The Chemical Bond in Phosphoranes. Comparative ab Initio Study of PH_3F_2 and the Hypothetical Molecules NH_3F_2 and PH_5

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Abstract: Ab initio SCF calculations are performed for the molecules NH_3, NH_2F, NH_3F^+, NH_3F_2, PH_3, PH_2F, PH_3F_2 (four isomers), PH_5, PH_4F, PH_2F_3 with different gaussian basis sets, with and without d functions on P, N, and F. NH_3F_2 is not stable with respect to $NH_2F + HF$ or the ion pair $NH_3F^+ F^-$ but probably is lower in energy than $NH_3 + 2F$ or $NH_3 + F_2$. PH_3F_2 is at least 170 kcal/mol below PH_3(planar) + 2F and by ~40 kcal/mol with respect to $PH_2F + HF$. The energy lowering due to d AO's on P is ~40 kcal/mol both in PH_3F_2 and PH_5. The role of d AO's both for the energy and the population analysis is compared for NH_3F_2 and PH_3F_2. Four isomers of PH_3F_2 are compared. In PH_5 correlation effects are accounted for as well. Conclusions are drawn as to the mechanism of the three-center four-electron bond and bonding in phosphoranes

1. Introduction

Molecules with pentacoordinated phosphorus are very interesting from the point of view of valence theory and have therefore been the object of several quantum chemical studies in the past few years (for rather up-to-date compilations see ref 2). Most of these studies were devoted either to the hypothetical molecule PH_5[2b,3] or to the well-known species PF_5.[2a,4,5] For either compound both semiempirical[2b,4,5] and ab initio[1,3] calculations have been published. In the most sophisticated paper on PF_5 by Strich and Veillard[2a] some calculations on other phosphoranes, in particular PF_4H, PF_3H_2, and PFH_4, are mentioned, not however on PH_3F_2, a molecule that has only recently been synthesized.[6]

In our opinion PH_3F_2 (that also represents PR_3F_2) is not only the simplest and most clear-cut example of a compound of "pentavalent" phosphorus but it also provides a prototype of a three-center four-electron bond like it occurs, e.g., in XeF_2. A careful analysis of the electron structure of PH_3F_2 may therefore (complementary to the study of the somewhat different molecule PF_5) serve to give insight into the mechanism of electron-rich chemical bonds.

As is well known two opposite views have been proposed to look at bonding in pentavalent phosphorus compounds (for historical reviews see ref 7 and 8): (a) one assumes sp^3d hybridization[9] at the P atom which leads to five covalent, though nonequivalent, bonds (three of them involve sp^2 hybrids on P, two of them pd hybrids); (b) one explains bonding without involving d AO's, through a three-center four-electron axial FPF bond, the three equatorial PH bonds being ordinary two-center two-electron bonds.[10]

We want to answer the following questions. 1. Which role do the d AO's of phosphorus play for bonding in pentavalent phosphorus compounds? Are they as important for PH_3F_3 as for PF_5? 2. How important is the particular value of the lowest ionization potential of P (or rather planar PH_3) for making PH_3F_2 a stable molecule? 3. How important is the electronegativity of the axial ligands (F in PH_3F_2) for making the three-center four-electron bond stable? 4. How important is back-bonding? 5. Why are there no compounds of "pentavalent" nitrogen?

To answer question 1 we have performed computations both with and without d functions in the AO basis. Question 2 is somewhat suggested by Pitzer's[11] correlation between stability of noble gas fluorides and the respective ionization potentials. To answer this question we have compared PH_3F_2 with the hypothetical molecule NH_3F_2. A comparison of PH_3F_2 and PH_5 served to study the role of the axial ligands and gives some information about the role of back-bonding. We have not performed calculations on PF_5 but our basis sets are sufficiently close to those of Strich and Veillard[2a] that their values can serve for reference to document differences between PH_3F_2 and PF_5.

The energy differences between different isomers of PH_2F_3 and PF_5 are directly related to the ease of isomerization by a pseudorotation[12] (or turnstile[13]) mechanism. In PH_3F_2, the equilibrium structure of which has most likely D_{3h} symmetry, the F atoms are equivalent and so are the H atoms. Isomerization can hence be studied less easily experimentally, since it does not lead to a scrambling of previously nonequivalent positions. We think that the energy differences between the isomers of PH_3F_2 deserve some interest nevertheless.

2. Choice of the Computation Method and the Basis Sets

The majority of the calculations reported here are of SCF type with basis sets of gaussian lobes. We went beyond the SCF approximation and calculated the correlation energy as well only for PH_5, using the IEPA-PNO, PNO-CI, and CEPA-PNO methods, respectively.[14-17] The reliability of the SCF approximation for the questions that we want to answer is discussed in sections 6 and 12. Here we point out that a comment on the change of the correlation energy is needed whenever we consider breaking of bonds (e.g., the energy difference between PH_3F_2 and PH_3 + 2F) but that we can rely on the change in correlation energy to be insignificant for dissociation of one closed shell molecule into two closed shell molecules (e.g., $PH_3F_2 \rightarrow PH_3 + F_2 \rightarrow PH_2F + HF$). Also equilibrium distances are usually rather well predicted by SCF calculations.

The basis sets were chosen as the smallest ones that are able to account for the effects that we want to study. The pilot calculations on smaller molecules described in section 3 led us to the following "standard" basis sets for the larger systems.

Hydrogen: a 4s Huzinaga basis[18] in the contraction (3,1), augmented by a p function (in all three directions) with $\eta = 0.65$. In some cases the p functions are omitted; this is then explicitly mentioned. For the axial hydrogens in PH_5 we used an additional s lobe with $\eta = 0.03$.

Nitrogen: (7s/4p) in the contraction (3,1,1,1,1/2,1,1).

Table I. Total and Atomization Energies (au) of NH_3(planar) for Different N Basis Sets

Basis	$-E_{tot}$	$-E_{bind}$
(7,4), no p on H	56.1404	0.2692
Std = (7,4), with p on H	56.1694	0.2982
$+d_{z^2}$ ($d\sigma$)	56.1695	0.2983
$+d_{xy} + d_{x^2-y^2}$ ($d\delta$)	56.1714	0.3002
$+d_{z^2} + d_{xy} + d_{x^2-y^2}$	56.1715	0.3003
(9,5), with p on H	56.1936	0.3014
$+d_{z^2}$ ($d\sigma$)	56.1937	0.3015
$+d_{xy} + d_{x^2-y^2}$ ($d\delta$)	56.1956	0.3034
$+d_{z^2} + d_{xy} + d_{x^2-y^2}$	56.1958	0.3036
Ref 19	56.2138	0.3132
Ref 21, SCF	56.2072	
With valence shell correlation	56.4318	
Exptl (ref 20)	56.5818	0.4606

Table II. Total and Atomization Energies (au) of PH_3(planar) for Different P Basis Sets

Basis	$-E_{tot}$	$-E_{bind}$
(9,5), with p on H	−342.1673	0.1731
$+d_{z^2}$ ($d\sigma$)	−342.1686	0.1744
$+d_{xy} + d_{x^2-y^2}$ ($d\delta$)	−342.1794	0.1854
$+d_{z^2} + d_{xy} + d_{x^2-y^2}$	−342.1806	0.1864
(10,6), without p on H	−342.2796	0.1557
Std = (10,6), with p on H	−342.3196	0.1957
$+d_{z^2}$ ($d\sigma$)	−342.3208	0.1969
$+d_{xy} + d_{x^2-y^2}$ ($d\delta$)	−342.3311	0.2072
$+d_{z^2} + d_{xy} + d_{x^2-y^2}$	−342.3322	0.2083
(12,9), with p on H	−342.3958	0.1982
$+d_{z^2}$	−342.3969	0.1993
$+d_{xy} + d_{x^2-y^2}$	−342.4085	0.2109
$+d_{z^2} + d_{xy} + d_{x^2-y^2}$	−342.4089	0.2122
Ref 22	−342.3974	0.2072
Ref 23, SCF	−342.4503	0.2121
With valence shell correlation	−342.6217	
Exptl (using data of ref 22)	−343.857	0.332

We also used this standard basis plus a d set with $\eta = 1.0$ (or, if indicated, $\eta = 0.9$).

