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Ab initio study of $FH-PH_3$ and $ClH-PH_3$ including the effects of electron correlation

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Ab initio calculations are carried out for $FH-PH_3$ and $ClH-PH_3$ using a basis set including two sets of polarization functions. Electron correlation is incorporated via Møller–Plesset perturbation theory to second and (in part) to third orders. The basis set is tested and found to produce satisfactory treatments of subsystem properties including geometries and dipole moments as well as the proton affinity and inversion barrier of PH_3. Electron correlation is observed to markedly enhance the interaction between PH_3 and the hydrogen halides. Its contribution to the complexation energy is 30% for $FH-PH_3$ and 50% for $ClH-PH_3$. Moreover, the equilibrium geometries of the complexes at correlated levels are quite different than SCF structures.

INTRODUCTION

The importance of hydrogen bonding has motivated a large number of quantum chemical studies of this phenomenon over the years. In contrast to the case of first-row hydrides which have been investigated to very high levels of theory,[1–3] relatively few studies of comparable accuracy have been carried out for the analogous second-row atoms.[4–7] This situation is paralleled to some extent by experimental work where data for the second-row hydrides has lagged behind the smaller atoms.[1] Recent pulsed–nozzle Fourier transform microwave spectroscopic work by Legon and Willoughby has detected formation of complexes between PH_3 and the halides HF, HCl, and HBr.[8–10] The geometries of these systems belong to the C_{3v} point group and contain a linear H-bond of the type XH--PH_3. Although it was possible to determine the equilibrium intermolecular distances, other features of the geometries as well as the magnitudes of the interaction energies remain unknown.

The objective of this paper is a theoretical study of complexes of PH_3 with HF and HCl. A basis set of sufficient flexibility is used to ensure proper treatment of various contributions to the interaction and to provide an adequate framework for evaluation of the effects of electron correlation. It is our intention to furnish information complementary to the experimental data and to elucidate the importance of electron correlation in these complexes. Moreover, comparison of the two systems at the correlated level will point out fundamental differences between the character of H-bonds involving first and second-row atoms as proton donors.

DETAILS OF CALCULATIONS

All calculations were carried out using the GAUSSIAN-80 package of computer programs.[11] Electron correlation was considered via Møller–Plesset perturbation theory to second (MP2) and third (MP3) orders (keeping the inner shells of first and second-row atoms frozen).[12,13] Our choice of basis set was a modified form of the standard 6-31G**.[14] For nonhydrogen atoms, an additional diffuse set of five *d* functions was added with $\zeta = 0.25$.[15] The contracted *d*-orbital exponent on *P* was optimized with respect to the SCF energy of the PH_3 molecule to be 0.80. All hydrogens were supplied with a diffuse set of *p* orbitals with $\zeta = 0.15$.[15] In the case of the H-bonding proton of HF and HCl, a second set of more contracted *p* functions was also included with exponent 1.1. We may therefore use the notation 6-31G** (2*p*,2*d*) to describe the basis set of HX and 6-31G** (1*p*,2*d*) for PH_3.

Geometry optimizations were carried out at the SCF and MP levels for the isolated HF and HCl subunits; PH_3 was optimized at the SCF level only. In line with the experimental information,[8–10] C_{3v} geometries were assumed for the complexes. The internal geometry of PH_3 was held fixed in its optimized structure while the intermolecular separation *R* (P--X) and *r*(HX) bond lengths were optimized.

RESULTS

Subunit properties

Before presenting our results for the complexes, we begin with an examination of the suitability of the basis set for this problem. The calculated properties of the various subunit molecules are presented in Tables I and II along with

TABLE I. Calculated properties of PH_3 and $(PH_4)^+$.

	6-31G**(1*p*,2*d*)	Lit.
	PH_3 (C_{3v})	
r(PH), Å	1.408	1.427[a]
θ(HPH), deg	94.8	93.2[a]
μ,D	0.653	0.574[b]
	PH_3 (D_{3h})	
r(PH), Å	1.375	1.379[c]
	$(PH_4)^+$ (T_d)	
r(PH), Å	1.388	1.392[d]

[a] Experimental value from Ref. 16.
[b] Experimental value from Ref. 17.
[c] Calculated with [642/31] basis set, Ref. 18.
[d] Calculated with CI/DZP method; Ref. 19.

