Tetrahedron Vol. 41, No. 22, pp. 5235 to 5240, 1985
Printed in Great Britain.

0040-4020/85 \$3.00 + .00

SUBSTITUENT EFFECTS IN SECOND ROW MOLECULES

MOLECULAR ORBITAL STUDIES OF PHOSPHORUS(III) COMPOUNDS

Eric Magnusson
Contribution from the Research School of Chemistry, Australian National University,
G.P.O. Box 4, Canberra, A.C.T., 2601, Australia

(*Received in UK* 10 *December* 1984)

Abstract—Substituent effects in directly bonded P(III) compounds are investigated by *ab initio* MO calculations of relative energies and the results compared with those for the corresponding nitrogen species. The investigation covers substitution by $X = BH_2, CH_3, NH_2, OH, F$ in PHX^-, PH_2X, and PH_3X^+ series molecules with some attention also to PX_3 and PX_3H^+ species. Except for compounds containing the π-acceptor substituent BH_2, σ-interactions dominate substitution behaviour but the second row species tolerate electron withdrawal better than their first row analogues, the severe destabilization of NH_2X and NH_3X^+ by σ-electron withdrawal being absent from PH_2X and PH_3X^+. In contrast to the σ-withdrawing NH_2 group, the PH_2 group is characterized as a mild σ-donor. PH^- is a σ-donor and PH_3^+ a σ-acceptor. π-Bonding to the second row atom is an important means of maintaining electroneutrality in the PH_3X^+ series, where $d\pi$ functions have a bigger role than $p\pi$ functions.

Substituent effects in the first row hydrides CH_4, NH_3, H_2O, and HF and related charged species NH_2^-, NH_4^+, OH^- have been subjected to theoretical analysis by Radom *et al.* who made particular use of substituent interaction energy calculations.[1] The results were readily accommodated by simple perturbation molecular orbital theory and the known characteristics of the substituents used.

In relative energy calculations the effect of errors inherent in the Hartree–Fock approach is minimized by comparing systems with the same number of bonds. The case of the amines is typical:

$$XNH_2 + H_2 \rightarrow NH_3 + XH.$$

In this case the substituent interaction energy measures the energy of the X—N interaction relative to the X—H interaction. Because of the exceptional strength of the X—H bonds, the interaction energy of this system is often negative and trends are more valuable than absolute values in rationalizing chemical behaviour.

Recently there have been several reports of high-level calculations of first row bases[2] which have concentrated on the calculation of accurate energies of protonation rather than an investigation of substituent effects but some conclusions about the nature of the bonding interactions and the effect of substituents were also drawn. Similar studies on some second row bases have also been published.[3]

Because of the importance of later main group molecules the relative energy approach is now extended to the second row by model calculations on some systems of phosphorus and, in other publications, on silicon and sulfur.[4] In this paper the series PH_2X, PH_3X^+, and PHX^- are treated ($X = H, BH_2, CH_3, NH_2, OH, F$) and, for $X = CH_3$ and F only, the trisubstituted species PX_3 and PX_3H^+. Not all the systems modeled correspond to compounds yet isolated but the calculations were carried out on complete series for ease of comparison with earlier work.

Method of calculation

The application of the Gaussian-80 series of programs[5] to compounds containing second row atoms at four basis set levels, with and without d-function supplementation, has been described separately.[6] The results selected for discussion in this paper are mainly from the calculations with the 6-31G## basis set.[6b,7] The geometries of all compounds were optimized at the 4-31G(#) level by the gradient technique.

Calculations on the anionic series compounds PHX^- were repeated with the use of diffuse s and p functions added to the 6-31G## basis, as recommended for first row anions by Spitznagel *et al.*[7] Preliminary calculations suggested the value $k = 0.03$ of the additional functions in the basis set, designated 6-31+G##. The corresponding first row NHX^- series were also restudied in this way, using the recommended 4-31+G(#) basis.[7]

RESULTS

Energy data (at 6-31+G##, 6-31G## and 4-31G(#) levels)[6b] and optimized geometries (4-31G(#) level) for the PHX^- series molecules are set out in Table 1 and Fig. 1, which also contain entries for $PH_2\cdot BH_2$ and $PH_3\cdot BH_2^+$. Data for the remaining members of the PH_2X and PH_3X^+ series are reported elsewhere.[6] Energy data at the 4-31+G basis set level for the NHX^- series compounds are also included in Table 1.