Fluorine: (7s/3p) in the contraction (3,1,1,1,1/2,1) but with the exponents of the p AO's scaled by a factor 1.15 and augmented by a "diffuse" p function with $\eta = 0.1173$, both the scaling factor and the additional function being optimized for F^-. In some calculations this standard basis plus d_{z^2}, d_{xz}, and d_{yz} functions with $\eta = 0.5$ were used.

Phosphorus: (10s/6p) in the contraction (4,6 × 1/3,1,1,1). Another basis for P is identical with this standard basis but contains a set of d AO's as well. The exponents were optimized individually in different cases. For PH_3F_2 different exponents for d_{z^2}/d_{xz} and d_{yz} on one side and d_{xy} and $d_{x^2-y^2}$ on the other side were allowed for (the fluorines being on the z axis). In some calculations a single exponent $\eta = 0.57$ was chosen for all the five d components. For NH_3, PH_3, and HF larger basis sets were used as well. They are indicated explicitly when they come up.

3. Study of NH_3, PH_3, HF, and F

Planar NH_3 and PH_3 had to be studied since we want to know the binding energy of NH_3F_2 and PH_3F_2 with respect to NH_3 + 2F and PH_3 + 2F. The molecules NH_3 and PH_3 also served for testing the basis sets. Several calculations on planar NH_3 are compared in Table I. Although the total energy depends very strongly on the basis size the binding energy (with respect to N + 3H) of 0.2982 au obtained with the standard basis differs by 1% from that from a (9,5) basis or by 2% from that from a (9,5) basis with a d set.

The value of Rauk et al.[19] of 0.3132 au obtained with a very large basis, which is close to the Hartree-Fock limit, is only "better" by 6% than our standard value. The experimental value is 0.4540 au[20] and the correlation error is much larger than the distance of our value to the Hartree-Fock limit.

We note that inclusion of d AO's on N to the standard basis improves the binding energy of NH_3 by 0.0019 au as far as d_{xy} and $d_{x^2-y^2}$ is concerned and by 0.0001 au for d_{z^2}. For symmetry reasons d_{xz} and d_{yz} do not contribute. One knows that d_{xz} and d_{yz} are important if one wants to account correctly for the inversion barrier of NH_3, but such small energy contributions (a few kilocalories per mole) are not relevant in the present context. For the standard basis calculations of planar NH_3 the geometry was optimized. An NH distance of $1.873a_0$ was found without d AO's on N and $1.870a_0$ with d AO's. The respective force constant for the pulsation vibration was found to be 25.27 and 26.21 mdyn/Å. The estimated exact values are $1.880a_0$ and 24.7 mdyn/Å.[21]

In the case of planar PH_3 (see Table II) the energy improvements due to d AO's are roughly an order of magnitude larger than in NH_3, namely 0.0120 for d_{xy} and $d_{x^2-y^2}$ and 0.0012 au for d_{z^2}. These values are almost independent on whether one starts from (9,5), (10,6), or (12,9) basis. The binding energy obtained with the standard basis, with and without d AO's, is −0.1957 and −0.2083 au, to be compared with the best published value of Lehn and Munsch[22] of −0.2072 au. With a very large basis (two d and one f sets on P) we recently got a Hartree-Fock binding energy of 0.2121 au.[23] For the PH distance and the force constant we find $2.58a_0$ (with d) ($2.62a_0$ in ref 22) and 13.84 mdyn/Å. The optimum exponent for the d AO's is $\eta = 0.925$. If one uses $\eta = 1$ (which we did) the energy is raised by roughly 0.0001 au. Since the F atoms in PH_3F_2 carry large negative charges and since we are also going to study ionic species like NH_3F^+-F^- our F basis must be equally appropriate for F and F^-. None of the smaller Huzinaga basis sets has this property. With the (7,3) basis the energy of F^- is 0.0051 au above the ground state energy of F whereas calculations at the Hartree-Fock limit[24] yield F^- 0.0501 au below F (with correlation this difference in the electron affinity is even 0.13 au).[25] The basis is obviously too poor for F^-. The (9,5) basis gives F^- more stable by 0.0222 than F, but it is much more effective to use the (7,3) basis with an additional "diffuse" p lobe of $\eta = 0.1$ which yields F^- more stable than F by 0.0502 au. With this basis set the energies of F and F^- are −99.2591 and −99.3093 au, respectively. Optimizing the scaling factor for the p AO's and the orbital exponent of the additional p function for F^-, which leads to our standard basis, lowers these values to −99.2682 and −99.3199 but changes the electron affinity of F only to 0.0513. We also used calculations on HF to check the quality of our basis. With the standard basis we get a binding energy of 0.1416 au which is improved by inclusion of d AO's on F to 0.1487 au; the (9,5) basis gives 0.1450 and 0.1501 au with d AO's on F. The best Hartree-Fock and "exact" values are 0.1611[26] and 0.225 au,[27] respectively.

We conclude that our standard basis sets are "well balanced", in particular that no spurious d AO contributions result from s or p unsaturations of the basis.

4. The Hypothetical NH_3F_2

The computed energies to which we refer in this and the following section are collected in Table III.

NH_3F_2 has not been observed experimentally. We first assumed that it has the structure of a trigonal bipyramid with the F atoms as axial ligands. The NH distance was kept fixed at its value for planar NH_3 ($1.87a_0$ = 0.99 Å) and the equilibrium NF distance was obtained as $3.22a_0$ (1.70 Å) irrespective of d AO's on nitrogen. In the standard

Table III. Summary of the Computed SCF Energies (Other Than Those of NH_3 and PH_3(planar))

Molecule (or atom)	Geometry	Basis	Energy, au
H		Std	0.4970
F		Std	−99.2686
F		Std	−99.3199
HF	$r = 1.73a_0$	Std, without p on H	−99.8905
	$r = 1.73a_0$	Std	−99.9098
F_2	$r = 2.68a_0$	Std	−198.4715
PH_3	C_{3v}, $r = r(PH) = 2.685a_0$, HPH = 93°50′	Std, without d on P	−342.3973
NH_3F_2	D_{3h}, $r(NH) = 1.87a_0$, $r(NF) = 3.22a_0$	Std, without p on H	−254.6386
	D_{3h}, $r(NH) = 1.87a_0$, $r(NF) = 3.22a_0$	Std	−254.6780
	D_{3h}, $r(NH) = 1.87a_0$, $r(NF) = 3.22a_0$	Std, with d on N	−254.6888
	D_{3h}, $r(NH) = 1.87a_0$, $r(NF) = 3.22a_0$	Std, only d_{z^2}, d_{xz}, d_{yz}	−254.6867
	D_{3h}, $r(NH) = 1.87a_0$, $r(NF) = 3.22a_0$	Std, with d on N and d on F	−254.7069
	C_{3v}, see text and Figure 1	Std, without p on H	−254.6560
	C_{3v}, see text and Figure 1	Std, with d on N	−254.7092
NH_2F	$r(NH) = 1.89a_0$, $r(NF) = 2.70a_0$, tetrahedral angles	Std, without p on H	−154.8045
NH_3F^+	$r(NH) = 1.92a_0$, $r(NF) = 2.77a_0$, tetrahedral angles	Std, without p on H	−155.0965
PH_2F	$r(PH) = 2.66a_0$, $r(PF) = 3.17a_0$, tetrahedral angles	Std, without p on H	−441.0669
	$r(PH) = 2.66a_0$, $r(PF) = 3.17a_0$, tetrahedral angles	Std, with d on P	−441.1298
PH_5	D_{3h}, $r_{ax} = 2.81a_0$, $r_{eq} = 2.58a_0$	Std	−343.4021
	D_{3h}, $r_{ax} = 2.81a_0$, $r_{eq} = 2.58a_0$	Std, with d on P	−343.4573
	C_{4v}, see text		−343.4490
PH_4F	Isomer I, see text	Std, with d on P (exponent 0.57)	−442.2857
	Isomer II, see text	Std, with d on P (exponent 0.57)	−442.2506
PH_3F_2	D_{3h}, $r(NH) = 2.58a_0$, $r(PF) = 3.31a_0$	Std, without p on H	−540.9648
	D_{3h}, $r(NH) = 2.58a_0$, $r(PF) = 3.31a_0$	Std	−541.0211
	D_{3h}, $r(NH) = 2.58a_0$, $r(PF) = 3.18a_0$	Std, with d on P	−541.1018
	D_{3h}, $r(NH) = 2.58a_0$, $r(PF) = 3.18a_0$	Std, with d on P and d on F	−541.1394
	D_{3h}, $r(NH) = 2.58a_0$, $r(PF) = 3.18a_0$	Std, with d on P, but a single d exponent (0.57)	−541.0976
	Structure II, see text		−541.0620
	Structure III, see text		−541.0469
	Structure IV, see text		−541.0795
PH_2F_3	See text		−639.8731

