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Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

Perturbation Approach to Spin-Coupling Constants in the Phosphorus(III) Compounds

EVGENY SHUSTOROVICH*

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The perturbation extension of the Pople–Santry theory developed earlier for treating the Fermi contact terms in reduced spin-coupling constants ${}^1K$(E–L) in substituted compounds $EL_{m-k}L'_k$ has been applied to main group "quasi lone pair" molecules, particularly to trigonal-pyramidal $P^{III}L_{3-k}L'_k$ ones. The three most important cases have been considered in detail, namely, for L = H, P^{III}, and F. The results obtained agree with experiment and explain the puzzling peculiarities of the observable ${}^1K(P^{III}\text{–}L)$ trends. The developed model permits both similarities and differences in the ${}^1K$(A–L) regularities for the A(HOS) vs. A(NHOS) compounds (highest vs. not highest oxidation states, respectively) to be explained and predicted.

Introduction

Recently[1,2] we have developed the perturbation extension of the Pople–Santry (P–S) theory[3] for treating the Fermi contact (FC) terms in reduced nuclear spin coupling constants ${}^1K$(E–L) in substituted compounds $EL_{m-k}L'_k$ where E is a transition-metal M or main-group element A. We have found that for "one-pronged" ligands L with valence *n*s orbitals[2] such as H or CR_3 changes in ${}^1K$(E–L) under substitution should typically follow changes in the s contribution to the E–L bond overlap population.[1] On the other hand, for "two-pronged" ligands L, such as F, with a low lying lone ns^2 pair,[2] changes in ${}^1K$(E–F) in $EF_{m-k}L'_k$ are of rather complicated character depending on E, L′, and even *k*.[2]

The P–S theory for the FC term in ${}^1K$(E–L) was originally developed in explicit form for the AL_4 T_d case.[3] One can show[2] that the simple and elegant P–S expression for the FC term holds for any compound EL_m where, first, *all* ligands L are geometrically equivalent and, second, only *one* central atom orbital, s_E, belongs to the totally symmetric irreducible representation A_1. The linear AL_2,[1] planar-trigonal AL_3,[1,2] tetrahedral AL_4,[1,2] square EL_4,[1] and octahedral EL_6[1,2] compounds are just such cases. It is another story, however, for octet angular AL_2 and trigonal-pyramidal AL_3 compounds where only the first condition is valid but not the second as *two* central atom orbitals, s_A and p_z, belong to the A_1 representation (see Table I). We can anticipate some peculiarities in the FC mechanism and therefore in trends of ${}^1K$(A–L) as compared, for instance, with those in linear AL_2 and trigonal-planar AL_3 compounds where A is of the highest oxidation state, A(HOS). We have recently developed a perturbation approach for treating the electronic structures and the substituent effects on the A–L bond lengths (strengths) in octet AL_2 and AL_3 molecules where A is not of the highest oxidation state, A(NHOS), and has quasi lone pairs (QLP).[4] In the present paper we will apply our perturbation approach to the substituent effects on spin-coupling constants ${}^1K$(A–L) in the mentioned QLP compounds.

Results and Discussion

The general LCAO MO form of the FC term is[3]

$$ {}^1K(\text{A–L}) = C\cdot\sum_i^{\text{occ}}\sum_j^{\text{unocc}}(\epsilon_i-\epsilon_j)^{-1}c_{iA}c_{iL}c_{jA}c_{jL} \qquad (1)$$

where *C* is some positive constant and the LCAO MO coefficients c_{iA}, c_{jL}, etc. correspond to the s parts of the occupied ψ_i and unoccupied ψ_j MO's with the energy gaps $E_{ij} = \epsilon_j - \epsilon_i > 0$. The valence A_1 MO's contributing to ${}^1K$(A–L) in octet AL_2 and AL_3 molecules (see Table I) have the following nodal structures[4]