Substituent interaction energies ($\Delta E(X, H)$) for the PHX^-, PH_2X and PH_3X^+ series are presented in Table 2, results being listed for calculations at 4-31G(#), 6-31G(#), 6-31G##, and 6-31+G## basis set levels (for anions, at 6-31+G## and 4-31+G levels). The substituent interaction energies refer to the reactions:

$$\left\{\begin{array}{l} PH_2X + H_2 \\ PHX^- \\ PH_3X^+ \end{array}\right. \rightarrow \left\{\begin{array}{l} PH_3 + HX \\ PH_2^- \\ PH_4^+ \end{array}\right.$$

Table 1. Calculated total energies (Hartrees) of PHX^- series molecules (X = H, BH_2, CH_3, NH_2, OH, F), $PH_2 \cdot BH_2$ and $PH_3 \cdot BH_2^+$ and NHX^- series molecules[a]

Basis set:	4-31G(#)	6-31G# #	6-31+G# #
PH_2^- (C_{2v})	−341.42534	−341.84015	−341.85587
$PH \cdot BH_2^-$ (C_s)	−366.69918	−367.13593	−367.14520
$PH \cdot CH_3^-$ (C_s)	−380.40306	−380.86975	−380.88348
$PH \cdot NH_2^-$ (C_s)	−396.37884	−396.86099	−396.88334
$PH \cdot OH^-$	−416.19603	−416.69675	−416.73400
PHF^- (C_s)	−440.20138	−440.70483	−440.73463
$PH_2 \cdot BH_2$ (C_s)	−367.29286	−367.70779	
$PH_3 \cdot BH_2^+$ (C_s)	−367.61536	−368.03073	
Basis set:	4-31+G		
NH_2^-	−55.44246		
$NH \cdot BH_2^-$	−80.74276		
$NH \cdot CH_3^-$	−94.40423		
$NH \cdot NH_2^-$	−119.35527		
$NH \cdot OH^-$	−130.15972		
$NH \cdot F^-$	−154.16560		

[a] Energies at all levels calculated at the 4-31G(#) optimized geometries.

Energies of protonation and deprotonation, both relative to those of the unsubstituted hydride PH_3, are presented in Tables 2 and 3 which also include comparative material from published work on the corresponding first row compounds. The relative energies refer to the processes:

$$PH_2X + PH_4^+ \rightarrow PH_3X^+ + PH_3$$

$$PHX^- + PH_2^- \rightarrow PHX^- + PH_3.$$

Figure 2 contains calculated interaction energies and σ and π bond orders for three second row series compounds with data for the corresponding nitrogen compounds. Taking the z-axis as the P—X internuclear axis, σ bond orders are Mulliken overlap populations for s and p_z orbital overlap; π bond orders refer to total p_x and p_y orbital overlap.

DISCUSSION

The series of substituents considered in this research comprises the methyl group, capable of behaving as a donor or an acceptor, and the series of σ-acceptors NH_2, OH, F which, by virtue of interactions with lone pairs of electrons, may also function as π-donors. Calculations were also carried out for substitution by the strong π-acceptor BH_2.

A useful guide to the nature of the interactions expected for the five substituents is given by the substituent scales recently proposed by Topsom and co-workers.[8] σ_F(theor.) is a field effect parameter, and σ_R(theor.) an indication of the size of the resonance interaction of a substituent with a benzene ring. σ_X(theor.) is a measure of group electronegativity on a scale in which the value for H is zero, so that negative

Table 2. Calculated substituent interaction energies for PHX^-, PH_2X, PH_3X^+ series molecules (X = BH_2, CH_3, NH_2, OH, F) with comparative data for NHX^-, NH_2X and NH_3X^+ series (kJ mol^{-1})[a,b,c]