basis without d AO's on N the total energy is −254.6780, i.e., 0.0287 au (18 kcal/mol) above the sum of the energies of NH_3(planar) + 2F in the same basis. (In a calculation without p AO's on H the total energy is −254.6386 au which is 0.0390 above the corresponding sum for NH_3 + 2F. This indicates that the p AO's on hydrogen stabilize NH_3F_2 with respect to NH_3 + 2F by about 0.01 au). The standard basis with d AO's gives a total energy of −254.6888, which is 0.0179 au (11 kcal/mol) above that of NH_3(planar) + 2F. Inclusion of just d_{z^2} lowers the (total) energy of NH_3F_2 by 0.0076 au and of d_{xz} and d_{yz} by 0.0021 au, whereas the three functions together lower the energy by 0.0087 au and the full d set by 0.0108 au (7 kcal/mol). Inclusion of a d set on F lowers the energy further by ~ 0.02 au (12.5 kcal/mol) to −254.7069 au, so that is practically equal in energy with planar NH_3 + 2F. We are pretty sure that with electron correlation NH_3F_2 in D_{3h} geometry will turn out to be significantly lower in energy than planar NH_3 + 2F, and even lower than pyramidal NH_3 + 2F (since NH_3(planar) and NH_3(pyramidal) differ by only 6 kcal/mol). For the isoelectronic ion $CH_3F_2^-$ Dedieu and Veillard[28] have found that the D_{3h} structure is not a minimum but rather a saddle point of the potential hypersurface and that $CH_3F_2^-$ is stabilized by a distortion to C_{3v} symmetry (see Figure 1).

We therefore investigated whether NH_3F_2 is stable with respect to a distortion to C_{3v} symmetry and found that it is not. We studied this deformation both with the standard basis without p AO's on H (I) and with the standard basis including a d set on N (II). The geometries that one obtains on imposing C_{3v} symmetry are shown in Figure 1 for both basis sets. Without p AO's on H and d AO's on N the energy lowering due to this deformation is 0.0174 au and with polarization functions it is 0.0204 au (13 kcal/mol). One sees from the geometry in Figure 1 and the population analysis in Table IV that the C_{3v} structure of NH_3F_2 is actually an ion pair NH_3F^+-F^- held together by the Coulomb attraction. The sum of the energies of isolated NH_3F^+ and F^- ions in the standard basis without d on H is −254.4164 which is ~0.24 au above the energy of the ion pair.

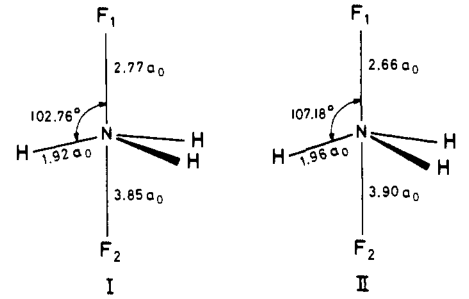

Figure 1. Optimum C_{3v} structure of NH_3F, calculated without (I) and with (II) polarization functions on N and H.

Table IV. Gross AO Populations[a]

Molecule	Basis	N or P							H_{eq} or F_{eq}				H_{ax} or F_{ax}					
		s	pπ	pσ	dσ	dδ	dπ	Σ	s	pπ	pσ	Σ	s	pπ	pσ	dσ	dδ	Σ
NH_3(planar)	Std, without p on H	3.47	2.28	2.00				7.75	0.75			0.75						
	Std	3.24	2.00	1.94				7.17	0.87	0.06	0.02	0.95						
	Std, with d on N	3.24	2.04	1.94	0.001	0.01		7.22	0.85	0.05	0.02	0.92						
$NH_3F_2(D_{3h})$	Std, without p on H	3.58	2.66	0.78				7.02	0.61			0.61	3.96	4.00	1.61			9.58
	Std	3.28	2.34	0.71				6.34	0.74	0.08	0.01	0.83	3.96					9.58
	Std, with d on N	3.29	2.34	0.71	0.03		0.006	6.37	0.74	0.07	0.01	0.82	3.96	3.98	1.63			9.58
	Std, with d on N and F	3.22	2.35	0.63	0.03	0.01	0.006	6.25	0.74	0.07	0.01	0.82	3.96	3.99	1.68	0.01	0.006	9.65
$NH_3F^+-F^-$	Std, without p on H	3.56	2.72	0.76				7.05	0.60			0.60	3.97	3.98	1.38			9.32[c]
(NH_3F_2/C_{3v})													3.97	4.00	1.88			9.84[d]
PH_3(planar)	Std, without p on H	5.44	5.82	4.00				15.25	0.92			0.92						
	Std	5.31	5.62	3.97				14.78	1.03	0.03	0.01	1.07						
	Std, with d on P	5.31	5.62	3.97	0.001	0.03		14.82	1.02	0.03	0.01	1.06						
$PH_5(D_{3h})$	Std, without d on P	5.28	5.63	2.98				13.88	1.11	0.03	0.003	1.15	1.32	0.004	0.02			1.34
	Std, with d on P	5.26	5.59	2.96	0.26	0.03		14.10	1.10	0.03	0.003	1.13	1.23	0.002	0.02			1.25
$PF_5(D_{3h})$[2a]	Without d on P							12.33				9.51						9.57
	With d on P	4.74	5.00	2.50	0.24	0.24	0.16	12.88	3.94	3.45	1.94	9.40	3.90	3.88	1.62			9.46
$PH_3F_2(D_{3h})$	Std without P on H	5.41	6.12	2.43				13.96	0.91			0.91	3.96	3.96	1.74			9.65
	Std	5.22	5.76	2.41				13.39	1.06	0.04	0.004	1.10	3.96	3.94	1.75			9.65
	Std with d on P	5.17	5.70	2.37	0.22	0.04	0.08	13.58	1.07	0.04	0.003	1.11	3.94	3.89	1.71			9.55
	Std, with d on P and F	5.15	5.68	2.35	0.22	0.04	0.08	13.51	1.07	0.04	0.003	1.11	3.95	3.90	1.73	0.007	0.004	9.56
PH_3F_2/EN3[b]	Std, with d on P	5.13	5.52	2.43	0.22		0.07	13.38	1.14	0.04	0.003	1.18	3.95	3.92	1.67			9.53
PH_3F_2/EN4[b]	Std, with d on P	5.06	5.30	2.47	0.22		0.08	13.13	1.25	0.05	0.003	1.30	3.96	3.90	1.62			9.48

[a] The basis sets are explained in section 2. Std means standard set. [b] EN3 and EN4 mean that an equatorial ligand with electronegativity 3 and 4 respectively in the Pauling scale is simulated through an increased nuclear charge on H. [c] F atom close to N. [d] F atom distant to N.

We did not inquire whether the C_{3v} structure is a real local minimum of the potential hypersurface, but we are sure that it cannot be the absolute minimum, since the sum of the energies of NH_2F + HF turns out to be lower than that of $NH_3F_2(C_{3v})$ by 0.039 au (25 kcal/mol, standard basis, without p on H). In the calculation of NH_2F tetrahedral angles were assumed and the NH distance was taken the same as in NH_3 (pyramidal, $r = 1.89a_0 = 1.00$ Å). The NF distance was optimized and found to be $2.689a_0$ (= 1.43 Å). While NH_3F_2 turns out to be unstable with respect to NH_2F + HF we find it stable with respect to $NH_3 + F_2$. In the standard basis without p on H $NH_3F_2(C_{3v})$ is lower in energy than NH_3(planar) + F_2 by 28 kcal and in the standard basis with d on N by 42 kcal/mol. (The values referring to pyramidal NH_3 are 22 and 36 kcal/mol, respectively.) One has to remember that in the Hartree-Fock approximation F_2 is not bound with respect to 2F, because the correlation energy contribution to the binding energy of F_2 is as large as 80 kcal/mol (for comparison H_2: ~ 25 kcal/mol, HF ~ 40 kcal/mol). If we assume that the correlation contribution for either of the two NF bonds is as large as that of a HF bond, the correlation contributions to the reaction $NH_3 + F_2 \rightarrow NH_3F_2$ should nearly cancel, so that we can in fact expect NH_3F_2 to be more stable than $NH_3 + F_2$ (and also with respect to NH_3 + 2F). For F_2 we have optimized the FF distance for our basis (see Table III).

