10.0	−9.7	−9.5	−8.6
	14s	C_s	−11.8	−10.2	−9.8	−9.6	−9.5	−9.1
PH_2	**15a′**	C_s	0.0	0.0	0.0	0.0	0.0	0.0
	15e″	C_s	−3.0	−3.3	−3.8	−3.7	−3.9	−3.3
	15s	C_{2v}	39.4					
	15a$_{\parallel}$	C_s	22.0	20.2	22.9	23.1	23.7	23.1
	15e$_{\parallel}$	C_{2v}	43.2	41.8	38.6	38.4	38.4	37.3
	15e′	C_s	2.0	1.8	1.0	0.8	0.5	0.7
	15e$_{\perp}$	C_{2v}	19.7	19.0	15.9	16.7	16.7	17.0
SH	**16a**	C_s	0.0	0.0	0.0	0.0	0.0	0.0
	16e$_{\perp}$	C_s	3.1	3.0	−0.3	−0.1	−0.7	−0.1
	16s	C_s	18.8	19.3	17.8	17.2	16.9	16.2
	16e$_{\parallel}$	C_s	14.5	14.0	10.4	10.2	9.6	8.8
Cl	**17a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0
	17e	C_{2v}	15.0	12.6	14.9	14.8	14.5	13.4
	17s	C_{4v}	35.4	35.8	31.5	31.3	30.6	29.7

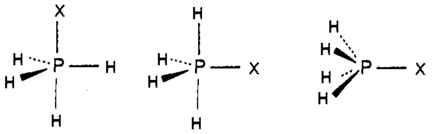
[a] Relative energies are in kcal mol⁻. [b] Zero point energies were calculated at 6-31G* and scaled by 0.89.

can be calculated from second-order perturbation theory, where F is the Fock operator and ϵ_σ and ϵ_{σ^*} are NBO orbital energies.

$$E_{\sigma\sigma^*} = -2\frac{(\sigma|F|\sigma^*)^2}{\epsilon_{\sigma^*} - \epsilon_\sigma}$$

We will use NBO analysis to examine the role of d orbitals in PH_5 and the π effects of some substituents. The conclusions quantify concepts established by previous workers. Table VI lists the natural charges of the PH_4X species. These are based on improved natural (localized) orbitals and overcome the large basis set sensitivity that mars Mulliken population analysis.

In this study, we consider these fundamental structural types: the apically substituted TP structure **a**, the equatorially substituted TP structure **e**, and the apically substituted SP structure s. The combination of the atomic number with these symbols represents the corresponding substituted conformation (for example, **3a**, **3e**, **3s** for PH_4Li). For some substituents, other conformations also were investigated, for example, to examine π-bonding effects.



a **e** **s**

X = **3**, Li; **4**, BeH; **5**, BH_2; **6**, CH_3; **7**, NH_2; **8**, OH; **9**, F; **11**, Na; **12**, MgH; **13**, AlH_3; **14**, SiH_3; **15**, PH_2; **16**, SH; **17**, Cl

"Apicophilicity" is a convenient measure of the relative energies of isomers. According to Holmes' recent definition,[20] the apicophilicity A is defined as $A = E_{(e)} - E_{(a)}$. Apicophilic ligands have positive and apicophobic ligands have negative A values. Similarly, the $E_{(s)} - E_{(a)}$ relative energies characterize the perferences for SP structures. In Tables IV and V, the apicophilicity values are given as the relative energy of the e conformation in the second line for each substituent subgroup. $E_{(s)} - E_{(a)}$ relative energies are given in the third line of the entry for each substituent.

Results and Discussion

PH_5. The trigonal-pyramidal (TP) and square-planar (SP) structures of PH_5 were optimized with various basis sets (Table I). Optimizations with 3-21G(*) and 6-31G* give quite similar geometries, whereas basis sets lacking d functions on phosphorus (such as 3-21G and 6-31G) result in longer P–H_e and P–H_a distances. As is well-known, the use of basis sets supplemented with d functions is necessary to obtain satisfactory geometries on second-row molecules, but correlation effects are minimal.

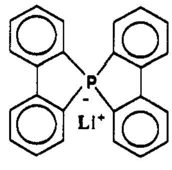
The general conclusion from many studies of phosphorus compounds[15,24] is that d functions serve as polarization functions. On the basis of NBO analysis, a simpler picture can be drawn of the role of d orbitals in PH_5. For the TP structure, the natural charges on P, H_a, and H_e are 0.64, −0.23, and −0.06, respectively (Table VI). The phosphorus inner shell 1s, 2s, and 2p natural atomic orbitals (NAO) are fully occupied, but 3s, 3p, and 3d have occupation numbers of 1.20, 3.08, and 0.08, respectively. The 3d (mainly $3d_{x^2-y^2}$ and $3d_{z^2}$) occupancy corresponds to only 1.8% of the total phosphorus valence electrons. This is much less than the 20% required by the conventional sp^3d hybridization model. The natural localized molecular orbitals (NLMOs) show the P–H_a bond to be polarized toward hydrogen (59% on H; 39% on P). The d function participation is only 3.3% in the P–H_a bond and 1.7% in the P–H_e bond. Hence, the sp^3d hybridization model does not apply. Actually, the P–H_a antibond consists mostly of phosphorus d orbitals. From second-order perturbation theory (NBO analysis of the Fock matrix), the charge delocalization from P–H_e to this P–H_a antibond contributes 35 kcal mol^{-1} to the total energy. The d orbital in PH_5 acts as an acceptor to allow the negatively charged hydrogens to donate electrons to the positively charged phosphorus. This is equivalent to saying that the d function has a polarization effect on phosphorus. In the C_{4v} PH_5 structure, d orbitals play the same role. The difference is that the negative charge is present largely on the four basal hydrogens rather than on the apical hydrogen.