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TABLE. II. Bond lengths and dipole moments of HX calculated with 6-31G**(2p,2d) basis set.

	SCF	MP2	Expt.
		HF	
r(HF), Å	0.900	0.922	0.917[a]
μ,D	1.812	1.849[b]	1.83[c]
		HCl	
r(HCl), Å	1.270	1.277	1.275[a]
μ,D	1.167	1.174[b]	1.09[d]

[a] Reference 20.
[b] SCF value at MP2 geometry.
[c] Reference 21.
[d] Reference 22.

TABLE III. Calculated proton affinity[a] of PH_3.

	This work	Ref. 19
ΔE^{SCF}	−198.1	−200.4
ΔE^{MP2}	−190.8	...
ΔE^{MP3}	−190.3	−193.7[b]
PA (0 K)[c]	183.2	186.6
PA (298 K)[d]	184.7	188.1
PA (expt.)[e]	185.6–186.6	

[a] All entries in kcal/mol.
[b] CI value.
[c] $PA = -(\Delta E^{MP3} + \Delta \text{ZPE})$; Δ ZPE = 7.1 kcal/mol from Ref. 19.
[d] PA (298 K) = PA (0 K) + $5/2\,RT$.
[e] From Refs. 23 and 24.

previous data from the literature for purposes of comparison. In addition to pyramidal PH_3, we have also optimized the geometry of planar PH_3 and the protonated $(PH_4)^+$, all at the SCF level, and included these in Table I as well. The calculated properties of pyramidal PH_3 are in satisfactory agreement with experiment: although the bond length is underestimated by 0.02 Å, the bond angle is a good approximation and, perhaps most important, the calculated dipole moment is within 14% of the experimental value. The dipole moments of planar PH_3 and tetrahedral $(PH_4)^+$ are of course identically zero; our optimized bond lengths are rather close to previous theoretical values, including a CI calculation for the protonated species.

The results of geometry optimizations of HF and HCl at both the SCF and MP2 levels are contained in Table II along with experimental data. It is clear that second-order correlation effects have a lengthening influence on each bond. This effect is particularly noticeable for HF where the bond length increases by 0.022 Å. The MP2 bond lengths are in excellent agreement with the experimental values. Moreover, as in the previous case of PH_3, we find good accord between the theoretical and experimental dipole moments. There is therefore reason to believe that the basis set being used here is capable of accurately treating the electrostatic component of the interaction energy in the complexes described below.

The attack of a naked proton on the P atom of PH_3 may be thought of as an extreme or limiting case of the approach of a hydrogen halide to form a H bond. The proton affinity of PH_3 should therefore serve as an appropriate (and particularly stringent) test of the adequacy of our basis set for study of the complexes. We have accordingly calculated the interaction energy of PH_3 with a proton and the results are presented in Table III. ΔE^{SCF} in the first row represents the difference in SCF electronic energy between the optimized geometries of pyramidal PH_3 and $(PH_4)^+$ listed in Table I. The suitability of our basis set is confirmed in part by the small magnitude of the basis set superposition error; a counterpoise calculation yields a BSSE of only 0.9 kcal/mol. This small value is particularly notable in light of the small distance between PH_3 and the proton in $(PH_4)^+$.

The next two rows contain analogous data calculated at the MP2 and MP3 levels, also using the SCF geometries. Note that the MP values of ΔE are less negative than ΔE^{SCF}, which corresponds to a repulsive contribution of correlation to the interaction between PH_3 and a proton. This observation is not surprising in light of previous work which suggests that the dipole moment of the base, and hence the electrostatic attraction with a proton, is reduced by correlation effects.[25–28] An additional factor is the better separation between electron pairs in PH_4^+ than in PH_3 which may be expected to lower the correlation energy in the protonated base. The magnitude of the reduction in proton affinity is on the order of 7 or 8 kcal/mol. (Calculation of the BSSE on the correlated levels indicates that this positive contribution would be enlarged by about 1.6 kcal/mol.) Hence, the reduction in the proton affinity by electron correlation is substantial and may certainly not be ignored.