5. PH_3F_2

PH_3F_2 was synthetized by Seel and Velleman.[6] It readily disproportionates to $PH_2F_3 + PH_3$ + HF but is stable enough to be characterized by its ir spectrum. The exact geometry of this molecule is not known, although there is no doubt that it is a trigonal bipyramid with the F atoms as axial ligands. We computed the energy of PH_3F_2 for such a structure first without d AO's on P, taking the PH distances the same as in planar PH_3 ($2.58a_0$ = 1.36 Å) and optimizing the PF distance, which resulted in $3.306a_0$ (1.75 Å).

The total energy (standard basis without d) was −541.0211 au which corresponds to a binding energy of −0.1643 au (103 kcal/mole) with respect to PH_3(planar) and 2F (without p AO's on H the total energy is 540.9648 au, and the binding energy is 0.1480 au as for NH_3F_2 these p AO's stabilized PH_3F_2 with respect to PH_3 + 2F by about 0.01 au). Subsequent optimization of the PH distance yielded $2.63a_0$; this value was however reduced to nearly $2.58a_0$ when d AO's on P were included in the basis. We therefore used $2.58a_0$ for all calculations. For the calculations with d AO's the exponents of the nonequivalent d functions were optimized individually and the best values were found to be

$$\eta = 0.925 \text{ for } d_{xy} \text{ and } d_{x^2-y^2}$$

$$\eta = 0.5 \text{ for } d_{z^2}, d_{xz} \text{ and } d_{yz}$$

The difference in the exponents comes from the different role of the respective d functions: d_{xy} and $d_{x^2-y^2}$ contribute to the PH bonds, d_{z^2} to the PF σ bond, and d_{xz} and d_{yz} to the PF π bond ("back-bonding"). One finds that the energy improvement due to d_{xy} and $d_{x^2-y^2}$ is about the same as in PH_3 so that they do not influence the binding energy much.

Inclusion of the d AO's to the basis reduces the PF distance from $3.306a_0$ (1.75 Å) to $3.185a_0$ (1.68 Å). The binding energy which was −0.1643 au without d AO's is −0.2258 au when d_{z^2}, d_{xz}, and d_{yz} are included. The improvement of the binding energy by d_{z^2} is 0.0408 au, that by d_{xz} and d_{yz} 0.0225 au, and that of the three together 0.0615 au (40 kcal/mol). An additional lowering of the energy is achieved by the inclusion of d_{xz}, d_{yz}, and d_{z^2} polarization functions with $\eta = 0.5$ on F. A calculation that included these d AO's on F in addition to the full d set on P

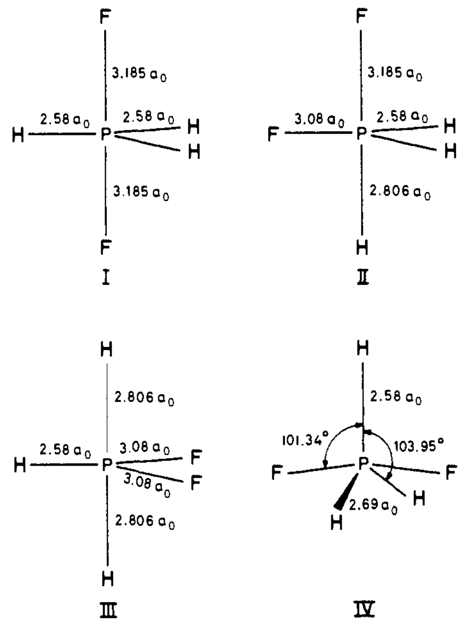

Figure 2. Geometries of four isomers of PH_3F_2.

led to a total energy of 541.1394 au and a binding energy of −0.2700 au (170 kcal/mol)

PH_3F_2 is, unlike NH_3F_2, quite strongly bound with respect to $PH_3 + 2F$; PH_3F_2 would be stable even without any contributions of d AO's on P. The contribution of 40 kcal/mol due to the d AO's is surely not negligible but is not large compared to the 103 kcal/mol from the calculation without d AO's and the 25 kcal/mol contribution of the d AO's on F.

One may be worried about the rather large contribution of the d AO's on F. However, the d AO's on F contribute about as much to the binding energy of F_2. The d AO's on F do not therefore affect the binding energy of PH_3F_2 with respect to PH_3(planar) + F_2 to an appreciable extent, whereas the d AO's on P contribute to the binding energy with respect to $PH_3 + F_2$ as much as to that with respect to $PH_3 + 2F$. Since a single d set on P lowers the energy of PH_3F_2 by as much as 40 kcal/mol one can estimate that a second d set and an f set may lead to an additional lowering of the order of magnitude of 10 kcal/mol, so that the real SCF binding energy is somewhat larger than the computed one.

PH_3F_2 is, unlike NH_3F_2, quite stable with respect to dissociation into $PH_2F + HF$. A calculation without p AO's on H and without d AO's on P yields PH_3F_2 0.0074 au (5 kcal/mol) lower than $PH_2F + HF$, whereas with p AO's on H and d AO's on P this difference is 0.0622 au (40 kcal/mol). One sees that the d AO's are quite decisive as far as the stability of PH_3F_2 with respect to $PH_3F + HF$ is concerned, whereas they do not matter for the respective stability of NH_3F_2.

For the calculation of PH_2F we assumed that all the angles are tetrahedral and that r(PH) is the same as in PH_3 (pyramidal equilibrium configuration). The PF distance was optimized to yield $r(\mathrm{PF}) = 3.17a_0$.

We studied three more isomers of PH_3F_2 (see Figure 2). For consistency's sake we used a single exponent ($\eta = 0.57$, cf. ref 2a) for the d AO's on P. In structure II, a trigonal bipyramid with one axial and one equatorial F, we used $r(\mathrm{PF_{ax}}) = 3.185a_0$ and $r(\mathrm{PH_{eq}}) = 2.58a_0$ as in structure I(D_{3h}), $r(\mathrm{PF_{eq}}) = 3.08a_0$ from our optimization for PH_4F, and $r(\mathrm{PH_{ax}}) = 2.806a_0$ from PH_5. The same values were used in structure III, a trigonal bipyramid with two equatorial F bonds. Structure IV is a square pyramid with the two F's at diagonal positions. The HPF and HPH angles were taken as 101.34 and 103.95° from ref 2a and 3, respectively. For $r(\mathrm{PH_{ap}})$ we choose the same value as for $r(\mathrm{PH_{eq}}) = 2.58a_0$; $r(\mathrm{PH_{bas}}) = 2.693a_0$ and $r(\mathrm{PF_{bas}}) = 3.133a_0$ were chosen as the mean values of the respective equatorial and axial distances.

The energies of the four isomers are given in Table III. One sees that structure I(D_{3h}) has the lowest energy of the four isomers. Structure IV is the only one that is somewhat competitive. It is, however, unlikely that structure IV represents a local minimum; there is probably a monotonic increase in energy in going from structure I via structure IV and II to structure III. Other square pyramidal structures are supposed to be much higher in energy.[3]

Since NH_3F_2 is stabilized by a deformation from the D_{3h} to a C_{3v} structure we checked whether PH_3F_2 (structure I) is stable with respect to the same kind of deformation. An out-of-plane displacement of the P atom by $0.2a_0$ (≈6% of the PF bond length) led to an increase of the energy from −541.1394 to −541.1317 au. We conclude that structure I represents in fact the equilibrium geometry. To state this with absolute certainty would require a few more calculations.