Frequency calculations show that the D_{3h} PH_5 structure is the energy minimum and the C_{4v} structure is the transition structure corresponding to the energy maximum in the Berry pseudorotation process.[7] At various basis set levels, namely 6-31G*, 6-31G**, 6-31G(2d,p) (with two sets of d orbitals on phosphorus), and 6-31G(2df,p) (with an additional f set on P), the energy difference between the two structures is almost constant at about 2.8 kcal mol^{-1}. The electron correlation correction reduces the difference. The MP4/6-31G*+ZPE relative energy (1.1 kcal mol^{-1}) is similar to that of full CI calculations (1.2 kcal mol^{-1}).[6b] These results calibrate the MP4SDTQ/6-31G*//6-31G* + ZPE theoretical level used in this work. Optimization at the MP2 level gave little change in geometry.

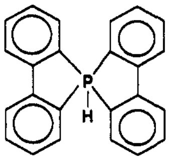
Note that the pentacoordinated phosphorane is thermodynamically unstable relative to phosphine and hydrogen. The TP structure of PH_5 is about 58 kcal mol^{-1} higher in energy than PH_3 + H_2 (Table I). However, the barrier for this decomposition should be about 36 kcal mol^{-1}.[6b] Hence, PH_5 may be an observable metastable species.

PH_4X (X = Li, Na, BeH, and MgH). Electropositive substituents often produce unusual behavior. For example, lithium and sodium reduce the planar-tetrahedral energy difference in CH_3–X derivatives significantly.[37] To our knowledge, there is no prior ab initio theoretical investigation on phosphorus substituted by the electropositive elements of the first and second rows. For acyclic and monocyclic five-coordinate phosphoranes, it is generally believed that the TP conformer is lower in energy compared to SP. We now inquire whether this generalization extends to electropositive ligands.

We find in fact that for PH_4X (X = BeH, Na, and MgH), the SP (**s**) and TP (**a**) conformations are energy minima with **s** being much more stable than **a**. For PH_4Li the **s** conformation is the only minimum, and the **a** (C_{3v}) structure is a second-order saddle point (Table II). At MP4/6-31G*//6-31G* + ZPE, the greater stabilities (in kcal mol^{-1}) of **s** over **a** conformers are Li, −28.4; Na, −23.4; BeH, −22.8; and MgH, −24.8. These SP structures are the first acyclic phosphoranes which are more stable as the square-pyramidal conformer. The XPH angles in these SP structures range from 101.3° to 102.9°, close to the value of 100.5° at 6-31G* in C_{4v} PH_5. Note that five point charges on the surface of a sphere in a C_{4v} geometry results in a least repulsion angle of 104.1°.[38] It is also noteworthy that the P–M bond length in SP is considerably shorter than that in TP. Experimentally, there is a proposed example of the **3s** type of structure (I) obtained by the reaction of the H-spirophosphorane (II, SP structure) with *tert*-butyllithium.[39]



I

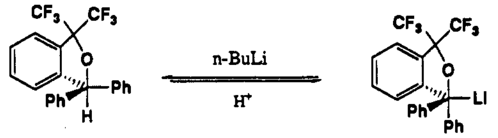


II

An analysis of the TP and SP HOMO's is instructive. The TP HOMO involves a nonbonding or slightly antibonding interaction between phosphorus and the apical ligands, with the larger coefficient associated with the apical ligands.[24] Thus, the electropositive ligand on the apical position raises the HOMO energy and makes the TP conformation unstable. On the other hand, the HOMO in SP comprises four basal ligands with two nodes, and there is almost no participation by the axial ligand. The electronegativity of the ligand at the axial position does not influence the HOMO. The natural charges on P, Li, H_a, and H_e are 0.24, 0.34, −0.25, and −0.04, respectively, in **3a**. The two positively charged centers P and Li raise the energy and make the TP structure unstable. Note that the charge on lithium is rather low and that the P–Li bond length in this structure, 2.80 Å, is rather long. The low charge on lithium was confirmed by an integrated projected electron density analysis. This result not only suggests that this structure has an important $H_4P^{\bullet}Li^{\bullet}$ character that results from the weakened P–Li bond but also implies that a single configuration Hartree–Fock approach may not suffice for this species. The qualitative result, however, is undoubtedly still sound. For the SP structure **3s**, the phosphorus is negatively charged (−0.25) and the lithium is more typically positively charged (0.89). This structure can be considered as a lithium–phosphoranide ion pair. These results imply that the relatively small conformational change from SP to TP is accompanied by profound changes in electronic structure.

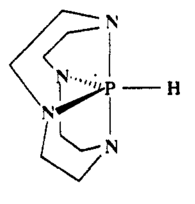
There are no stationary points corresponding to the equatorially substituted structures. Optimizations starting from a C_{2v} equatorial structure ended with the SP structure. The structures in Table VII were only partially optimized by setting two XPH_a angles at 90°. In the **e** conformation, the P–M bond is longer than that in SP but much shorter than that in apically substituted TP. The charge distribution is similar to the **s** conformation. As a rough comparison, Li_3P and Na_3P have been shown to have structures of the Na_3As type. In crystals of these compounds the P atoms are surrounded by five metal atoms in a trigonal-bipyramidal configuration. The P–Na bond length at the equatorial position in Na_3P is 2.88 Å, which is not too much longer than the value of 2.70 Å in **11e**. The P–Na bond length at the axial position in Na_3P is 2.93 Å, which is much shorter than the 3.27 Å in **11a**.[40] Relative energies show that PH_4X_e is about 20 kcal mol^{-1} more stable than PH_4X_a. Therefore, if ring structures block the formation of the SP conformation, the equatorial structure would be the preferred conformation.

A good example has been provided by Ross and Martin.[41] They reported a stable monocyclic triarylalkoxyphosphorane and a monocyclic phosphoranide anion. The slowness of the proton exchange between III and IV clearly indicates the equatorial preference of the P–Li bond over the apical position.