$$\psi_3(3a_1) = s + p_z - \sigma^{(+)} \qquad (2)$$

$$\psi_2(2a_1) = -s + p_z + \sigma^{(+)} \qquad (3)$$

$$\psi_1(1a_1) = s + p_z + \sigma^{(+)} \qquad (4)$$

where the nodeless ψ_1 and one-node ψ_2 are occupied but the two-node ψ_3 is vacant. It is of great importance that in *all* octet AL_2 and AL_3 molecules the $\psi_2(2a_1)$ has the same nodal structure (3) corresponding to the p bonding but s antibonding.[4] The immediate consequence from eq 3 and 4 is a well-known fact that the A(NHOS)–L bonds are usually of less s character than the A(HOS)–L bonds[4] (cf. eq 10 and 11). The same nodal structures (2)–(4) remain in our approximate

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* Address all correspondence to the author at: Chemistry Division, Research Laboratories, Eastman Kodak Co., Rochester, N.Y. 14650.

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Table I. Assignment of Orbitals in Octet AL_2 and AL_3 Compounds

compd	symmetry	irreducible representation	orbitals[a,b] A	L	
AL_2	C_{2v}	A_1	s	$\sigma^{(+)} = (1/2^{1/2})(\sigma_1 + \sigma_2)$	$[s_F]_{A_1} = (1/2^{1/2})(s_1 + s_2)$
			p_z		
		B_1	p_x		
		B_2	p_y	$\sigma^{(-)} = (1/2^{1/2})(\sigma_1 - \sigma_2)$	$[s_F]_{B_2} = (1/2^{1/2})(s_1 - s_2)$
AL_3	C_{3v}	A_1	s	$\sigma^{(+)} = (1/3^{1/2})(\sigma_1 + \sigma_2 + \sigma_3)$	$[s_F]_{A_1} = (1/3^{1/2})(s_1 + s_2 + s_3)$
			p_z		
		E[c]	p_y	$\sigma^{(-)} = (1/6^{1/2})(2\sigma_1 - \sigma_2 - \sigma_3)$	$[s_F]_E = (1/6^{1/2})(2s_1 - s_2 - s_3)$

[a] Enumeration of ligands and directions of the coordinate axes are obvious (for clarity see, for instance, Figure 1 in ref 4). [b] One-pronged ligands (H, CR_3, etc.) have only the $\sigma^{(\pm)}$ group orbitals; two-pronged ligands F have also the $[s_F]$ ones (see the text). [c] The second E component, p_x and $(1/2^{1/2})(\sigma_2 - \sigma_3)$, $(1/2^{1/2})(s_2 - s_3)$, is not needed for the ensuing consideration.

Table II. Typical Values of ${}^1J(P^{III}-H)$, Hz[a]

L′	H	CH_3	CF_3	C_6H_5	F
PH_2L'	182–189	186.4	180–181	195–201	
PHL_2'	182–189	191.6	217–218	214–218 (239)	182

[a] All data were taken from ref 5a.

diagonalization scheme for octet AL_m where (2)–(4) are replaced by (5)–(7), $\psi_1(1a_1)$ being bonding, $\psi_{\bar{1}}(2a_1)$ nonbonding, $\psi_3(3a_1)$ antibonding, namely

$$\psi_3(3a_1) = b(\mu s + \nu p_z) - a\sigma^{(+)} \tag{5}$$

$$\psi_{\bar{1}}(2a_1) = \nu s - \mu p_z \tag{6}$$

$$\psi_1(1a_1) = a(\mu s + \nu p_z) + b\sigma^{(+)} \tag{7}$$

where μ, ν, a, and b are some variable coefficients.[4] Remember that the form (5)–(7) is the closest analogue of the A_1 MO's of the A(HOS)L_m compounds where only s_A belongs to the A_1 representation, so that there are only two A_1 MO's, occupied bonding $\psi_1(1a_1)$ (eq 9) and unoccupied antibonding $\psi_2(2a_1)$ (eq 8) with the nodal structures (11) and (10), respectively.