6. The Hypothetical PH_5

PH_5 has been studied previously by several authors[2b,3] mainly as a simple model for PF_5. We are interested in the questions whether PH_5 is stable with respect to $PH_3 + 2H$ and whether it is stable with respect to a deformation from D_{3h} to C_{3v} symmetry, and in similarities and differences between PH_3F_2 and PH_5.

For all calculations of PH_5 we used the standard basis including d AO's on P with $\eta = 0.925$ for d_{xy} and $d_{x^2-y^2}$ and $\eta = 0.5$ for d_{z^2}, d_{xz}, and d_{yz}, but in addition the basis sets of the axial H atoms were augmented by a diffuse s lobe with $\eta = 0.03$ (that is appropriate for H^-) since these atoms were expected to carry an appreciable negative charge.

For PH_5 not only SCF calculations but also calculations that account for electron correlation were performed. The IEPA-PNO,[14] CEPA-PNO,[15] and PNO-CI[16] methods are described in detail elsewhere.[17] We have used a localized representation.

Assuming D_{3h} geometry and taking $r(\mathrm{PH_{eq}}) = 2.58a_0$ as in PH_3F_2 the equilibrium value $r(\mathrm{P\text{-}H_{ax}}) = 2.806a_0$ was found.

The total energies on the SCF levels including valence shell electron correlation in the IEPA-PNO, PNO-CI, and CEPA-PNO levels are

$$E_{\mathrm{SCF}} = -343.4573 \text{ au}$$

$$E_{\mathrm{IEPA}} = -343.6694 \text{ au}$$

$$E_{\mathrm{CEPA}} = -343.6529 \text{ au}$$

$$E_{\mathrm{CI}} = -343.6388 \text{ au}$$

the respective values for PH_3(planar), H_2, and their sum are: (E_{SCF}) −342.3960, 1.1286, 343.5246 au; (E_{IEPA}) −342.5653, 1.1625, 343.7278 au; (E_{CEPA}) −342.5512, 1.1625, 343.7137 au; (E_{CI}) −342.5414; 1.1625, 343.7039.

Chart I.

	with respect to PH_3+2H	with respect to PH_3+H_2
SCF	−0.0613 au	+0.0673 au
IEPA	−0.1041 au	+0.0584 au
CEPA	*−0.1017* au	*+0.0608* au
CI	−0.0974 au	+0.0651 au

The binding energies of PH_5 with respect to $PH_3 + 2H$ and with respect to $PH_3 + H_2$ are in Chart I. The CEPA values are expected to be closest to reality and are therefore italic. One sees that PH_5 is bound by 64 kcal/mol with respect to $PH_3 + 2H$ but it is unstable with respect to PH_3(planar) + H_2 by 38 kcal/mol. One also sees that electron correlation stabilizes PH_5 compared to $PH_3 + 2H$ by 0.04 au (25 kcal/mol) but that the energy difference between PH_5 and $PH_3 + H_2$ is little affected by correlation.

One may say that the axial H-P-H bond is rather tight, but that PH_5 is unstable with respect to $PH_3 + H_2$ since the H_2 bond is so strong.

A calculation without d AO's yields an SCF energy of −343.4021 for $PH_5(D_{3h})$; the stabilization due to d AO's amounts hence to 0.0552 au (34 kcal/mol); it is rather close to that obtained for PH_3F_2.

A possible alternative to the D_{3h} structure is the tetragonal pyramid with C_{4v} geometry. We assumed the same angles as in tetragonal PH_3F_2 and also took over $r(\text{P-H}_{\text{bas}})$ from PH_3F_2, whereas $r(\text{P-H}_{\text{ap}})$ was chosen as $2.62a_0$ (1.39Å). The energies in the different approximations and the corresponding differences to the D_{3h} structure are in Chart II. Taking again the CEPA value as the most reliable one we find the C_{4v} structure 0.004 au (2.5 kcal/mol) above the D_{3h} structure. With more careful optimization of the geometry this difference will probably get smaller again though we do not expect that it changes its sign.

Chart II.

	E_{tot}, au	ΔE, au
SCF	−343.4490	+0.0083
IEPA	−343.6669	+0.0025
CEPA	*−343.6492*	*+0.0037*
CI	−343.6341	+0.0047

On the SCF level the energy difference is 5.0 kcal/mol, to be compared with the 3.9 kcal/mol of ref 3, whereas the extended Hückel value of 2.1 kcal/mol[2b] is surprisingly close to our value that includes correlation effects.

Since the D_{3h} structure of PH_5 does not represent the absolute minimum of the potential hypersurface we wondered whether it is at least a local minimum. To answer this question turned out to be a much harder task than we anticipated. One has namely to calculate the full valence force field including all cross terms and from this then the normal coordinates, and one has then to demonstrate that deformations along any of the normal coordinates lead to an increase of the energy. This investigation is not completed and will be published elsewhere. We have so far shown definitely only that the D_{3h} structure is stable with respect to deformations to C_{3v} symmetry, i.e., that PH_5 does not prefer an ion cluster PH_4^+-H^- like NH_3F_2 does.

7. PH_4F and PH_2F_3

Since PH_3F_2 is a stable molecule and PH_5 is not one wonders whether PH_4F is stable. The geometry assumed by Strich and Veillard[2a] for PH_4F is somewhat unrealistic; we therefore used our experience and additional optimization to get better distances. We considered two isomers.

Isomer I was taken as an ideal trigonal bipyramid with an axial F atom and the respective optimized distances from PH_5 and PH_3F_2, namely $r(\text{PH}_{\text{eq}}) = 2.58a_0$, $r(\text{PH}_{\text{ax}}) = 2.806a_0$, $r(\text{PF}) = 3.184a_0$.

In isomer II the F atom is equatorial. The PF distance was optimized and obtained as $r(\text{PF}) = 3.08a_0$; the other distances were taken from PH_5, namely $r(\text{PH}_{\text{eq}}) = 2.58a_0$, $r(\text{PH}_{\text{ax}}) = 2.806a_0$.

From the energies collected in Table III one sees that isomer II lies 23 kcal/mol above isomer I (Strich and Veillard[2a] found a difference of 16 kcal/mol), but that the more stable isomer I has an energy of 0.0214 au (13.4 kcal/mol) above that of PH_3(pyramidal) + HF.

We did not investigate the ion pair PH_4^+-F^-, which may compete with PH_3 + HF. For PH_2F_3 we only considered the structure which is suggested from spectroscopic evidence,[29] namely a trigonal bipyramid with two axial and one equatorial F. The angles were taken for idealized geometry (as if the molecule had D_{3h} symmetry). The bond distances were first taken from PH_4F and PH_3F_2 which led to $E = -639.8687$ au. Then we shortened the PF distances by 2%, taking care of the fact that the PH_2F_3 is somehow between PH_3F_2 and PF_5. This lowered the energy by 0.0044 au (2.8 kcal/mol). The energy given in Table III was obtained for $r(\text{PF}_{\text{ax}}) = 3.12a_0$, $r(\text{PF}_{\text{eq}}) = 3.02a_0$, $r(\text{PH}) = 2.58a_0$. A comparison of $2 \times PH_3F_2$ and of $PH_2F_3 + PH_4 + HF$ yields $2 \times PH_3F_2$ lower by 0.015 au (9.4 kcal/mol). This value can probably be reduced by ~5 kcal/mol if one optimizes the geometry of PH_2F_3 (which has only C_{2v} symmetry) more carefully. If one considers further that there should be a hydrogen-bonded interaction between PH_3 + HF one expects $2 \times PH_3F_2$ to be very close in energy to the disproportionation products $PH_2F_3 + PH_3 + HF$. The disproportionation should require practically no activation energy. Only very accurate calculation could decide on whether PH_3F_2 is really unstable with respect to disproportionation, as is suggested from experiment.[6]

8. Population Analysis

Some insight into the nature of the chemical bond in the molecules studied here can be gained from a population analysis. If the FXF bond (X = N, P) is a pure three-center four-electron bond the F atoms should have a negative charge of about −0.5. If, on the other hand, there are two covalent axial XF bonds involving dp hybrids, only a small negative charge on F is expected, but a d AO on P should be occupied by 1.0 electron.

Some care is necessary since atomic populations are not uniquely defined and depend to some extent on the basis used.