III IV

Some bicyclic phosphoranes with Li cation in the equatorial position have been reported.[42] Most recently, the X-ray crystal structure was reported[42c] of THF-solvated lithium cyclenphosphoranide, $[Li(THF)cyclenP]_x$, via deprotonation of the PH group of the cyclen V with butyllithium. This is the first X-ray structural determination of a deprotonated phosphoranide. Because of the ring structure in the ligands, this Li phosphoranide cannot adopt an SP structure. The lithium compound has a polymeric structure in which each lithium is coordinated to two apical nitrogens in different cyclen moieties rather than to phosphorus. The equatorial N–P–N angle in the phosphoranide is considerably smaller than that in the neutral compound, indicating the trend toward the SP structure. From the discussion above, it can be expected that for a monomeric phosphoranide salt that is free from ring strain the SP structure would be the favored conformation.



V

PH_4BH_2 and PH_4AlH_2. There are several conformations to be considered for PH_4X in which X = YH_2. For X = BH_2 and AlH_2 the substituent groups are planar (or nearly planar) but can have several types of orientation.

PH_4BH_2 is found computationally to be a flexible species. The apical structure $\mathbf{5a}_{\parallel}$ with a planar BH_2 lying in the C_s plane of

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(36) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (d) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7362. (e) Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969.

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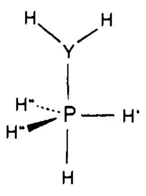
(39) Hellwinkel, D. *Chem. Ber.* **1969**, *102*, 528.

(40) Brauer, G. E.; Zintl, Z. *Physik. Chem.* **1937**, *37B*, 327.

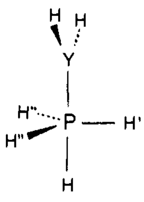
(41) Ross, M. R.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1234.

(42) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4623. (b) Trippett, S.; Whittle, P. J. *J. Chem. Soc., Perkin Trans. I* **1975**, 1220. (c) Lattman, M.; Olmstead, M. M.; Power, P. P.; Rankin, W. H.; Robertson, H. E. *Inorg. Chem.* **1988**, *27*, 3012.

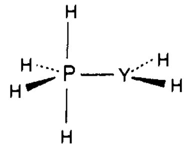
the PH_4 group ($\parallel$) has nearly the same energy as **5a**$_{\perp}$ in which the essentially planar BH_2 is rotated 90° with respect to the position in **5a**$_{\parallel}$. The structure **5a**$_{\parallel}$ is a transition state with an imaginary frequency of 73.7i cm^{-1}. The structure **5a**$_{\perp}$ is an energy minimum. The equatorial structure **5e**$_{\parallel}$, 13.0 kcal mol^{-1} more stable than **5a**$_{\perp}$, is the lowest energy stationary point on the PH_4BH_2 potential surface. In **5e**$_{\parallel}$, BH_2 lies in the equatorial plane. The optimal H_aPB angle is 91.06° and is slightly greater than 90°. If the planar BH_2 is rotated by 90° and the angle H_aPB is kept at 90° during the optimization, the resulting structure **5e**$_{\perp}$ is 7.2 kcal mol^{-1} less stable than **5e**$_{\parallel}$ at our highest level (Table IV). The optimization of this equatorial structure with only C_s symmetry results in a $(PH_3)(BH_3)$ complex with staggered C_{3v} symmetry that is more stable than **5e**$_{\parallel}$ by 65.6 kcal mol^{-1} at 6-31G*. This complex is simply a Lewis acid–base complex between BH_3 and PH_3 and is not a phosphorane.



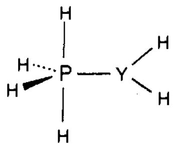
a$_{\parallel}$



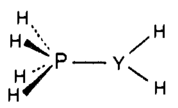
a$_{\perp}$



e$_{\parallel}$



e$_{\perp}$

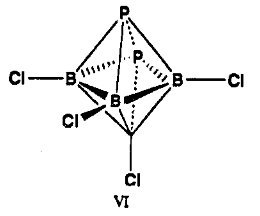


s

Y = B, Al, N, P

The π conjugation effect in the **5e**$_{\parallel}$ conformation has already been rationalized by McDowell and Streitwieser.[24] On the basis of NBO analysis, the apical hydrogen in **5e**$_{\parallel}$ has a charge of –0.27. The π effect comes from the electron delocalization of the P–H_e σ bond to antibonding P–B. Second-order perturbation theory estimates this charge donation to be about 16.9 kcal mol^{-1}. The larger H_aPB angle favors this charge donation. This kind of charge transfer can also be regarded as an anomeric effect. It has been demonstrated that the anomeric effect is strongest at C, N, P, and S centers.[43]

The SP structure **5s** is only 3.5 kcal mol^{-1} higher in energy than **5e**$_{\parallel}$. The P–B bond length in PH_4BH_2 changes but little among the various isomers. No B–P bond length data have been reported for pentacoordinate phosphoranes. In the recently published[44] structure of $P_2B_4Cl_4$, VI, P assumes an inverted tetracoordinated geometry with a B–P bond length of 2.0 Å.



VI

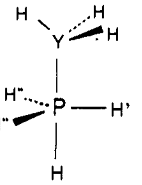
PH_4AlH_2 behaves quite similarly to PH_4BH_2. The equatorial isomer, **13e**$_{\parallel}$, is the global minimum. The next most favorable structure, the SP conformation, **13s**, is only 3.3 kcal mol^{-1} less stable than **13e**$_{\parallel}$, but **13s** is a transition state as is the apically substituted **13a**$_{\parallel}$ which has the highest energy. No corresponding **a**$_{\parallel}$ stationary point was found for PH_4AlH_2. PH_4BH_2 and PH_4AlH_2 are the "turning points" for the first- and second-row series, respectively. When more electronegative groups are present, the TP structures are more stable than the SP isomers.