$$\psi_2(2a_1) = b's - a'\sigma^{(+)} \tag{8}$$

$$\psi_1(1a_1) = a's + b'\sigma^{(+)} \tag{9}$$

$$\psi_2(2a_1) = s - \sigma^{(+)} \tag{10}$$

$$\psi_1(1a_1) = s + \sigma^{(+)} \tag{11}$$

Because absolute values of the LCAO MO coefficients in (2)–(4) or (5)–(7) as well as the substituent effects strongly depend on the relative electronegativities of A and L,[4] it makes sense to consider some typical cases rather than to look for some universal solution. As ${}^{31}P$ is the most intensively studied[5] of the central atoms A in question, we will consider the regularities of ${}^1K$(A–L) in $AL_{m-k}L'_k$ for A = P^{III}, $m = 3$, for three most important cases, namely, L = H, P^{III}, and F.

The $PH_{3-k}L'_k$ Case. Let us begin with PH_3 where L = H has a pure s valence orbital. From (1) and (5)–(7) we have

$${}^1K(P^{III}-H)_{PH_3} = |\mathrm{const}|\cdot\frac{a^2b^2\mu^2}{3E_{13}} \tag{12}$$

which is always positive and smaller than ${}^1K$(P–H) for any P(HOS)H_m compound where from (1) and (8) and (9)

$${}^1K(P-H)_{PH_m} = |\mathrm{const}|\cdot\frac{a'^2b'^2}{mE'_{13}} \tag{13}$$

Indeed, $ab < a'b'$, $E'_{13} \simeq E_{13}$,[6] and $\mu < 1$ and $m > 3$. The same conclusion can also be easily obtained from eq 1 and 2–4 because the contributions from ψ_1 (eq 4) and ψ_2 (eq 3) will be of opposite sign, the former being positive and bigger in absolute value as in PH_3 $\psi_1(1a_1)$ is mainly of the s character.[4]

From our previous analysis[1] we know that a better acceptor L′ can only increase the values of ${}^1K$(P–H) (eq 13) because such L′ will increase the s character of the A–L bonds in A(HOS)$L_{m-k}L'_k$ compounds.[7,8] In fact, the magnitude of ${}^1J$(P–H) in PH_3, ca. 185 Hz, is smaller than any ${}^1J$(P–H) in all the known compounds of P^{IV}, P^{V}, and P^{VI}, ca. 450–1075 Hz,[5a,9] where the s character of the P–H bonds is obviously larger.[5a,4,7,8]

As far as ${}^1K$(P–H) in $PH_{3-k}L'_k$ are concerned, the substituent effects on the s character of the A–L bonds in A(NHOS)$L_{m-k}L'_k$[4] should be, as a rule, rather similar to those in A(HOS)$L_{m-k}L'_k$.[1,7,8] Thus, for better acceptors L′ the values of ${}^1J(P^{III}-H)$ should be larger or, at least, not smaller than that in PH_3 and increase monotonically as k increases. Again, the known experimental data[5a] agree with this conclusion. Some examples are given in Table II. Not surprisingly, the lack of a strictly defined relationship between the s character of the A–L bonds and the values of ${}^1K$(A–L)[1,7,8] produces an