We have calculated the Mulliken gross populations[30] and summed them over all AO's of the same symmetry. We get for each atom separate s, p, and d populations (also the components p_x, p_y, p_z, etc., are defined), but it is not meaningful (it is only so for a minimum basis set) to distinguish between 1s, 2s, and 3s populations, etc. These populations are defined for the total electron distribution but also for any occupied orbital, be it canonical or localized.

The total populations are collected in Table IV. One first notes that the population of the hydrogen s AO's is rather different for the same molecule depending on whether or not p AO's of hydrogen are included. It seems that by allowing for a polarization of the H atom it becomes more attractive and therefore higher populated. The increase of the hydrogen population is between 0.15 and 0.22 electron in all cases. One also realizes that this increased population of hydrogen goes at the expense of N or P and the sum of the populations of the XH_3 unit is almost unaffected and so is the total population of the fluorines.

Taking this into account one realizes that the population of the hydrogens is about 0.10 larger in planar PH_3 compared to planar NH_3 and about 0.30 larger in PH_3F_2 compared to NH_3F_2. The ratio of the s to the ($p_x + p_y$) populations of the valence shell is 1.47:2.28 (1.24:2.04) in NH_3 and 1.44:1.82 (1.31:1.62) in PH_3 (values in parentheses refer to calculations with p AO's on the hydrogens). For genuine sp^2 hybridization this ratio would be 1:2. Hence the p_x and p_y AO's are much less populated (in PH_3 still less than in NH_3) than what is expected for the appropriate hybrids.

In $NH_3F_2(D_{3h})$ either F atom has a negative charge of −0.58 which can be compared with the value of −0.5 given by simple Hückel theory for a four-electron three-center bond assuming the same α for N (or P) and F. (In the C_{3v} structure one F has a charge of -0.32 and the other -0.84.) The negative charge of the F atoms in PH_3F_2 is -0.65 and hence larger than in NH_3F_2 (in agreement with the increased electronegativity difference) if one omits d AO's in the basis. In NH_3F_2 inclusion of d AO's has practically no effect on the charges on the F atoms, and the d AO's are almost unpopulated. In PH_3F_2 the d population is nonnegligible (0.21 for d_{z^2} and 0.07 for $d_{xz} + d_{yz}$, compared to 0.03 and 0.006 for NH_3F_2) but not very large. One sees that the d AO's of P are populated at the expense of the fluorines, which are by about 0.1 less negative if d AO's on P are taken into account. Inclusion of d AO's on F has little effect on the populations, although it lowers the energy considerably.

Comparing NH_3 with NH_3F_2 one sees that the bulk of the charge transferred to the fluorines is taken from N (~0.8 units) and the rest (~0.4) from the hydrogens. On nitrogen p_z loses about 1.2 units whereas s, p_x, and p_y gain charge. In PH_3F_2 as compared to PH_3 practically the whole charge transferred to the fluorines comes from P and there essentially from p_z. If we consider that the FXF bond is mainly formed by p_z of X and p_z of the two F one realizes that this four-electron three-center bond is highly ionic both in NH_3F_2 and in PH_3F_2; in the latter the increased electronegativity difference is attenuated by the larger participation of d AO's.

The question "sp^3d hybridization" or "three-center four-electron bond" can be answered easily. The ratio of the s, p, and d valence AO populations should be 1:3:1 for sp^3d hybridization; the actual ratios are 1.29:3.05:0.03 in NH_3F_2 and 1.20:2.12:0.21 in PH_3F_2. These ratios together with the documented ionicity establish that three-center four-electron bonds are present, but that they are stabilized by a slight contribution of d AO's.

Back-bonding is obviously not really important for PH_3F_2 (and still less for NH_3F_2). The d_{xz} and d_{yz} AO's of P that carry back-bonding are together only populated by 0.07 electron, at the expense of the p_x and p_y AO's of F.

In PH_5 the axial H atoms, which play the role of the F atoms in PH_3F_2, carry a negative charge of 0.34 if no d AO's on P are allowed for and of 0.25 if d AO's are included. From simple MO theory one would expect 0.5 for a genuine three-center four-electron bond. The small electroaffinity of H obviously does not allow such a high negative charge. In fact the sum of the negative charges in the three equatorial H atoms (0.39) is not very different from that on the two axial H atoms (0.50). The population of d_{z^2} (0.26) is even somewhat higher than that in PH_3F_2 (0.21), but there is obviously no back-bonding at all in PH_5.

A certain equilibration of the effective charges on the ligands, somewhat in contrast to the predictions of simple MO theory, is also observed for PF_5. Strich and Veillard[2a] found total electron populations of 9.40 and 9.46 for equatorial and axial PF bonds respectively and a total population of 12.88 for P (compared to our values of 13.51 in PH_3F_2 and 14.10 in PH_5).

The total population of the d AO's is appreciably higher in PF_5 (0.64) than in PH_3F_2 (0.34), but on closer inspection one sees that the population of d_{z^2} does not vary much (0.24 in PF_5 vs. 0.22 in PH_3F_2) and the main difference lies in the population of $d_{xy} + d_{x^2-y^2}$ (0.24 in PF_5 vs. 0.04 in PH_3F_2). The AO's d_{xy} and $d_{x^2-y^2}$ can only contribute to the equatorial PF bonds. Their strong population in PF_5 indicates that d AO's are about equally important for the equatorial and for the axial PF bonds. In the sp^3d hybridization model d_{xy} and $d_{x^2-y^2}$ are completely ignored.

It seems that in PF_5 the difference between the nonequivalent PF bonds is as much attenuated as it can be. The ratio between the s, p, and d_{z^2} valence AO population on P is 0.74:1.50:0.24 and hence somewhat closer to the sp^3d hybridization ratio than in PH_3F_2. Nevertheless, we think that even in PF_5 the d AO's on P should be more looked at as polarization functions than in terms of a hybridization model that involves d AO's.

If one tries to simulate PF_5 by increasing the nuclear charge on hydrogen in PH_3F_2 such as to account for the electronegativity of fluorine, one is only partially successful. According to ref 3 nuclear charges of 1.117 and 1.243 are equivalent to electronegativities of 3 and 4 respectively in the Pauling scale.

One sees from Table IV that on going from PH_3F_2 via PH_3F_2(EN3) to PH_3F_2(EN4) the electron population on H increases by ~0.2 units, that on F decreases by 0.1 units, and that on P decreases by ~0.5 units. Only the charges found on F are close to those of PF_5;[2a] the hydrogens (simulating fluorines) have somewhat too little charge (without p's on H these charges would be even smaller) and P has somewhat too high electron population. The d population on P is well accounted for as far as d_{z^2} is concerned (0.22 in PH_3F_2(EN4) compared to 0.24 in PF_5) but the population of d_{xz} and d_{yz} is a factor 2 too small (0.08 compared to 0.16), i.e., back-bonding in the three-center FPF bond is underestimated. The d_{xy} and $d_{x^2-y^2}$ orbitals were not considered in this comparison because they have only a population of 0.036 in PH_3F_2 and are unlikely to be higher populated in the simulated PF_5, whereas in "real" PF_5 they have a population of 0.24 mainly due to polarization of the equatorial PF bonds and equatorial PF-quasi-back-bonding, which can of course not be simulated by H with an extra positive charge.

9. Discussion of the MO Energies

In Table V the orbital energies of the interesting molecules are compiled in such a way that MO's that correspond to each other are on the same line. The energies of the MO's involved in the three-center four-electron bond are italicized. In looking for an essential difference between NH_3 and PH_3 (both planar) one realizes that the orbital energies of the p_z lone pairs, that are via Koopmans' theorem related to the respective ionization potentials, differ appreciably, being 0.2865 au (7.8 eV) for PH_3 and 0.3787 au (10.3 eV) for NH_3. This difference is in contrast to the rather close experimental vertical ionization potentials[31] (NH_3: 10.85 eV; PH_3: 9.9 eV) but one has to note that the latter correspond to the pyramidal equilibrium geometries and that the lone pair in NH_3 is more like an sp^3 hybrid and that in PH_3 more like a pure s AO, though both are hybrids.