Table VI. Natural Charges[a] of PH_4X

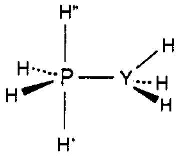
X	no.	P	YH_n	H_a	H_e
H	**1a**	0.64		–0.23	–0.06
	1s	0.61		–0.01	–0.15
Li	**3a**	0.24	0.34	–0.25	–0.04
	3e	–0.14	0.84	–0.31	–0.04
	3s	–0.25	0.89		–0.16
BH_2	**5e**$_{\parallel}$	0.53	0.08	–0.27	–0.04
CH_3	**6a**	0.84	–0.41	–0.22	–0.00
NH_2	**7e**$_{\perp}$	1.07	0.44	–0.22	–0.00
	7e$_{\parallel}$	1.08	0.47	–0.22	–0.00
PH_2	**15e**$_{\perp}$	0.60	–0.13	–0.17	–0.06
	15e''	0.55	–0.00	–0.23	–0.05' –0.04''
OH	**8a**	1.04	–0.64	–0.21	–0.07'' –0.05'
	8e$_{\perp}$	1.13	–0.56	–0.22' –0.16''	–0.09
SH	**16a**	0.66	–0.48	–0.20	0.01'' 0.00'
	16e$_{\perp}$	0.68	–0.23	–0.17' –0.17''	–0.06
F	**9a**	1.07	–0.70	–0.21	–0.05
	9e	1.13	–0.65	–0.15	–0.09
Cl	**17a**	0.73	–0.76	–0.11	0.04
	17e	0.73	–0.93	0.10	0.00

[a] Natural charges were calculated at 6-31G*//6-31G*. See text for the corresponding structures. Primes and double primes refer to nonequivalent hydrogens as indicated in the structural figures.

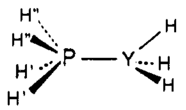
PH_4CH_3 and PH_4SiH_3. The geometries of PH_4CH_3 and PH_4SiH_3 are summarized in Table VIII. Three conformations (**a**, **e**, and **s**) were calculated.



a



e



s

Y = C, Si

Both the apical and equatorial species are minima. For **6a** and **14a**, YH_3 is staggered with resect to $P(H_e)_3$. For **6e** and **14e**, YH_3 is also staggered with respect to $P(H_e)_2$. The P–C bond length (1.847 Å) in **6e** is longer than in CH_3PF_4 (1.780 Å),[45a] and $(CH_3)_2PF_3$ (1.798 Å)[45a] but close to that in $(CH_3)_3F_2$ (1.813 Å).[45b] At our highest level the apicophilicity of the CH_3 group is only –0.9 kcal mol^{-1}. Thus, the CH_3 group in PH_4CH_3 has relatively little preference for either position. The apicophilicity of –7.0 kcal mol^{-1} given by Holmes[23] may be due to the steric interactions and ring strain in more highly substituted phosphorus. In contrast to CH_3, the SiH_3 group is quite apicophobic; the A value is –8.6 kcal mol^{-1} at our highest level. The **6s** and **14s** structures are both second-order saddle points; **14s** is almost as stable as **14e** and **6s** is only 3.2 kcal mol^{-1} higher than **6a**. The P–C bond length (1.832 Å) in **6s** is quite close to that in a number of spirocyclic phosphoranes (SP). For example, in an adamantane-substituted spirocyclic phosphorane, the P–C bond length is 1.836 Å.[46]

PH_4NH_2 and PH_4PH_2. The geometries of the PH_4NH_2 isomers are listed in Table IX. In addition to the conformations considered for PH_4BH_2 and PH_4AlH_2, in which the substituents are planar, we must now also consider conformations with pyramidal groups.

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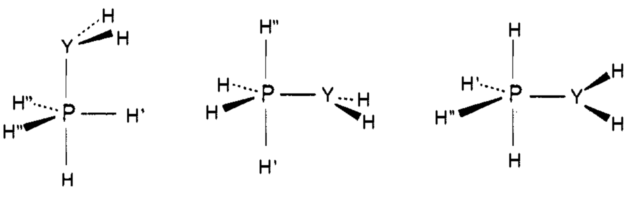


a' e' e''

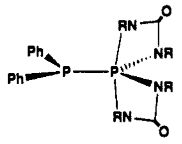
Y = N, P

In the apical position, the pyramidal NH_2 structure **7a′** is 1.3 kcal mol^{-1} more stable than the planar NH_2 structure **7a**$_{\|}$. Note that the pyramidal NH_2, as expected, is staggered with respect to an equatorial H. In the equatorial position the structure **7e**$_{\perp}$, in which NH_2 is planar and the nitrogen lone pair is in the equatorial plane, is the global minimum, probably because of π-bonding effects. With this isomer, the NH_2 apicophilicity is −7.2 kcal mol^{-1}. Holmes' apicophilicity of NH_2 was −6.8 kcal mol^{-1} when the π-bonding effect of NH_2 in the equatorial position was included.[23] Structure **7e**$_{\|}$, with a planar NH_2 lying in the equatorial plane, is 24.6 kcal mol^{-1} higher in energy than **7e**$_{\perp}$. This result is essentially the same as Veillard's value (25 kcal mol^{-1}).[13] If the NH_2 in this position is allowed to adopt a pyramidal conformation (**7e′**), the energy is still 18.1 kcal mol^{-1} higher than that of **7e**$_{\perp}$. Note in this structure that the NH_2 group is staggered with respect to an H_a rather than a farther H_e. A SP structure **7s** with C_{2v} symmetry can be located at 3-21G(*) but at 6-31G* it converts to structure **7e**$_{\perp}$.

Although the bonding in PH_4NH_2 has been discussed by many authors,[11,13,24] NBO analysis provides a simple interpretation for the π-bonding effect in equatorial PH_4NH_2. Consider the two **7e**$_{\perp}$ and **7e**$_{\|}$ conformers. In **7e**$_{\perp}$, the lone pair on the nitrogen delocalizes its electron to $\sigma^*(P{-}H_e)$. The second-order perturbation energy contribution corresponding to this hyperconjugation is 15.2 kcal mol^{-1}. In **7e**$_{\|}$, the nitrogen lone pair delocalizes to $\sigma_{(P-Ha)^*}$. The n → $\sigma_{(P-Ha)^*}$ interaction is much less, only 3.3 kcal mol^{-1} from NBO analysis. The total hyperconjugation energy difference between **7e**$_{\perp}$ and **7e**$_{\|}$ ($15.4 \times 2 - 3.3 \times 2 = 24.2$ kcal mol^{-1}) is in excellent agreement with the relative energy (24.6 kcal mol^{-1}) at 6-31G*. Corresponding to the anomeric effect, the P–N bond length is much shorter in **7e**$_{\perp}$ (1.675 Å) than in **7e**$_{\|}$ (1.713 Å). Moreover, if the NBO's of $\sigma_{(P-He)^*}$ and $\sigma_{(P-Ha)^*}$ are deleted from the basis sets in the calculations, **7e**$_{\perp}$ and **7e**$_{\|}$ become degenerate. In other words, the rotation barrier of P–NH_2 disappears after deleting the $\sigma_{(P-He)^*}$ and $\sigma_{(P-Ha)^*}$. Therefore, the π-effect mainly comes from the anomeric effect in which the lone pair of the substituent interacts with the P–H antibonding σ^* (n → σ^*).