		X = BH_2	CH_3	NH_2	OH	F
PHX^-	6-31+G# #	74.8	−110.7	−94.5	−61.9	−0.5
	6-31G# #	91.7	−105.5	−111.9	−89.5	−37.5
	4-31G(#)	133.8	−93.7	−70.4	−30.4	39.7
PH_2X	6-31G# #	−15.7	−77.3	−67.0	−57.6	−26.4
	4-31G(#)	−16.6	−75.1	−36.4	−29.3	−4.3
PH_3X^+	6-31G# #	0.2	−12.9	3.7	−30.8	−43.8
	4-31G(#)	11.5	−4.0	35.7	6.0	−49.4
NHX^-	4-31+G	203.2	−135.5	−177.2	−170.7	−99.2
	4-31G	270.7	−92.6	−155.3	−144.8	−87.7
NH_2X	4-31G	128.6	−127.1	−210.7	−254.9	−290.4
NH_3X^+	4-31G	−18.4	−82.7	−216.7	−324.1	−418.3

[a] Substituent interaction energies refer to the reactions:

$$\left\{\begin{matrix} PH_2X + H_2 \rightarrow \\ PHX^- \\ PH_3X^+ \end{matrix}\right. \left\{\begin{matrix} PH_3 + HX \\ PH_2^- \\ PH_4^+ \end{matrix}\right.$$

[b] All results from calculations on 4-31G(#)-optimized structures (4-31G-optimized structures for NHX^- compounds).

[c] Results from NH_2X, NH_3X^+ and NHX^- 4-31G level calculations from refs. 1*a*,*b*.