The proton affinity at 0 K is obtained by subtracting from the MP3 value the difference in zero-point vibrational energy between PH_3 and $(PH_4)^+$, Δ ZPE, taken from Ref. 19. Finally, translational and Δ PV corrections totaling $5/2\,RT$ must be included to arrive at a value adjusted to 298 K. Our data compares quite favorably with previous calculations involving an STO basis set of near Hartree–Fock limit quality and including correlation via configuration interaction.[19] Indeed, our final estimate of 184.7 kcal/mol for the proton affinity of PH_3 at 298 K is quite close to experimental values contained in the last row of Table III.

As a final test of our basis set, we examine the inversion motion of pyramidal PH_3 which goes through a D_{3h} planar structure as the transition state. The differences in energy between these two geometries (Table I) are listed in the first column of Table IV at SCF and correlated levels. Also provided are the results of previous calculations involving ex-

TABLE IV. Calculated inversion energy barriers[a] for PH_3.

	This work	b	c
SCF	38.82	37.79	36.77
MP2	34.86	...	...
MP3	34.80	34.52[d],35.35[e]	...

[a] All entries in kcal/mol.
[b] Reference 29; [7421/31].
[c] Reference 18; [642/31].
[d] IEPA-PNO.
[e] CEPA-PNO.

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tended basis sets.[18,29] At the SCF level, our barrier of 38.82 kcal/mol is slightly higher than those of the previous work. Inclusion of correlation via MP2 or MP3 reduces this barrier by 4 kcal/mol to a value in excellent agreement with calculations involving both IEPA and CEPA treatments with a very large basis set including *f* orbitals.[29] We therefore conclude that the basis set and theoretical procedures being used here lead to a variety of calculated properties in good accord with previous high-quality theoretical studies as well as available experimental information.

Complexes

The calculated properties of the complexes of PH_3 with HF and HCl are compiled in Table V along with theoretical data recently obtained by Hinchliffe using a basis set containing single sets of polarization functions at the SCF level.[5] The first two rows of data indicate the strong effects of correlation upon the equilibrium geometry of each complex. Second-order perturbation theory reduces the R (P–X) intermolecular separation by 0.16 Å for H_3P–HF and by 0.36 Å in the complex with HCl. Whereas large discrepancies exist between the SCF and experimental distances, the MP2 values concur with experiment quite nicely.

Correlation has a significant effect also upon the internal HX bond lengths. It was noted previously (see Table II) that these bonds are lengthened by correlation effects in the isolated HX subsystems. However, the increases in these bond lengths are even greater in the complexes. To amplify this point, the third row of Table V contains the increase in the r(HX) bond length which occurs as a result of complex formation at each level of theory. It may be seen that the HF bond is lengthened by 0.006 Å at the SCF level but by twice this amount when the comparison in bond length between HF and FH–PH_3 is made at the MP2 level. Similar results are noted for HCl where the SCF and MP2 bond length elongations are 0.004 and 0.011 Å, respectively.

The above effects of correlation upon the equilibrium geometries are fully consistent with the enhancement of the H-bond energy apparent from the next two rows of Table V. ΔE^{SCF} corresponds to the interaction energy computed at the SCF level using geometries optimized at the level indicated at the top of each column (SCF or MP2); analogous considerations apply to ΔE^{MP2}. Thus, the complexation energy of FH–PH_3 at the SCF level is −4.14 kcal/mol with SCF geometries and the somewhat smaller value of −3.82 if MP2 geometries are used. Comparison of the fourth and fifth rows of Table V illustrates the effects of correlation in stabilizing the two complexes. Using geometries appropriate to each level, correlation increases the H-bond energy of FH–PH_3 from −4.14 kcal/mol to −6.03, an increase of 46%; the corresponding enhancement in ClH–PH_3 is over 100%. Thus, second-order correlation effects are responsible for 1/3 of the total interaction energy in the first complex and 1/2 in the second. Clearly, any treatment of these systems which neglects correlation will be subject to large errors and will be ignoring a major stabilizing force.