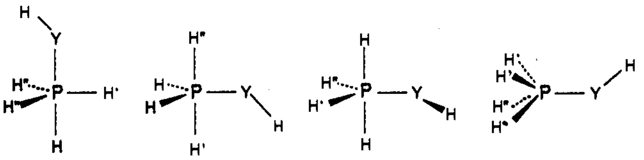
In contrast to the π-bonding effect of an NH_2 group, a PH_2 group strongly prefers the pyramidal conformation. In the apical position, the planar PH_2 structure **15**$_{\|}$ is a transition state 23.1 kcal mol^{-1} less stable than the pyramidal **15a′** (analogous to **7a′**), a local minimum. In the equatorial position, the lowest energy conformation is **15e″** with a pyramidal PH_2. None of the other equatorial stationary points is a local minimum. The alternative structure **15e′** in which the PH_2 group is staggered with respect to H_a is the transition state for rotation of pyramidal PH_2 group in the equatorial position. The 4.0 kcal mol^{-1} rotation barrier is much lower than the NH_2 rotation. In the two planar equatorial conformations (C_{2v}), the PH_2 plane is coplanar with the equatorial plane in **15e**$_{\|}$ and orthogonal to the equatorial plane in **15e**$_{\perp}$. These conformers, **15e**$_{\|}$ and **15e**$_{\perp}$, are 40.6 and 20.3 kcal mol^{-1}, respectively, less stable than **15e″**. The 20.3 kcal mol^{-1} energy difference between **15e**$_{\|}$ and **15e**$_{\perp}$ does demonstrate π-bonding participation in the **15e**$_{\perp}$ conformer that is only little less than that in PH_4NH_2 case. The substituted SP structure **15s** corresponds to a stationary point at 3-21G(*) but not at 6-31G*.

Structure VII is the first X-ray structure of a phosphorane with a phosphorus substituent that is not part of a ring system.[46] In VII the Ph_2P group is twisted so that the phosphorus lone pair is directed between the apical and equatorial orientations of the phosphorane moiety and does not correspond to either **15e′** or **15e″**. Unfortunately, the spiro four-membered rings introduce such distortion that VII is not a good model system for unstrained phosphoranes. Nevertheless, VII does show that the phosphino group is pyramidal, and the observed P–P bond length of 2.214 Å is close to our calculated value of 2.211 Å in **15e″**.



VII

PH_4OH and PH_4SH. Four possible conformations investigated are as follows:



a e$_{\perp}$ e$_{\|}$ s

Y = O, S

In the equatorial conformations the PYH plane can be either perpendicular (⊥) or coplanar (‖) with respect to the equatorial plane. Conformations **8a** and **16a** have H–Y staggered with respect to H_ePH_e. The **a** and **e**$_{\perp}$ structures were fully characterized by frequency calculations and are minima on the PES. At our highest level, the apicophilicities of OH and SH are 0.4 and −0.1 kcal mol^{-1}, respectively. Thus, if ring strain and steric effects are omitted, OH and SH groups have little positional preference. The empirical OH apicophilicity value of Holmes,[23] 1.3 kcal mol^{-1}, is slightly higher than our value of 0.4. Note the importance in these cases of using a polarized basis set and including some electron correlation. For example, at the SCF level, the apicophilicity of SH is 3.1 kcal mol^{-1} at 3-21G(*) and 3.0 kcal mol^{-1} at 6-31G*. Electron correlation changes the sign of the apicophilicity. At MP4SDTQ/6-31G*, the value is −0.7 kcal mol^{-1}. After the ZPE correction, the final value is −0.1 kcal mol^{-1}.

The other conformations are stationary points that are not minima on the PES. Rotating the H–Y group by 90° results in conformations **8e**$_{\|}$ and **16e**$_{\|}$, which are 11.2 and 8.9 kcal mol^{-1} higher in energy than **8e**$_{\perp}$ and **16e**$_{\perp}$, respectively. The bond angles at oxygen and at sulfur in PH_4OH and PH_4SH are instructive. The POH angles are 114.4° in **8a**, 112.0° in **8e**$_{\perp}$, and 115.8° in **83**$_{\|}$; the oxygen is approximately sp^3 hybridized. On the other hand, the PSH angle is 100.4° in **16a**, 99.5° in **16e**$_{\perp}$, and 94.3° in **16e**$_{\|}$; the sulfur bonds, as expected, have much greater p character. Again, the rotation barrier arises from the hyperconjugation of the Y lone pairs with the P–H antibonding σ^*. The OH substituent exhibits more anomeric effect than the SH substituent. For example, in **8e**$_{\perp}$ the n → σ^* interaction corresponds to 13.9 kcal mol^{-1}, whereas in **16e**$_{\perp}$ the value decreases to 10.1 kcal mol^{-1}.