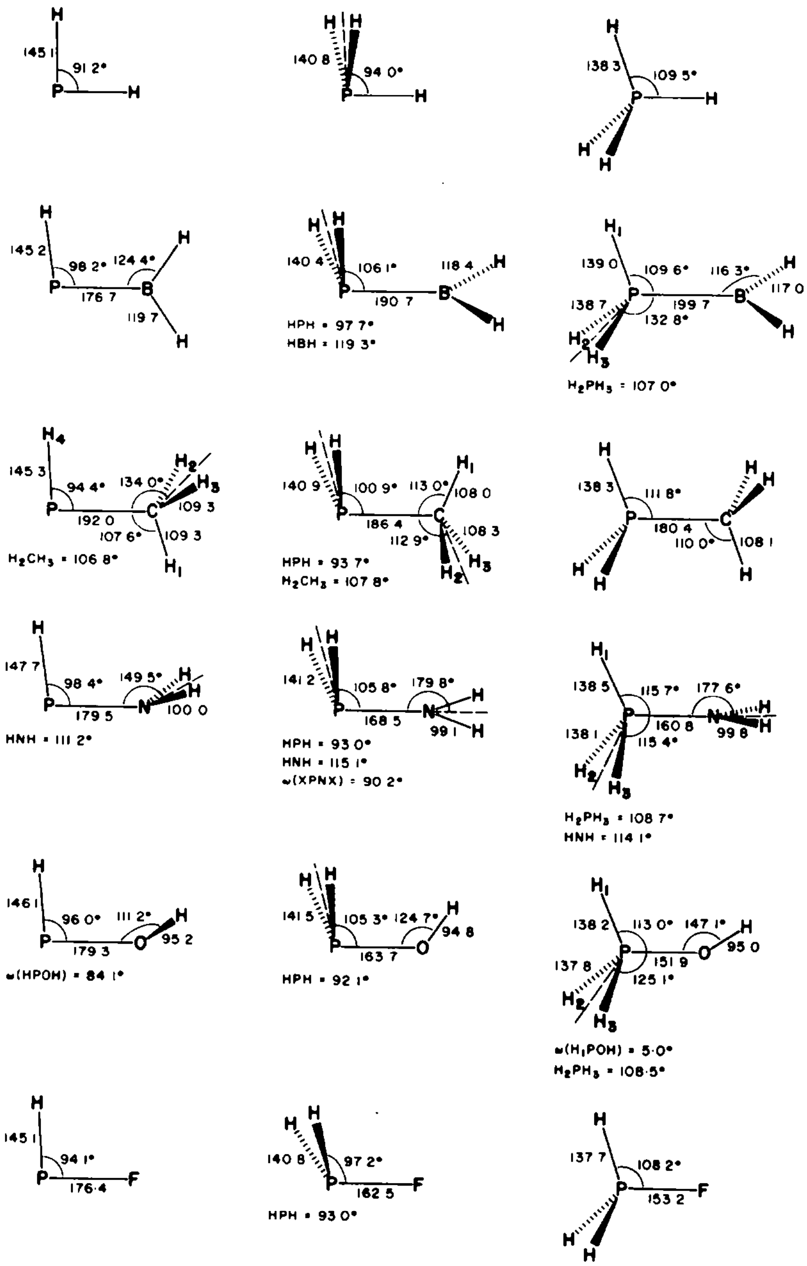

Fig. 1. Optimized geometries (4-31G(#) level) for PHX^-, PH_2X and PH_3X^+ series molecules (bond lengths in pm, bond angles in degrees).

Table 3. Relative protonation and deprotonation energies of PH_2X series molecules (X = BH_2, CH_3, NH_2, OH, F) with comparative data for NH_2X compounds[a]

		X = BH_2	CH_3	NH_2	OH	F
Relative protonation energies						
PH_2X	6-31G# #	15.9	64.4	70.7	26.8	−17.5
	4-31G(#)	28.1	71.2	72.1	35.2	−45.1
NH_2X	4-31G	−110.3	44.4	−6.0	−69.2	−127.9
Relative deprotonation energies						
PH_2X	6-31+G# #	91.4	−35.6	−58.0	−32.6	3.8
	6-31G# #	107.4	−28.2	−44.9	−31.9	−11.1
	4-31G(#)	150.4	−18.5	−34.0	−1.1	44.1
NH_2X	4-31+G	74.6	−8.4	33.5	84.2	191.2
	4-31G	142.1	34.5	55.4	110.1	202.7

[a] Details as for Table 2.

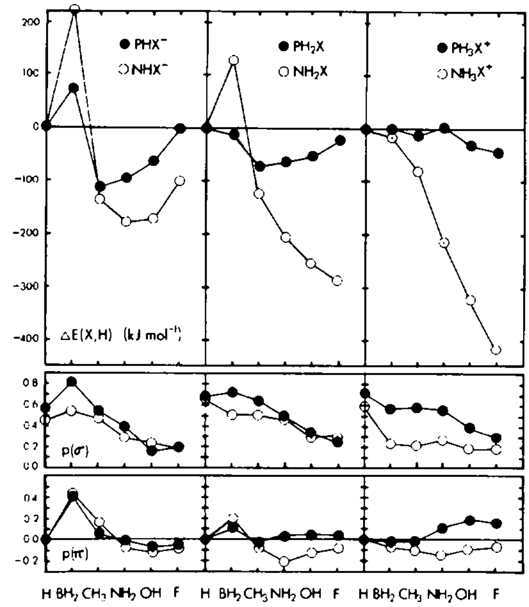

Fig. 2. Interaction energies (kJ mol^{-1}) and calculated σ and π bond orders for PH_2X and PH_3X^+ series molecules (6-31G##//4-31G(#) level calculations) and PHX^- series molecules (6-31+G##//4-31G(#) level). Parallel results are included for NHX^-, NH_2X and NH_3X^+ series (4-31G//4-31G level calculations); energy data from refs. 1*a*,*b*.

values for less electronegative groups should be expected.

Group X:	BH_2	CH_3	NH_2	OH	F
σ_X(theor.)	−0.09	0.17	0.33	0.43	0.52
σ_F(theor.)	0.06	−0.02	0.16	0.31	0.49
σ_R(theor.)	0.51	−0.03	−0.48	−0.44	−0.34

Comparison between first and second row systems is possible with the use of the values for the same parameters calculated by Topsom's procedures[8] for PH_2, PH^-, and PH_3^+:

Second row center:	PH_2	PH^-	PH_3^+
σ_X(theor.)	−0.05	−0.17	0.08
σ_F(theor.)	0.09	−2.12	2.18
σ_R(theor.)	−0.08	−0.80	0.09

These figures suggest that the PH_2 group will act as a weak σ-acceptor, with weak π-donor ability in conditions that favour it. The responses to substitution by the X = BH_2, H_3, NH_2, OH, F series should be very much less pronounced than those shown by NH_2.[1] By extension, donor–acceptor interactions between substituents and the PH^- and PH_3^+ groups are predicted to be weaker than in first row cases. However, Topsom's theoretical substituent scales take no account of the possible involvement of d functions, widely considered to play a small role in bonding to second row elements, even those of normal valency,[9] and it is of interest to observe the effect of their inclusion.