Table III. Assignment of Orbitals in Some 14e A_2L_{2m} Compounds

compd	symmetry	irreducible representation	orbitals A	L[c]
P_2L_4[a]	C_{2v}	A_1	$(1/2^{1/2})(s_1 + s_2)$, $(1/2^{1/2})(p_{z_1} + p_{z_2})$	$(1/2)(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
			$(1/2^{1/2})(p_{x_1} - p_{x_2})$, $(1/2^{1/2})(p_{y_1} - p_{y_2})$	
		A_2		$(1/2)(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
		B_1	$(1/2^{1/2})(s_1 - s_2)$, $(1/2^{1/2})(p_{z_1} - p_{z_2})$	$(1/2)(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$
			$(1/2^{1/2})(p_{x_1} + p_{x_2})$	
		B_2	$(1/2^{1/2})(p_{y_1} + p_{y_2})$	$(1/2)(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)$
C_2L_6[b]	D_{3h}	A'_1	$(1/2^{1/2})(s_1 + s_2)$, $(1/2^{1/2})(p_{z_1} - p_{z_2})$	$(1/6^{1/2})(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$
		A''_2	$(1/2^{1/2})(s_1 - s_2)$, $(1/2^{1/2})(p_{z_1} + p_{z_2})$	$(1/6^{1/2})(\sigma_1 + \sigma_2 + \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$
		E'	$(1/2^{1/2})(p_{x_1} + p_{x_2})$	$(1/2(3^{1/2}))(2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6)$
			$(1/2^{1/2})(p_{y_1} + p_{y_2})$	$(1/2)(\sigma_2 - \sigma_3 + \sigma_5 - \sigma_6)$
		E''	$(1/2^{1/2})(p_{x_1} - p_{x_2})$	$(1/2(3^{1/2}))(2\sigma_1 - \sigma_2 - \sigma_3 - 2\sigma_4 + \sigma_5 + \sigma_6)$
			$(1/2^{1/2})(p_{y_1} - p_{y_2})$	$(1/2)(\sigma_2 - \sigma_3 - \sigma_5 + \sigma_6)$

[a] The z axis is two fold; the x axis coincides with the $P_{(1)}$-$P_{(2)}$ line. [b] The z axis is threefold and coincides with the $C_{(1)}$-$C_{(2)}$ line. [c] Enumeration of ligands begins with those bonded to the $A_{(1)}$ atom. See also footnotes a and b.

unusual series of donor abilities of L′; for instance, F has weaker influence than CF_3 or C_6H_5 (see Table II). Similar things, however, also take place for the $A(HOS)H_{m-k}L'_k$ compounds.[1]

The $^1K(P^{III}–P^{III})$ Case. One of the most intriguing problems of NMR theory is the negative values of $^1K(P^{III}–P^{III})$[5a] as well as of some $^1K(P^{III}–C^{IV})$[5a,11] and $^1K(Se^{II}–C^{IV})$,[11] though *all* $^1K(A–A')$ where A and A′ do not have QLP's (are of the highest oxidation states) are positive.[5,10–12] This reversal of the sign of $^1K(A–A')$ has been explained[11] by the contribution of "the indirect FC term". We will show that in our model this reversal can be naturally explained by the different FC mechanism for $^1K(A–A')$ depending on the presence, or lack, of lone or quasi lone pairs on atoms A and A′.

Let us compare $^1K(A–A)$ for two isoelectronic 14e molecules, P_2L_4 and C_2L_6, the former A being P^{III} (NHOS) and the latter C^{IV} (HOS). It is easy to show[13] that in the framework of our orthogonalization procedure for producing QLP's (see the relationships 17′–19′ in ref 4) the results for $^1K(A_{(1)}–A_{(2)})$ do not depend on the conformation of A_2L_{2m} so that we arbitrarily choose C_{2v} for P_2L_4 and D_{3h} for C_2L_6 (their eclipsed forms). The combinations $s_1 + s_2$ and $s_1 - s_2$, the only ones contributing to $^1K(A_{(1)}–A_{(2)})$, enter the A_1 and B_1 representations in P_2L_4 C_{2v} and A'_1 and A''_2 in C_2L_6 D_{3h} as seen from Table III. For A'_1 and A''_2 in C_2L_6 we have three-orbital bondings (the 3 × 3 determinants) among the relevant s, p_z, and σ_L orbitals which are quite similar to those in the octet AL_2 and AL_3 molecules considered elsewhere.[4] Though for A_1 and B_1 in P_2L_4 there are some extra p_x and p_y orbitals (see Table III), they are orthogonal to the s, p_z, and σ_L combinations. Thus, in both C_2L_6 and P_2L_4 we have the relevant 3 × 3 determinants which can be reduced to the 2 × 2 + 1 × 1 forms by our orthogonalization scheme.[4] For example, for the A_1 representation of P_2L_4 we have

$$\phi_1 = \mu(2^{-1/2})(s_1 + s_2) + \nu(2^{-1/2})(p_{z_1} + p_{z_2}) \tag{14}$$

$$\phi_2 = \nu(2^{-1/2})(s_1 + s_2) - \mu(2^{-1/2})(p_{z_1} + p_{z_2}) \tag{15}$$

$$\langle \phi_1 | \sigma^{(+)} \rangle = \langle \phi_1 | (1/2)(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \rangle = 0 \tag{16}$$