The conformational preferences of **8e**$_{\perp}$ and **16e**$_{\perp}$ over **8e**$_{\|}$ and **16e**$_{\|}$ have important chemical significance. The "ring strain" rule states: "Four- or five-membered cyclic systems preferentially span axial–equatorial position".[22] Certainly, ring strain is one of the factors. But for oxygen- and sulfur-containing rings, the ⊥ rather than the ‖ conformational preference of an equatorial P–O–R or P–S–R bond is another important factor responsible for the axial–equatorial conformation. This can be accounted for as follows. Strain-free OH and SH ligands have little positional preference. But in a small-membered diequatorial ring, the OR and SR groups have to assume unfavorable conformations in which the OR or SR rings are coplanar with the equatorial plane. This effect contributes as instability of about 11 kcal mol^{-1} for each oxygen and about 9 kcal mol^{-1} for each sulfur. Moreover, it has been shown that six- or larger-membered rings also prefer axial–equatorial conformations.[49] This conformational preference effect

Table VII. Optimized HF/6-31G* Geometries[a] of PH_4X (X = Li, Na, BeH, MgH, F, and Cl)

X	no.	sym	P–X	P–H_a	P–H_e	YPH_a	YPH_e	Y–H
Li	**3a**	C_{3v}	2.802	1.477	1.419		92.60	
	3e	C_{2v}	2.386	1.553	1.398	90.00[b]	119.96	
	3s	C_{4v}	2.376		1.457		102.72	
Na	**11a**	C_{3v}	3.274	1.461	1.397		89.19	
	11e	C_{2v}	2.704	1.555	1.398	90.00[b]	121.78	
	11s	C_{4v}	2.677		1.458		102.88	
BeH	**4a**	C_{3v}	2.252	1.481	1.424		92.69	1.347
	4e	C_{2v}	2.103	1.498	1.407	90.00[b]	115.52	1.330
	4s	C_{4v}	2.090		1.448		101.27	1.329
MgH	**12a**	C_{3v}	2.862	1.478	1.404		91.48	1.759
	12e	C_{2v}	2.508	1.502	1.408	90.00[b]	115.46	1.714
	12s	C_{4v}	2.481		1.450		101.46	1.710
F	**9a**	C_{3v}	1.657	1.440	1.386		89.31	
	9e	C_{2v}	1.623	1.414	1.403	84.54	128.44	
	9s	C_{4v}	1.565		1.431		101.35	
Cl	**17a**	C_{3v}	2.495	1.412	1.373		81.56	
	17e	C_{2v}	2.975	1.369	1.385	58.91	128.09	
	17s	C_{4v}	2.024		1.432		100.51	

[a] Bond lengths in Å, angles in deg. [b] Angles fixed for optimization.

Table VIII. Optimized HF/6-31G* Geometries[a] of PH_4X (X = CH_3, SiH_3, OH, and SH)

X	no.	sym	P–Y	P–H_a	P–H_e	YPH_a	YPH_e	θ	H_ePH_e
CH_3	**6a**	C_{3v}	1.904	1.464	1.409		91.13		
	6e	C_s	1.847	1.473′ 1.468″	1.405	88.93′ 92.13″		91.08″	118.97
	6s	C_s	1.832		1.442′ 1.442′		102.97′ 100.83″		87.42′ 87.74″
SiH_3	**14a**	C_{3v}	2.407	1.462	1.409		90.52		
	14e	C_s	2.275	1.483′ 1.473″	1.410	95.29′ 89.54″		91.67″	121.98
	14s	C_s	2.265		1.443′ 1.444″		102.45 99.32″		88.03′ 87.86″
OH	**8a**	C_s	1.704	1.450	1.389′ 1.395″		89.41′ 92.74″	89.00	116.21″
	8e$_{\perp}$	C_s	1.644	1.446′ 1.421″	1.403	87.75′ 85.05″		89.98′	104.76
	8e$_{\parallel}$	C_s	1.665	1.431	1.410′ 1.403″	87.55	130.94′ 122.91″		
	8s	C_s	1.614		1.442′ 1.430″		102.84′ 101.44″		87.03′ 88.23″
SH	**16a**	C_s	2.389	1.435	1.384′ 1.382″		83.01′ 98.69″	84.00	117.87″
	16e$_{\perp}$	C_s	2.152	1.436′ 1.435″	1.403	88.67′ 84.14″		91.56′	107.58
	16e$_{\parallel}$	C_s	2.242	1.425	1.410′ 1.404″	86.83	131.71′ 119.25″		
	16s	C_s	2.105		1.438′ 1.435″		101.55′ 100.25″		88.10′ 88.25″

[a] Bond lengths in Å, angles in deg. See text for the corresponding structures. θ is the dihedral angle of H_ePYH_a. Primes and double primes refer to nonequivalent hydrogens as indicated in the structural figures.

at the equatorial position must be more important than the ring strain in such cases.

PH_4F and PH_4Cl. The equatorially substituted structures **9e** and **17e** are not minima on the PES but are transition states between the two equivalent apically substituted isomers. The P–F bond (1.623 Å) in **9e** is much longer than that in CH_3PF_4 (1.543 Å) or in HPF_4 (1.55 Å).[50] In **17e**, P and Cl have natural charges of +0.73 and −0.93, respectively. This structure is better considered as a $PH_4^+Cl^-$, phosphonium chloride edge-associated ion pair, isomer even though it is not an energy minimum. The PES surface is rather flat with respect to the P–Cl bond distance, and its character is sensitive to the basis set level. At the Hartree–Fock level, the standard 6-31G* basis set gives a single minimum corresponding to a phosphonium chloride structure. A comparable computation with two sets of d orbitals on phosphorus (exponents of 0.22 and 0.77 compared to the single exponent of 0.55 in 6-31G*) gave a second minimum corresponding to a phosphorane structure.