In situations where both σ- and π-type interactions can occur, it is necessary to determine which of the two is mainly responsible for the trends in the energy data or if both are contributing equally. Judicious use of electron population data may sometimes serve this purpose (see Fig. 2).

Conformations and geometries of the substituted compounds. In the few places wnere comparison is possible, the conformations and molecular dimensions obtained by geometry optimization at the 4-31G(#) level (Fig. 1) correspond closely to the experimentally determined values.[10] For X = CH_3, NH_2, OH, F the P—X bond distances are longer in the anionic series than in the corresponding neutral compounds (average lengthening 10 pm) and shorter in the cationic series (average shortening 7 pm) which are similar to the figures for the corresponding NHX^-, NH_2X and NH_3X^+ series. As in substitution of nitrogen compounds by the π-acceptor BH_2, the P—B distances increase from $PH \cdot BH_2^-$ to $PH_2 \cdot BH_2$ to $PH_3 \cdot BH_2^+$, and by about the same amount, 20–25 pm.[1a,7] The P—X bonds are generally quite shorter than the sum of the covalent radii, particularly for the OH and F substituted compounds, in which the shortening is in the 10 to 20 pm range.

At the supplemented 4-31G basis set level, XPH and HPH bond angles are some 10° lower than XNH and HNH bond angles, simply because of steric constraints around the larger second row core.

The 4-31G(#) optimized conformations of the substituted phosphorus compounds are similar to those of the first row analogues[1] but the amino group is usually in a conformation which leaves the PNH_2 fragment more closely planar than pyramidal. In the OH-substituted phosphorus compounds the POH bond angle is usually larger than it is in the corresponding first row compounds.

Substituent effects. The results obtained by Radom *et al.* for the sequence of changes induced in NHX^-, NH_2X and NH_3X^+ compounds by substitution with CH_3, NH_2, OH and F (Fig. 2) invite explanation in terms of σ-electron withdrawal from nitrogen; π-interaction with these substituents is too weak to mention.[1] Charge transfer away from nitrogen is expected to stabilize the anion and destabilize the cation, and this is observed, the neutral series being in an intermediate stabilizing position. However, π-interactions are much more important in the BH_2-substituted molecules as the results show dramatically in the comparison between the NH^- group (where π-bond formation is facilitated by the presence of a lone pair on the charged nitrogen species) and the NH_2 and NH_3^+ groups (where π-donation is much less likely).

The trends in the data for the P-containing species are most easily rationalized by ignoring π-electron interactions and classifying PH_2 as a mild σ-electron donor, PH_3^+ as a σ-acceptor and PH^- as a σ-donor. The exception is the strong π-interaction with BH_2 in the anionic PHX^- series, but there is also a case for including π-interactions in explaining the data for the PH_2X and PH_3X^+ series.

The greatest contrast between 1st and 2nd row results is found in the rising trend in the neutral PH_2X series molecules. On this data NH_2 is a σ-electron acceptor and PH_2 as σ-electron donor, which is not unreasonable in view of the positions of the groups in the electronegativity scale.

PH_3^+ may be classified as a σ-acceptor and a weak π-acceptor, the trend down the series NH_2, OH, and F being due to the fact that destabilizing σ-electron withdrawal prevails over the expected favourable effect of π-electron gain. π Bond orders (Fig. 2) are moderate but the favourable effect is insufficient to reverse the effect of σ-electron withdrawal by the σ-acceptor substituents. Calculated values of the pσ density on phosphorus show a big response to the σ-electron acceptors (a drop of 0.7 e over the $X = BH_2 \cdots F$ sequence) but the equivalent rise in pπ density is only 0.05 e.