Preserving only the s parts of the MO's contributing to $^1K(P_{(1)}–P_{(2)})$, we obtain

$$\psi_3 = b\phi_2 - a\sigma^{(+)} = b\nu(2^{-1/2})(s_1 + s_2) + \ldots \tag{17}$$

$$\psi_2 = \phi_1 = \mu(2^{-1/2})(s_1 + s_2) + \ldots \tag{18}$$

$$\psi_1 = a\phi_2 + b\sigma^{(+)} = a\nu(2^{-1/2})(s_1 + s_2) \ldots \tag{19}$$

where ψ_1 (eq 19) and ψ_2 (eq 18) are occupied but ψ_3 (eq 17) is vacant, so that the A_1 contribution (eq 20) to $^1K(P^{III}–P^{III})$ will be strongly negative. Similarly, for the B_1 representation,

$$^1K(P–P)_{A_1} = -\frac{a^2b^2\nu^4}{E_{13}} - \frac{b^2\mu^2\nu^2}{E_{23}} << 0 \tag{20}$$

replacing $s_1 + s_2$ and $p_{z_1} + p_{z_2}$ in eq 14–19 with $s_1 - s_2$ and $p_{z_1} - p_{z_2}$, we have practically the same *negative* contribution of the eq 20 form. Though the cross terms of the A_1 and B_1 MO's will give *positive* contributions to $^1K(P–P)$, one can show[13] that their absolute value will be smaller so that $^1K(P^{III}–P^{III})$ in P_2L_4 will be *always negative* regardless of the nature of L and conformation of P_2L_4, in complete agreement with experiment.[5,14]

It is another story for C_2L_6. Here we again have the contributing MO's of the eq 17–19 type within the A'_1 and A''_2 representations including $s_1 + s_2$ and $s_1 - s_2$, respectively. As C_2L_6 has the doubly degenerate E′ and E″ representations (see Table III), the contributing A'_1 and A''_2 MO's have different occupations unlike P_2L_4 where the contributing A_1 and B_1 MO's are occupied in the same manner corresponding to the 3σ–4e bonding. As seen from Table III, the electronic configuration of C_2L_6 will be $(1a_1')^2(1a_2'')^2(1e')^4(1e'')^4(2a_1')^2|(2a_2'')^0$ ... so that the biggest contribution to $^1K(C^{IV}–C^{IV})$ is obtained from the $2a_1' \rightarrow 2a_2''$ ($s_1 + s_2 \rightarrow s_1 - s_2$) transition which, according to eq 1, will be *positive.* Thus, the values of $^1K(C^{IV}–C^{IV})$ should be positive practically for all the C^{IV} compounds, and only in some exceptionally strained molecules with very small s character in the C–C bond (these bonds should be very long) can one anticipate finding $^1K(C–C) < 0$, as indeed occurs.[10,12]

Clearly, the values of $^1K(P^{III}–C^{IV})$ should be intermediate and therefore may be of any sign, in agreement with experiment.[5a,11] The behavior of Se^{II} is obviously similar to that of P^{III}.[11] Finally, P^{IV}, P^{V}, and P^{VI} should behave similarly to C^{IV} and other A(HOS) atoms rather than P^{III}, which also agrees with experiment.[5a,10]