The apically substituted structures **9a** and **17a** are energy minima with bond lengths similar to experimental values. Note that P has a higher natural charge in **9a** (+1.07) than in **17a** (+0.73). Structures **9s** and **17s** are transition states, much higher in energy than **9a** and **17a**, respectively. The apicophilicities of F and Cl have been calculated, compared, and discussed based on PH_4X structures,[20,24] but such treatments are clearly not appropriate because of the high degree of ion pair character in the equatorial conformers, PH_4F (**9e**) and PH_4Cl (**17e**). Experimentally, the evidence suggests that both ionic and phosphorane forms can exist for chlorophosphoranes and fluorophosphoranes.[51] For example, tetraphenylfluorophosphorane exists as an ionic

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Table IX. Optimized HF/6-31G* Geometries[a] of PH_4X ($X = BH_2$, AlH_2, NH_2, and PH_2)

X	no.	sym	P–Y	P–H_a	P–H_e	YPH_a	YPH_e	H_ePH_e	H_ePH_a
BH_2	**5a**$_{\perp}$	C_s	2.020	1.472	1.437′ 1.418″		88.85′ 93.19″	118.44″	88.03′
	5e$_{\parallel}$	C_{2v}	1.923	1.501	1.401	91.06	119.28		
	5s	C_{2v}	1.947		1.445		101.25		
	5a$_{\parallel}$	C_s	2.021	1.472	1.416′ 1.425″		94.22′ 90.46″	120.39″	88.45′
AlH_2	**13a**$_{\parallel}$	C_s	2.553	1.468	1.420′ 1.414″		91.45′ 91.84″	118.93″	88.04′
	13e$_{\parallel}$	C_{2v}	2.362	1.475	1.424	96.98	116.75		
	13s	C_{2v}	2.365		1.447		101.11		
NH_2	**7a**′	C_s	1.779	1.459	1.405′ 1.396″		94.25′ 89.60″	123.49	85.75
	7a$_{\parallel}$	C_s	1.757	1.463	1.403′ 1.396″		87.10′ 94.06″	118.23″	88.48′
	7e$_{\perp}$	C_{2v}	1.675	1.449	1.405	87.44	121.82		
	7e$_{\parallel}$	C_{2v}	1.713	1.448	1.441	91.23	120.64		
	7e′	C_s	1.752	1.464′ 1.436″	1.407	89.12′ 90.25″		111.63	
PH_2	**15a**′	C_s	2.391	1.452	1.398′ 1.397″		91.12′ 90.25″	120.55″	90.71′
	15a$_{\parallel}$	C_s	2.700	1.414	1.373′ 1.371″		77.00′ 83.15″	120.84″	
	15e$_{\perp}$	C_{2v}	2.165	1.440	1.405	86.07	121.70		
	15e$_{\parallel}$	C_{2v}	2.336	1.416	1.410	87.21	121.26		
	15e″	C_s	2.221	1.464	1.405′ 1.402″	89.13	119.68′ 125.93″		
	15e′	C_s	2.261	1.460′ 1.456″	1.408	90.08′ 90.04″		119.46	

[a] Bond lengths in Å, angles in deg. See text for the corresponding structures. Primes and double primes refer to nonequivalent hydrogens as indicated in the structural figures.

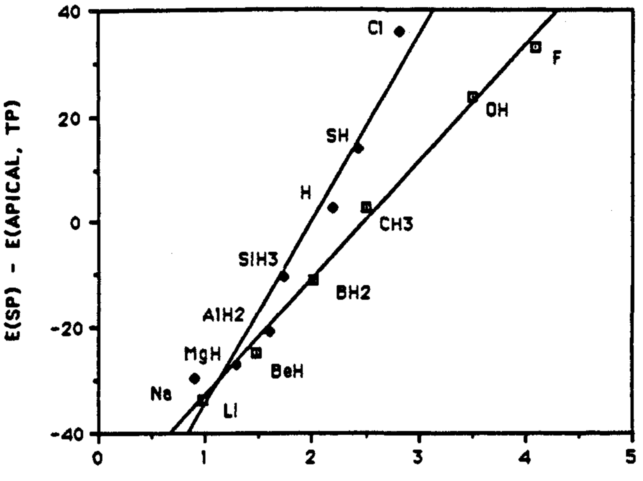

Figure 1. Correlation of energy differences between SP and TP **a** conformations and electronegativities.

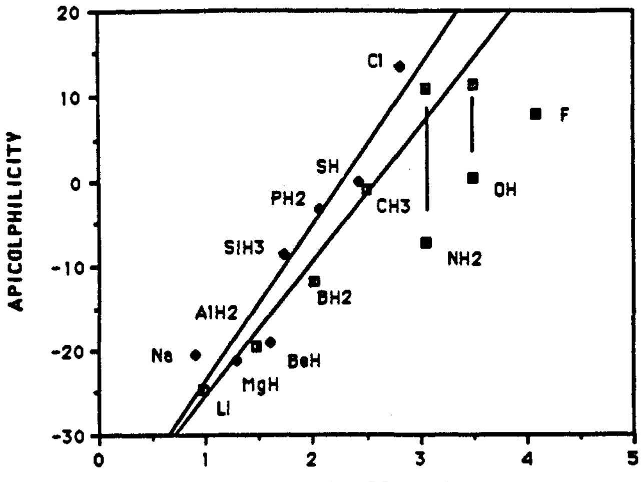

Figure 2. Correlation of energy differences between TP **a** and **e** conformations (apicophilicities) and electronegativities.

monomer, as an apically substituted molecular monomer, and as a dimer.[52]

The HF structure of **17a** depends somewhat on the basis set used. A change in the phosphorus d exponent in 6-31G* from that normally used, 0.55 to 0.47, results in a shortening of the P–Cl bond to 2.459 Å. The use of two sets of d orbitals as above produced a further shortening to 2.422 Å with only small changes in the P–H bonds. Analysis of the molecular orbitals show small increases in the contributions of the more diffuse d functions to the HOMO and to the antibonding π-molecular orbitals; the smaller d exponents promote polarization of electron density in the PH_4 group away from the negative chlorine.

Relative Energy Correlation. The electronegativity rule says that the most electronegative groups prefer apical locations.[21] Holmes's apicophilicities do indeed vary almost linearly with electronegativity.[23] As discussed above, inductive effects dominate in the **a** and **s** conformations. Hence, the energy differences between **s** and **a** conformations should correlate with the electronegativities, and Figure 1 shows this to be the case. Note, however, that first- and second-row groups show different correlation lines.