The pπ–pπ interactions in PH_3X^+ compounds are necessarily hyperconjugative, a fact reflected in the weakening of the P—H bonds in the interaction with the π-acceptor BH_2, as attested both by bond orders and bond lengths. The pπ–pπ part of the π-interactions between phosphorus and the π-donors NH_2, OH, F is too small to produce an identifiable effect; in any case, electrostatic (field) effects are the likely cause of any bond length changes with these substituents.

Analysis of the bond order results lends support to the above assignments, π-bonding having relatively little impact on the effect of σ-electron withdrawal by the substituents in the neutral and anionic series. Comparison of $\Delta E(X, H)$ trends across the substituent sequences with the calculated P—X bond orders shows an overall correspondence between the two. It is clear from the results for the charged nitrogen species that non-bonded interactions are important as well as the nature of the M—X bond; this is not repeated in the 2nd row molecules. However, in the PH_3X^+ compounds, the effect of π-interactions is much more important, recalling the importance of π-bonding in the iso-structural, iso-electronic SiH_3X series.[4a] As in SiH_3X compounds, a large part of the π overlap density in the PH_3X^+ series molecules is provided by d functions.[9a] Electron population data show that the d-type polarization functions reduce the progressive inductive withdrawal of charge from phosphorus by 0.1–0.2 e.

Polarization functions for second row atoms in supplemented basis sets are quite diffuse (exponents are obtained by optimization) but the size of the exponent increases from 0.45 to 0.55 to 0.65 from silicon to sulfur and the 0.55 value for phosphorus is sufficient to allow moderate dπ–pπ overlap (2pπ–3dπ overlap integrals are 0.16, 0.21 and 0.25 for Si—N, P—N and S—N bonds). The levels of utilization in the series considered here, especially in the PH_3X^+ series, require them to be regarded as intermediate between polarization functions (functions added to improve flexibility in the wavefunction) and actual valence orbitals (high-lying, but accessible).

The dπ contributions to P—X bonding are always favourable. Without these interactions, non-bonded repulsions would oblige the π bond orders in the PH_2X and PHX^- series compounds to be negative, as they are in the NH_2X and NHX^- series. Comparison calculations, performed with and without d function supplementation, show bond shortening in all the substituted compounds, but it is greatest (*ca* 10 pm) in the case where the d function contribution to bonding is the highest (PH_3X^+).[9a]

The pattern of π-bonding interactions in the neutral and anionic series is as follows. Broadly, the pπ–pπ interactions are anti-bonding in PHX^- and slightly anti-bonding in the neutral PH_2X compounds. The d function contribution increases as the charge on phosphorus moves to positive values. The net effect of the pπ- and dπ-interactions is bond weakening in the anions and very slightly bond strengthening in the neutral phosphines. The main reason for the rather small role for π-bonding in the PH_2X and PHX^- series is conformational. Since the interactions between the lone pairs on PH_2 and X are necessarily destabilizing, conformations are adopted in which they are minimized. Thus, the lone pair directions are perpendicular in the minimum energy conformations (gauche) of $PH_2 \cdot NH_2$ and $PH_2 \cdot OH$. For these compounds there is a 35 kJ mol^{-1} energy advantage gained by rotation about the P—X bond from the eclipsed conformation.

The characterization of PH_3^+ as a weak σ-acceptor and a weak π-acceptor is consistent with ESR and electrochemical results for P and N ring compounds, explained in terms of P-ring hyperconjugation.[11] Also relevant to the calculated properties of the PH_2 and PH_3^+ groups are ^{13}C-NMR measurements on PR_2-substituted benzene made by Modro, who obtained values of the inductive and resonance parameters for PMe_2 of $\sigma_I = 0.06$ and $\sigma_R = -0.02$.[12] The values for the PH_2 group should be quite close to these. For phosphonium compounds, however, NMR measurements point to the existence of a strong resonance component.[13]

Tri-substituted compounds. Data for the tri-substituted PX_3 and PX_3H^+ compounds (methyl and fluorine substituents only) are given in Table 4; calculations were performed at the 4-31G(#) level.