Comparing NH_3F_2 to PH_3F_2 one finds that the levels of the π AO's of F in NH_3F_2 (3E′ and 1E″) are only split by ~0.02 au but they are split by ~0.07 au in PH_3F_2 (~0.05 without d AO's). In both cases 1E″ is lower. Since there is no other E″ MO and since the increase of the splitting due to d (i.e. due to back-bonding) is only 0.02 (in PH_3F_2) the splitting is probably due to an "interaction" of 3E′ with other E′ MO's and not to a direct interaction of the π AO's of the fluorines. The MO energy of a fluorine π AO in HF (in the same basis) is 0.6517 au; the corresponding MO energies in PH_3F_2 and NH_3F_2 are in agreement with the somewhat higher negative charge on F in the latter compound.

Now, according to simple MO theory, the nonbonding $6A_1'$ MO that is part of the three-center four-electron bond should be built up from p_z AO's of the fluorines and have the same energy as the fluorine p AO. In NH_3F_2 the energy of this "nonbonding" MO is as much as ≈0.1 au higher than that of the E″ π MO (which is regarded as a "true"

Table V. Orbital Energies (Negative, in au) (the Orbitals Involved in the Three-Center Four-Electron Bond are Italic)

Label for PH_3F_2	$PH_3F_2(D_{3h})$ With d	$PH_3F_2(D_{3h})$ Without d	$PH_5(D_{3h})$ With d	$PH_5(D_{3h})$ Without d	$PH_3(D_{3h})$	$NH_3(D_{3h})$	$NH_3F_2(D_{3h})$	HF	Pictorial assignment
$1A_1'$	80.117	80.143	80.005	80.030	79.905	15.501	15.838		1s (P, N)
$1A_2''$	26.292	26.274					26.265	26.335	1s (F)
$2A_1'$	26.292	26.274					26.265		1s (F)
$3A_1'$	7.649	7.679	7.540	7.570	7.455				2s (P)
$2A_2''$	5.538	5.568	5.428	5.458	5.344				2p (P)
$1E'$	5.538	5.568	5.431	5.460	5.345				2p (P)
$4A_1'$	1.575	1.568					1.552	1.625	2s (F)
$3A_2''$	1.567	1.561					1.518		2s (F)
$5A_1'$	0.952	0.969	0.918	0.937	0.842	1.110	1.300		a_1 (XH)
$2E'$	0.706	0.714	0.593	0.603	0.556	0.636	0.882		e' (XH)
$4A_2''$	*0.689*	*0.685*	*0.565*	*0.575*	*0.287*	*0.379*	*0.682*	0.773	a_2'' (FXF)[a] or p_z (F)
$1E''$	0.625	0.611					0.587	0.652	π (F)
$6A_1'$	*0.566*	*0.543*	*0.325*	*0.305*			*0.481*		a_1' (FXF)[a]
$3E'$	0.554	0.557					0.566		π (F)

[a] Or HXH.

nonbonding MO); in PH_3F_2 the respective difference is ≈ 0.05. In either molecule the formally nonbonding MO of the three-center bond is appreciably destabilized (and hence in a sense antibonding), more in NH_3F_2 than in PH_3F_2. (Of course part of this "destabilization" can come from "interaction" with other A_1' MO's like the similar "destabilization" of E' with respect to E'', but unpublished model calculations where such an interaction is excluded demonstrated similar destabilization of the formally nonbonding MO.)

The binding $4A_2''$ MO of the three-center bond has about the same energy in PH_3F_2 and NH_3F_2. We further note that although in NH_3 the highest occupied MO is about 0.1 au lower in energy than in PH_3, in NH_3F_2 vs. PH_3F_2 the P compound has the lower highest occupied MO (by ~0.08 au).

10. Orbital Contraction, 3d vs. 4s Participation

If one plots the expansion coefficients of the gaussians in one orbital as a function of the orbital exponent one gets a maximum for what one may call the "optimum exponent", which is rather insensitive to the size of the expansion. In the free P atom the optimum exponents for 1s, 2s, 2p, 3s, and 3p are roughly 45, 2, 3, 0.2, and 0.2 respectively. We conclude that a spectroscopic 3d AO should have $\eta \approx 0.2$ (or rather less since it is expected to be more shielded than 3s and 3p), whereas a polarization-type 3d should have roughly the same η as the 3s and 3p that it polarizes. In the MO's of the PH bonds in PH_3 the optimum exponents are not much changed; in PH_3F_2, however, one finds for 3s and 3p in the 5A′ and 2E′ MO's 0.5 and 0.4, i.e., the optimum exponents of 3s and 3p are multiplied by roughly a factor of 2. This is a semiquantitative illustration of what is usually referred to as "orbital contraction" as a consequence of the effective positive charge on P. The optimum exponent for a d AO in PH_3F_2 is close to 0.5, hence similar to that of the "contracted" 3s and 3p AO's, but far from that of a spectroscopic 3d AO. At variance with the large optimum exponent of 0.5 for s in the $5A_1'$ MO (see Table IV) that has to do with the PH bonds, the optimum exponent of s in the (formally nonbonding) $6A_1'$ MO is only 0.13. In $6A_1'$ this "diffuse" s AO enters with a coefficient 0.18 that is close to that of the d_{z^2} AO (0.16). One is tempted to state that we are in fact dealing with a 4s AO of P which is involved in $6A_1'$ to about the same extent as $3d_{z^2}$, although it is not too meaningful to assign quantum numbers to AO's in a molecule unless one has used a minimal basis. We also note that in order to compare the size (the "bohr radius") of an AO one should not just compare the orbital exponents but also consider that a d AO contains a factor r^2, a p AO only a factor r. We ignore this since our argument is only semiquantitative anyway.

11. Role of the Ionization Potential of XH_3 (X = P, N) and Electron Affinity of F (with respect to H) for the Stability of the Three-Center Bond

The simplest realistic model of a four-electron BAB bond (with two electrons from A and one from either B) consists probably in building this bond in two steps: (a) formation of $AB^+ + B^-$; (b) "resonance" stabilization to BAB.

The energy involved in step (a) consists of: (1) the ionization potential of A; (2) the electron affinity of B; (3) the net Coulomb interaction at the equilibrium distance between AB^+ and B^-; (4) the covalent binding energy between A^+ and B.

According to simple MO theory step (b) should amount to an energy gain of $(\sqrt{2} - 1)$ times the binding energy of A and B^+ if this bond is ideally covalent, and to zero if this bond is purely ionic. So we expect something of the order of 20% of this binding energy, i.e., at best 20 kcal/mol, a quantity that is almost negligible with respect to the other energies that we discuss.

If the ABA bond is not completely a three-center four-electron bond, but is appreciably stabilized through d AO's, we have to add another step: (c) stabilization through participation of d AO's.

Using this simple model, identifying the ionization potential of XH_3 with the respective MO energy, taking the experimental electron affinity of F (3.5 eV = 0.13 au) assuming a Coulomb attraction of 0.24 au[32] (corresponding to a distance of $4.3a_0$ between ideal point charges), taking 0.08 au for the AB^+ binding energy, and taking the improvements due to d AO's from our calculations, we get the binding energies (au) (with respect to XH_3 + 2F (2H)) in Chart III. These values are in very rough agreement with those actually calculated. We can say that the difference in binding energy of PH_3F_2 and NH_3F_2 is to roughly 50% due to the difference in ionization potentials of NH_3 and PH_3(planar) and to 50% due to d AO's.

Chart III.

	NH_3F_2	PH_3F_2	PH_5
a1	0.38	0.29	0.29
2	−0.13	−0.13	−0.03
3	−0.24	−0.24	−0.24
4	−0.08	−0.08	−0.08
c	−0.00	−0.06	−0.06
	−0.07	−0.22	−0.13

12. Reliability of the Results

The basis sets were chosen so that with relatively little computational effort they account for energy *differences* rather close to those obtained at the Hartree–Fock-limit; i.e., the deficiencies of our basis sets are mainly intraatomic. The errors that are still present in the computed energy differences are hence due to correlation. We see from the results for PH_5 that, in fact, the binding energy with respect to $PH_3 + 2H$ is strongly underestimated in the Hartree-Fock approximation (by ≈ 0.04 au = 25 kcal/mol), whereas the error in the binding energy with respect to $PH_3 + H_2$ is in error by only ≈ 3 kcal/mol. We expect something similar for NH_3F_2 and PH_3F_2, i.e., that the binding energies with respect to $XH_3 + 2F$ are substantially higher (in absolute value) than those calculated in Hartree-Fock approximation (~ 0 and 170 kcal/mol, respectively), whereas those with respect to $XH_3 + F_2$ (or $XH_2F + HF$) should be close to the actual ones (see also the end of section 4).