The $PF_{3-k}L'_k$ Case. Let us begin with PF_3. Remember that the general P–S expression (eq 1) can be reduced to an elegant expression (eq 21) where $K_{13} > 0$, $K_{23} < 0$, $|K_{13}| < |K_{23}|$[2,3] only

$$^1K(A–F) = K_{13} + K_{23} = \frac{b^2x_s^2}{E_{13}} - \frac{a^2b^2x_s^2}{E_{23}} < 0 \tag{21}$$

for unsubstituted AF_m where, first, all fluorines are geometrically equivalent and, second, there is only one central orbital, s_A, within the A_1 representation. For PF_3 the first condition is fulfilled but not the second as the A_1 representation includes also the p_z orbital (see Table I). In the framework of the P–S theory[2,3] the s parts of the MO's contributing to $^1K(A–F)$ in AF_m, angular AF_2, and trigonal-pyramidal AF_3, will be (see Table I and eq 5–7)

$$\psi_3' = b\mu[s_A] - m^{1/2}b(\mu x_s + \nu x_p)[s_F]_{A_1} \tag{22}$$

$$\psi_2' = \nu[s_A] - m^{1/2}(\nu x_s - \mu x_p)[s_F]_{A_1} \tag{23}$$

$$\psi_2' = a\mu[s_A] - m^{1/2}a(\mu x_s + \nu x_p)[s_F]_{A_1} \tag{24}$$

$$\psi_1' = [s_F]_{A_1} + m^{1/2}(x_s + x_p)[s_A] \tag{25}$$

where the parameter $x_p > 0$[2] is similar to the P–S parameter $x_s > 0$,[3] $x_p << x_s$.[2] It is obvious that the usual P–S MO's for AF_m,[2,3] are obtained from eq 22–25 under condition 26 leading

$$x_p = 0, \quad \mu = 1, \quad \nu = 0 \tag{26}$$

to eq 21. Besides a new parameter x_p, the presence of the p_z orbital results in another important modification of eq 21; namely, we have *two negative* terms of the K_{23} type corresponding to two contributing MO's, ψ_2' (eq 23) and ψ_2' (eq 24). It should be stressed that this result is quite general and does not depend on our orthogonalization scheme (eq 5–7) because it is determined by the universal nodal structures (eq 2–4).[15] All the necessary details for constructing the MO's of the eq 22–25 type can be found in ref 2.

Thus, neglecting $x_p << x_s$[2,13] we obtain from eq 1 and 22–25

$$^1K(P–F)_{PF_3} = \frac{b^2x_s^2\mu}{E_{13}} - \frac{a^2b^2x_s^2\mu^2}{E_{23}} - \frac{b^2x_s^2\mu\nu}{E_{23}} \tag{27}$$

where because of

$$E_{23} < E_{23}, \quad a^2 < 1, \quad \nu < \mu < 1^4 \tag{28}$$

we decrease both K_{13} and K_{23} (increase the absolute value of K_{23}) in eq 21 so that

$$^1K(P–F)_{PF_3} << {}^1K(P–F)_{PF_m}, \quad m > 3 \tag{29}$$

In other words, $^1K(P–F)$ in PF_3 should be more negative, i.e., bigger in absolute value, than that in any compounds of P^{IV}, P^{V}, or P^{VI}, in complete agreement with experiment (the value of $^1J(P–F)$ in PF_3 is −1420 Hz compared to a range from

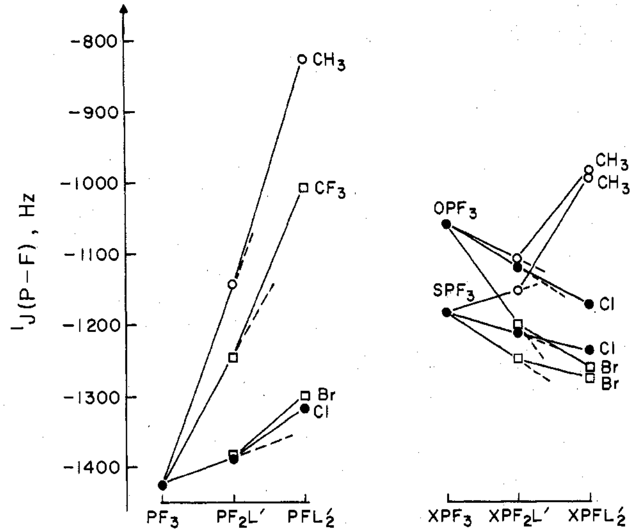

Figure 1. Experimental values of ^1J(P–F) in some $PF_{3-k}L'_k$ and $XPF_{3-k}L'_k$ compounds.[5] Straight lines were drawn through the PF_3(XPF_3) and PF_2L'(XPF_2L') points to show the positive deviation from linearity.