The results on the fully substituted molecules provide information about the effect on phosphorus donor–acceptor properties of progressive addition of substituents, it being obvious that the $\Delta E(X, H)$ values for tri-substitution are far from three times the values for mono-substitution. This implies non-additivity, resulting from interaction between different P—CH_3 and P—F bonds.

The departure of $\Delta E(X, H)$ values from linearity in the degree of substitution is equal to the relative energy of the bond separation process:

$$2PH_3 + PX_3 \rightarrow 3PH_2X$$

$$2PH_4^+ + PX_3H^+ \rightarrow 3PH_3X^+$$

For X = F, these are large and positive, which is interpreted to mean that P—F interaction becomes progressively more stabilizing as fluorine atoms are added, in contrast to the opposite effect of added methyl groups. For the bond separation processes above, the substituent interaction energies are:

($\Delta E(X, H)$; kJ mol^{-1})	$X = CH_3$	X = F
PH_2X	−28.0	153.1
PH_3X^+	−51.2	103.3

These responses are to be expected if PH_2 is a mild σ-

Table 4. Calculated substituent interaction energies of PX_3, PX_3H^+ series molecules ($X = CH_3$, F)[a,b]

$P(CH_3)_3$	−253.6
PF_3	148.5
$P(CH_3)_3H^+$	−63.2
PF_3H^+	−45.2

[a] Interaction energies refer to the processes:

$$PX_3 + 3H_2 \rightarrow PH_3 + 3HX$$

$$PX_3H^+ + 3H_2 \rightarrow PH_4^+ + 3HX.$$

[b] 4-31G(#)//4-31G(#) level calculations.

donor interacting with a σ-electron donor (X = CH_3) and a σ-electron acceptor (X = F).

In the PX_3H^+ compounds the effects of donation by CH_3 and withdrawal by F are partly quenched by the weak σ-acceptor character of the second row group. The results suggest that σ-withdrawal and π-donation are in competition, also attested by the very large d function occupation in PF_3H^+ (q(3d) = 0.58) chiefly in dπ orbitals.

Protonation and deprotonation. Although the relative energy results listed in Table 3 were obtained to allow study of substituent effect trends, comparison with experiment is possible for the methyl compounds (Taft's compilation[16]). The protonation ΔH values, relative to the protonation of PH_3, are 64.4 kJ mol^{-1} (PH_2CH_3) and 161.5 kJ mol^{-1} ($P(CH_3)_3$).[16] The calculated values are 64.4 kJ mol^{-1} and 190.4 kJ mol^{-1}, respectively.

These processes conform to the "isodesmic" criterion[15] and interaction energies are therefore expected to be less sensitive to basis set variation than those mentioned above. The relative protonation energy values for the substituted phosphines PH_2X (the difference between ΔE(X, H) for the PH_3X^+ and PH_2X species) are seen to drop very rapidly across the series, the destabilization of PH_3X^+ being reinforced by the stabilization of PH_2X. Although the nitrogen interaction energies change much more rapidly in response to NH_2, OH and F substitution, the effects on NH_2X and NH_3X^+ are opposed and the trend across the series is close to that for PH_2X basicity.

The reverse situation is found for PH_2X and NH_2X deprotonation energies, the extreme sensitivity of the NH_2X proton abstraction process to substitution being the result of progressive destabilization of the neutral acid added to stabilization of the anion through the series. The two effects are opposed in the phosphorus series and the overall response to substitution is small.

CONCLUSIONS

Relative energy calculations show that σ-interactions usually dominate substituent effects in directly bonded phosphines (PH_2X) and in the related anionic (PHX^-) and cationic (PH_3X^+). Compared with the corresponding nitrogen species, responses of the second row compounds to σ-donor/σ-acceptor interactions are smaller, as are also π-interactions. Except for X = BH_2, where π-donation dominates the differences between PHX^-, PH_2X, and PH_3X^+, the 2nd row series show only a shadow of the progressively stronger destabilization produced by σ-withdrawal from NH^-, NH_2, and NH_3^+.