We would like to make one last point concerning the interaction energies. In consideration of effects of electron correlation, it has become a fairly routine practice to apply an appropriate post-SCF procedure to a geometry of the complex which has been optimized only at the SCF level. Since this geometry does not coincide with the minimum in the correlated potential surface, this practice is subject to some error. The large differences observed between SCF and MP2 geometries for the complexes considered here would be expected to lead to especially inaccurate results. The errors introduced by this procedure may be seen by comparison of the values of ΔE^{MP2} in the SCF and MP2 columns of Table V. Use of the SCF geometry of FH–PH_3 leads to an MP2 interaction energy of −5.65 kcal/mol, underestimating the correlation contribution by 0.4 or 20%. The difference in the case of ClH–PH_3 is 0.6 kcal/mol which represents 30% of the true correlation component of the interaction energy.

Also included in Table V are the SCF dipole moments of the complexes computed for the SCF and MP2 geometries. Of particular interest are the enhancements of these moments produced as a result of the molecular interaction. This information is provided as $\Delta\mu$ in the last row of the table which is calculated as the difference between the dipole moment of each complex and the sum of isolated subsystem dipoles. The increases in dipole moment are quite substantial, amounting to almost 1 D. In contrast to the larger effects of correlation found for the ClH–PH_3 system with regard to properties previously discussed, the enhancement of the dipole moment of FH–PH_3 is greater than for ClH–PH_3, particularly when SCF geometries are considered.

TABLE V. Calculated properties of complexes.

	FH–PH_3				ClH–PH_3			
	SCF	MP2	a	expt.	SCF	MP2	a	expt.
R (P--X), Å	3.455	3.291	3.529	3.31[b]	4.166	3.802	4.210	3.88[c]
r(HX), Å	0.906	0.934	0.905		1.274	1.288	1.274	
Δr (HX), Å	0.006	0.012	0.007		0.004	0.011	0.004	
ΔE^{SCF}, kcal/mol	−4.14	−3.82	−3.70		−2.14	−1.48	−2.01	
ΔE^{MP2}, kcal/mol	−5.65	−6.03	...		−3.73	−4.35		
μ^{SCF},D	3.281	3.490	...		2.478	2.779	...	
$\Delta\mu^{SCF}$,D	0.816	0.988	...		0.658	0.952	...	

[a] Reference 5; SCF/DZP calculations.
[b] Reference 9.
[c] Reference 8.

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One potential source of error in the calculations of the complexes is the truncation of the perturbation series at second order. While higher-order terms may have some effect upon our results, we believe that these changes will be quite small. This belief is based in part on the very small third-order effects noted above for the proton affinity and inversion barrier and on previous work by ourselves and by Pople.[3] Due to the low value of the BSSE noted above for the interaction of a proton with PH_3, it is our expectation that superposition errors will be of little account in the complexes where the distances between subsystems are much longer.

One last remark concerns a comparison of the complexes formed between PH_3 and the hydrogen halides in Table V and its interaction with a proton in Table III. One clear distinction between the two types of complexes is the fact that, whereas electron correlation reduces the interaction with a proton, an opposite effect of increased complexation energy is observed for the H-bonded systems. This disparate behavior may be explained as follows. The dominant force in the interaction of the base with a proton is the ion-dipole term of the Coulomb energy. Correlation is known to diminish the dipole moment of the base[25–27] and thereby reduce the interaction energy. Similar decreases in dipole moment of both the base and hydrogen halide may be expected to depress the Coulomb attraction in the H-bonded systems as well. However, the inclusion of the dispersion attraction in correlated treatments more than compensates for this and the net result is an increase in the H-bond energy. Due to the absence of electrons on H^+, there is no possibility of dispersion in the interaction of a base with a proton.

CONCLUSIONS

From the calculations reported here, it is concluded that the interaction energy in FH–PH_3 is somewhat greater than for the HCl complex. Electron correlation plays a major part in the stabilization of both complexes although the effects are generally stronger in the latter system containing two second-row atoms. The contribution of correlation amounts to half of the total interaction energy of ClH–PH_3 and over 30% in FH–PH_3. The equilibrium geometries of both complexes are also substantially affected by correlation which markedly reduces the intermolecular separation and magnifies the lengthening of the HX bond which occurs as a result of complexation.

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