For those molecules which have been treated previously by ab initio calculations, namely PH_5 and PH_4F, we claim that our results are more reliable since we have used better balanced basis sets and spent more care on geometry optimizations. The populations tabulated in this paper should not be taken too literally mainly in view of their basis dependence, but the discussed differences between different molecules are surely significant. The same is true for the orbital energies.

13. Conclusions

(1) PH_3F_2 is a more typical example of a molecule with one electron-rich three-center bond and three ordinary bonds than is PF_5 or PH_5 where the difference of the two kinds of bonds is much attenuated.

(2) Molecules like PH_3F_2 or PF_5 would be stable without any participation of d AO's on P. The d AO's stabilize the FPF bond (by ≈ 40 kcal/mol) but they are not essential.[33] The stabilization through d AO's is about the same in PH_5 as in PH_3F_2, but it is one order of magnitude smaller in NH_3F_2. The population of the d_{z^2} AO of P is ≈ 0.02 in NH_3F_2 and ≈ 0.22 in PH_3F_2,; i.e., in either molecule it is much less than what is required for sp^3d hybridization. The surprisingly high d populations found in CNDO calculations[4] are an artifact of the CNDO scheme and deserve no further comment.

(3) A decisive factor for the stability of XH_3F_2 with respect to $XH_3 + 2F$ is the ionization potential of the p_z AO of planar XH_3. The lower ionization potential of planar PH_3 (orbital energy 7.8 eV) compared to NH_3 (10.3 eV) is to a large part responsible for the fact that PH_3F_2 is a stable molecule whereas NH_3F_2 is not. Similarly important is the large electron affinity of F. That PH_5 is not stable is in part due to the small electron affinity of H.

(4) In PF_5 the equatorial PF bonds render the P atom very positive (+2.1 compared to +1.4 in PH_3F_2) and stabilize indirectly the axial three-center bond. This extra stabilization results mainly from a stronger electrostatic attraction: the d_{z^2} participation is not increased compared to PH_3F_2 and back-bonding only slightly so. The axial PF bond length in PF_5 is 1.57 Å compared to 1.68 Å in PH_3F_2.

(5) The presence of back-bonding is demonstrated by the population of $d_{xz} + d_{yz}$ of 0.08 in PH_3F_2 and 0.16 in PF_5 accompanied by a similar decrease of $(p_x + p_y)$ population on F. In PH_3F_2 the energy improvement due to back-bonding is ≈ 15 kcal/mol (roughly half the energy improvement due to participation of d_{z^2}). In PF_5 an analysis of back-bonding is obscured by the fact that d_{xz} and d_{yz} can also participate in back-bonding with the equatorial F atoms. In PF_5 there is also a strong polarization of the equatorial PF bonds and some inplane "quasi-back-bonding" (there is no in-plane σ–π separation) documented by a population of 0.24 of $d_{xy} + d_{x^2-y^2}$ (compared to only 0.04 in PH_3F_2). There is no back-bonding possible in PH_5.

(6) Both PH_3F_2 and PH_5 in D_{3h} geometry are stable with respect to deformation to C_{3v}, whereas NH_3F_2 is not. PH_3F_2 and PH_5 want to have a symmetric axial bond, whereas NH_3F_2 prefers to consist of an ion pair NH_3F^+-F^-. The reason for this difference is not yet understood since according to simple MO theory the symmetric structure should be more stable by about 10 to 20 kcal/mol. Possibly the larger d participation in the P compounds is responsible for the preference to the symmetric structure, though the existence of the symmetric FHF^- proves that symmetric structures are possible without d participation. In NH_3F_2 the D_{3h} structure is only 12 kcal/mol above the C_{3v} structure.

(7) One can say that in PH_3F_2 the 3s and 3p AO's are contracted significantly compared to those in the P atom and that there is the participation of a 4s-like AO in the $6A_1'$ MO. The d AO in PH_3F_2 and PF_5 is rather different from a spectroscopic d AO. It is roughly as contracted as 3s and 3p.

(8) XH_3F_2 need not be a stable molecule, even if it is bound with respect to $XH_3 + 2F$ and even with respect to $XH_3 + F_2$. Another decomposition is that into XH_2F + HF. In fact NH_3F_2 is stable with respect to $NH_3 + F_2$ but not with respect to NH_2F + HF, whereas $PH_3F_2(D_{3h})$ is lower in energy than all other arrangements of the same atoms.

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Group Theoretical Selection Rules for the Transition States of Chemical Reactions

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Abstract: The transition state of a chemical reaction is the lowest barrier separating reactants and products on a potential energy surface. As such it is a critical point on the surface and its force constant matrix has exactly one negative eigenvalue. The corresponding eigenvector is defined to be the transition vector for the reaction. Schur's lemma implies that the transition vector will belong to one of the symmetry species of the transition state point group provided sufficient care is taken in the choice of the coordinate system. Consideration of the effect of transition state symmetry operations on the reactants and products and on the paths joining them to the transition state leads to a series of theorems governing the transformation properties of the transition vector. In some cases these requirements are incompatible with the known transformation properties of the available symmetry species for the proposed transition state. It is shown that such "transition states" are forbidden; i.e., they cannot be the lowest barriers separating reactants from products. The concept of symmetry forbidden transition states is applied to a series of reactions of gradually increasing complexity. Included (among others) are the classic H + H_2 exchange reaction, the T + CH_4 displacement reaction, the olefin metathesis reaction, the inversion of cyclohexane, and the Cope reaction.

I. Introduction

The concept of the transition state plays a central role both in the formal theory of reaction rates and in the way in which the chemist actually visualizes a reaction. The experimental determination of transition state geometries, however, is a very difficult problem. It is in fact probably fair to say that no currently available experiment or combination of experiments can yield anything better than a fuzzy view of the transition state of any particular reaction. It is natural, therefore, that there has in recent years been a series of attempts to calculate transition state energies and geometries by the various quantum mechanical techniques that were developed for equilibrium states. We shall refer to many of these computations in the body of this paper. The methods employed range from simple Hückel theory to the most expensive ab initio calculations. There have also been papers dealing with the special properties of transition states and with the problems involved in finding these states on a potential surface.

Murrell and Laidler[2a] have emphasized the requirement that the transition state force constant matrix have exactly one negative eigenvalue and have given a formal proof of this condition. Murrell and Laidler also tried to use their theorem to derive selection rules for transition state geometries. In doing so they made no use of group theory and were led into some unwarranted assumptions that destroyed the validity of some of their conclusions. These errors were later pointed out by Murrell and Pratt.[2b]

In this paper we will, like Murrell and Laidler, be looking for selection rules and will make extensive use of the Murrell and Laidler (hereafter M-L) theorem. We avoid the traps associated with faulty geometric intuition by combining the M-L theorem with formal group theory.[3] It might be mentioned that the M-L theorem also has important consequences which go beyond the scope of the present paper. It has been shown elsewhere,[4] for example, that M-L often requires that off-diagonal bond interaction force constants play a dominant role in the transition state, in marked contrast to their ordinarily minor role in equilibrium states.

Salem et al.[5] have defined as "narcissistic reactions" those in which reactants and products are related to one another via some improper rotation. They also discuss conditions which make a symmetric transition state probable or improbable for these reactions and stress the computational advantages associated with knowing the symmetry properties of the transition state prior to carrying out a computer search. These ideas can be generalized. We show that proper as well as improper rotations can convert reactants into products. Moreover, as indicated above, one can in many cases make *rigorous* statements concerning the allowed symmetry of the transition state for such reactions.

To a certain extent the computational advantage of knowing the symmetry of a transition state is the same as in knowing the symmetry of an equilibrium state; it enables one to reduce the number of coordinates that must be varied in the search for the transition state. Since the number of points required to map out a potential surface varies exponentially with the number of internal coordinates and since most reactions of interest involve a large number of coordinates the computational gain in reducing the number of coordinates can be very great. One practical way of achieving this gain is through the introduction of symmetry adapted coordinates. The search for the transition state can then be restricted to the subspace of fully symmetric coordinates.