The groups may be characterized as follows:

(a) PH_2 is a weak σ-donor.
(b) PH^- is a σ-donor and a π-donor.
(c) PH_3^+ is a weak σ-acceptor and a weak π-acceptor, the latter function being due to a marginal bonding role for d functions.

REFERENCES

[1a] NH_2X, OHX, FX, OX^-, NHX^- : A. L. Hinde, A. Pross and L. Radom, *J. Computational Chem.* **1**, 118 (1980); [b]NH_3X^+, CH_3X, BH_3X^- : A. Pross and L. Radom, *Tetrahedron* **36**, 673 (1980); [c]CH_2X^- : A. Pross, D. J. DeFrees, B. A. Levi, S. K. Pollack, L. Radom and W. J. Hehre, *J. Org. Chem.* **46**, 1693 (1981).

[2] J. E. Del Bene, M. J. Frisch, K. Raghavachari and J. A. Pople, *J. Phys. Chem.* **86**, 1529 (1982); A. Scheiner, *Chem. Phys. Lett.* **93**, 540 (1982); R. A. Eades, D. A. Weil, D. A. Dixon and C. H. Douglass, Jr., *J. Phys. Chem.* **85**, 981 (1981).

[3] C. Glidewell and C. Thomson, *J. Computational Chem.* **3**, 495 (1982); D. S. Marynick, K. Scanlon, R. A. Eades and D. A. Dixon, *J. Phys. Chem.* **85**, 3364 (1981).

[4a] Substituted silicon compounds SiH_3X, SiH_2X^-, *Tetrahedron* (1985), in press; [b]substituted sulfur compounds SHX, SX^-, SH_2X^+, *Tetrahedron* (1985), in press.

[5] J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn and J. A. Pople, *Quantum Chemistry Program Exchange* **12**, 406 (1980).

[6a] E. A. Magnusson, *J. Computational Chem.* **5**, 612 (1984); [b]The basis sets designated 4-31G(#) and 6-31G## in this work contain five d-functions rather than the six recommended by M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.* **104**, 2797 (1982). The use of five d functions facilitates comparison of results obtained with and without supplementation. The results differ in energy but not in any other significant way.

[7] G. W. Spitznagel, T. Clark, J. Chandrasekhar and P. v. R. Schleyer, *J. Computational Chem.* **3**, 363 (1982); J. Chandrasekhar, J. G. Andrade and P. v. R. Schleyer, *J. Am. Chem. Soc.* **103**, 5609 (1981).

[8] R. D. Topsom, *Accts. Chem. Res.* **16**, 292 (1983), and references therein; *J. Am. Chem. Soc.* **106**, 7 (1984).

[9a] E. A. Magnusson, *Accts. Chem. Res.* (1985), in press; [b]D. A. Dixon, T. H. Dunning, Jr., R. A. Eades and P. G. Gassman, *J. Am. Chem. Soc.* **105**, 7011 (1983).

[10] W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.* **104**, 5039 (1982).

[11] W. Kaim, U. Lechner-Knoblauch, P. Hanel and H. Bock, *J. Org. Chem.* **48**, 4206 (1983); C. K. White and R. D. Rieke, *Ibid.* **43**, 4638 (1978).

[12] T. A. Modro, *Can. J. Chem.* **55**, 3681 (1977).

[13] G. P. Schiemenz, *Angew. Chem. Int. Ed. Engl.* **7**, 545 (1968).

[14] As reported elsewhere,[6a,9a] the addition of d functions to minimal basis sets exaggerates their importance to the energies and the wave functions of second row molecules. However, both the energy increment and the level of utilization of d functions are stable for supplemented 3-21G, 4-31G and 6-31G basis sets, suggesting that the "superposition effect" is small in basis sets of split-valence quality or better.

[15] W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, *J. Am. Chem. Soc.* **92**, 4796 (1970).

[16] R. W. Taft, personal communication. Similar values from a variety of sources are cited by A. Ikuta, P. Kebarle, G. M. Bancroft, T. Chan and R. J. Puddephatt, *J. Am. Chem. Soc.* **104**, 5899 (1982).