–1200 up to –700 Hz for P^{IV}, P^V, and P^{VI} [5]). It should be stressed that this trend of $|^1K(\text{P–F})|$ is just *opposite* to that of $|^1K(\text{P–H})|$ as we have seen above.

Substitution effects on ^1K(P–F) in the $PF_{3-k}L'_k$ series have been treated along the same lines as earlier[2] for the A(HOS) compounds. One can show[13] that for PF_2L' the dominant corrections are the linear ones to K_{23} in eq 21 which are of the general form (30) where the expression in brackets is some

$$\Delta K_{23} = [a^2 - b^2, E_{23}, \bar{E}_{23}]\delta\alpha_p' > 0 \qquad (30)$$

function of the parameters shown and $\delta\alpha_p'$ (eq 31) is the usual

$$\delta\alpha_p' = \langle\sigma_{L'}|H|\sigma_{L'}\rangle - \langle\sigma_L|H|\sigma_L\rangle \qquad (31)$$

perturbation parameter.[7,8] The big positive value of ΔK_{23} (eq 30) is determined by two factors: (i) $a^2 - b^2 > 0$ and (ii) $\bar{E}_{23} < E_{23}$. The positive difference $a^2 - b^2 > 0$ is similar to that for some A(HOS) compounds, namely, $CF_{4-k}L'_k$, $XPF_{3-k}L'_k$, and SeF_5L' considered earlier.[2] The second factor is specific to the A(NHOS) compounds where s_A contributes to *two* occupied valence orbitals (cf. eq 2–4 and 5–7 with eq 8–11). Furthermore, one can show[13] that the overwhelming positive corrections to K_{23} level the difference between one- and two-pronged substituents L′ (remember that one-pronged L′, to first-order perturbation theory, influence mainly K_{13} making ΔK_{13} positive[2]). As ΔK_{23} (eq 30) is proportional to $\delta\alpha_p'$ (eq 31), we can predict that in PF_2L', changes in ^1K(P–F) should be *positive* and bigger in absolute value the better donor is L′. Finally, we can anticipate for $PF_{3-k}L'_k$, similar to the A(HOS)$F_{m-k}L'_k$ cases,[2] *positive* deviations of changes in ^1K(P–F) from additivity (linearity) as k increases. Indeed, all these model conclusions agree with experiment[5] (Figure 1).

Let us summarize some principal differences in the ^1K(P–F) trends for $P^{III}F_{3-k}L'_k$ vs. $XP^VF_{3-k}L'_k$ (X = O, S), which follow from our model: (1) the magnitude of $|^1K(\text{P–F})|$ must be bigger for PF_3; (2) in the $PF_{3-k}L'_k$ series all the corrections should be positive unlike the case of the $XPF_{3-k}L'_k$ series where the corrections may be of both signs depending on L′;[2] (3) the one-pronged substituents L′ such as H or CH_3 should have influence in the $PF_{3-k}L'_k$ series similar to that of the two-pronged ones such as Cl, Br, OR, etc., i.e., in accordance with their usual donor abilities; in the $XPF_{3-k}L'_k$ series the influences of the one- and two-pronged L″s are rather different.[2] All the above is clearly seen in Figure 1.

Conclusion

The previous[4] and present works represent, to our knowledge, the first attempt to develop an analytical perturbation LCAO MO approach for treating various properties of main group angular and trigonal-pyramidal compounds. This approach proved to be rather effective for consideration of many peculiarities of these QLP compounds. It is a straightforward matter to extend our analysis to other QLP polyhedra such as ClF_3 C_{2v}, SF_4 C_{2v}, IF_5 C_{4v}, etc.[16] In general, the developed perturbation model[1,2,4,7,8] permits both similarities and differences between the A(HOS) and A(NHOS) compounds to be explained and predicted on a general analytical basis so that this model can stimulate new research.

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