Apicophilicities, the energy difference between **a** and **e** conformations, of second-row groups also correlate linearly with electronegativities (Figure 2). Since the equatorial SH group follows this correlation, π-effects must be negligible. Indeed, the effects of the second-row groups in both **a** and **e** conformations are dominated by inductive effects. In contrast, many of the apicophilicities of the first-row groups do not correlate with electronegativities. In Figure 2, the lower points for NH_2 and OH are far from the correlation line. However, the inductive and π-contributions to apicophilicity can be dissected. The π-effect can be largely eliminated by a 90° rotation of the NH_2 and OH substituents. In this way, the inductive apicophilicity contributions are 10.9 kcal mol^{-1} for NH_2 (from **7e**′) and 11.6 kcal mol^{-1} for OH (from **8e**$_{\parallel}$). The resulting inductive apicophilicity does correlate linearly with electronegativities (Figure 2, upper points). Note that BH_2 also falls off the line from Figure 2. From the deviation, the inductive apicophilicity and the π-conjugation energy of BH_2 are deduced to be −11.2 and 4.1 kcal mol^{-1}, respectively. However, based on the relative energy of $\mathbf{5e}_\perp$, the inductive apicophilicity is indicated to be only −5.8 kcal mol^{-1}. This discrepancy is probably due to the only partial optimization of structure $\mathbf{5e}_\perp$ (the H_ePB angle was fixed at 90°) which raises its energy.

Conclusions

The relative energies, calculated at MP4SDTQ/6-31G*+ZPE, for both TP and SP conformations reveal inherent substitution effects. Some of the energy differences are quite close to empirical apicophilicity values or experimental energy differences of more highly substituted compounds. The SP structures for PH_4X (X = Li, Na, BeH, and MgH) are the most stable conformations. The apicophilicities of CH_3, OH, and SH are small. The preferential Y–H orientation in equatorial PH_4OH and PH_4SH is orthogonal to the equatorial plane. This preference is an important factor in determining the conformations of cyclic phosphorane systems. Our apicophilicity scale (in kcal mol^{-1}) is OH (0.4) > SH (−0.1) > CH_3 (−0.9) > PH_2 (−3.3) > NH_2 (−7.2) > SiH_3 (−8.6). PH_4F and PH_4Cl are not suitable for apicophilicity evaluation because of their ionic character.

Substituent effects on pentacoordinated phosphoranes can be divided into inductive (or σ) and π-bonding effects. Inductive effects dominate in the SP and apically substituted TP conformations, and the relative energies correlate with the electronegativities. π-Interactions play an important role in the equatorially substituted TP conformations of NH_2 and OH. After dissection and delection of these π-bonding effects, the inductive contribution remaining also correlates with electronegativity.

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Assessing Molecular Similarity from Results of ab Initio Electronic Structure Calculations

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Abstract: A new molecular similarity index, called the number of overlapping electrons (NOEL), is proposed. This similarity index can be computed very rapidly from the natural orbitals and their occupation numbers of the molecules under comparison. The low computational cost makes it possible to optimize the mutual orientation of molecules by maximizing NOEL. The magnitude of NOEL is related to the number of electrons in the molecular fragment common to both molecules. The new approach is illustrated on the examples of benzene, aniline, nitrobenzene, and 4-nitroaniline molecules and the acetate, isoxazole 3-oxide and isoxazole 5-oxide anions.

Introduction

In its early stages, chemistry has been mainly the science of comparing and classifying molecules and chemical reactions. Only in the last 50 years has it become possible to rationalize the observed properties of molecules by using the first principles of quantum mechanics. The properties that have rigorous theoretical definitions, such as energies and multipole moments, are easily amenable to theoretical approaches. On the other hand, properties of more intuitive nature, such as reactivity, aromaticity, or similarity, are more difficult to quantify.

Pharmacologists, toxicologists, and medicinal chemists find it particularly convenient to discuss and classify the physiological action of molecules by using instinctive measures of molecular similarity. For example, the taste of various substances is usually believed to be related to their molecular shape.[1] Organic chemists constantly use the concept of molecular similarity by invoking the notions of functional groups and synthons. Yet, the attempts to rigorously define the molecular similarity are quite scarce in the chemical literature. One of the obvious reasons is that certain arbitrary assumptions have to be necessarily made in order to judge the similarity of molecules from the results of quantum-mechanical calculations. The first assumption is that of molecular rigidity because calculations involve the Born–Oppenheimer approximation, which freezes the positions of the nuclei. The second assumption is of a more philosophical nature. One has to postulate that similar molecules have similar electron distributions. Third, one has to adopt a particular form of the functional which yields the numerical magnitude of the molecular similarity. As in the case of the definition of atomic charges, a plethora of choices are obviously possible; we insist, however, that any acceptable measure of the molecular similarity should conform to the following rules: (1) It should be derivable from the wave functions of the molecules in question alone. It should not depend upon either explicit or implicit assumptions about the basis sets used in calculations or the level of theory employed. (2) It should have some clearly recognizable physical or mathematical interpretation. (3) It should be computationally feasible. In particular, it should allow for optimization of the mutual orientation of the molecules in question by means of maximization of the similarity measure.

Although substantial progress have been recently achieved in quantification of the three-dimensional shape and similarity of molecules,[2] the only reported practical calculations involve a similarity index based on the electron density that has been put forward by Carbo, Leyda, and Arnau.[3] If the molecules under comparison, A and B, have the electron densities $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$, respectively, then the similarity index reads

$$R_{AB} = \int \rho_A(\vec{r})\rho_B(\vec{r})\, d\vec{r} \Big/ \left[\int \rho_B^2(\vec{r})\, d\vec{r} \int \rho_B^2(\vec{r})\, d\vec{r}\right]^{1/2} \quad (1)$$

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(2) Mezey, P. G. *J. Comp. Chem.* **1987**, *8*, 462. Mezey, P. G. *J. Math. Chem.* **1988**, *2*, 299, 325.

(3) Carbo, R.: Leyda, L.; Arnau, M. *Int. J. Quantum Chem.* **1980**, *17*, 1185.

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