Photoelectron Spectra of Group 5 Compounds. Part IV.[1] A Study of the E–X Bond in R_3EX Compounds (R = Me or F; E = N or P; X = O or S)

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The He(I) photoelectron (p.e.) spectra of the isoelectronic C_{3v} compounds Me_3NO, Me_3PO, Me_3PS, and F_3PS are discussed and assigned by comparison with the p.e. spectra of the parent bases R_3P and R_3N and with reference to CNDO and EHMO calculations. Bond descriptions for the E–X multiple bonds (σ donation, p_π–d_π back donation) have been critically revised taking into account the variation of the central atom E, of the acceptor X, and of the substituent R, and symmetry arguments. Inductive, hyperconjugative, and d-orbital effects have been determined by the CNDO method.

VARIOUS models have been proposed to describe multiple bonding in R_3EX systems in order to reflect differences in E–X bond orders, bond distances, or nucleophilicities. The models range from (a) to (d). While the equivalent

$$\begin{array}{cccc} R_2\overset{+}{E}{-}\overset{-}{X} & R_3E{\rightarrow}X & R_3E{=}X & R_3E{\equiv}X \\ \text{(a)} & \text{(b)} & \text{(c)} & \text{(d)} \end{array}$$

formulations (a) and (b) are generally accepted for amine oxides, (c) and (d) are used to indicate p_π–d_π interactions[2] as was reported for phosphine complexes in numerous *ab initio* (*e.g.* Me_3PO[3,4] and F_3PX[4-9]) and semiempirical calculations (R_3EO[10-12a] and R_3PX[13,14]).

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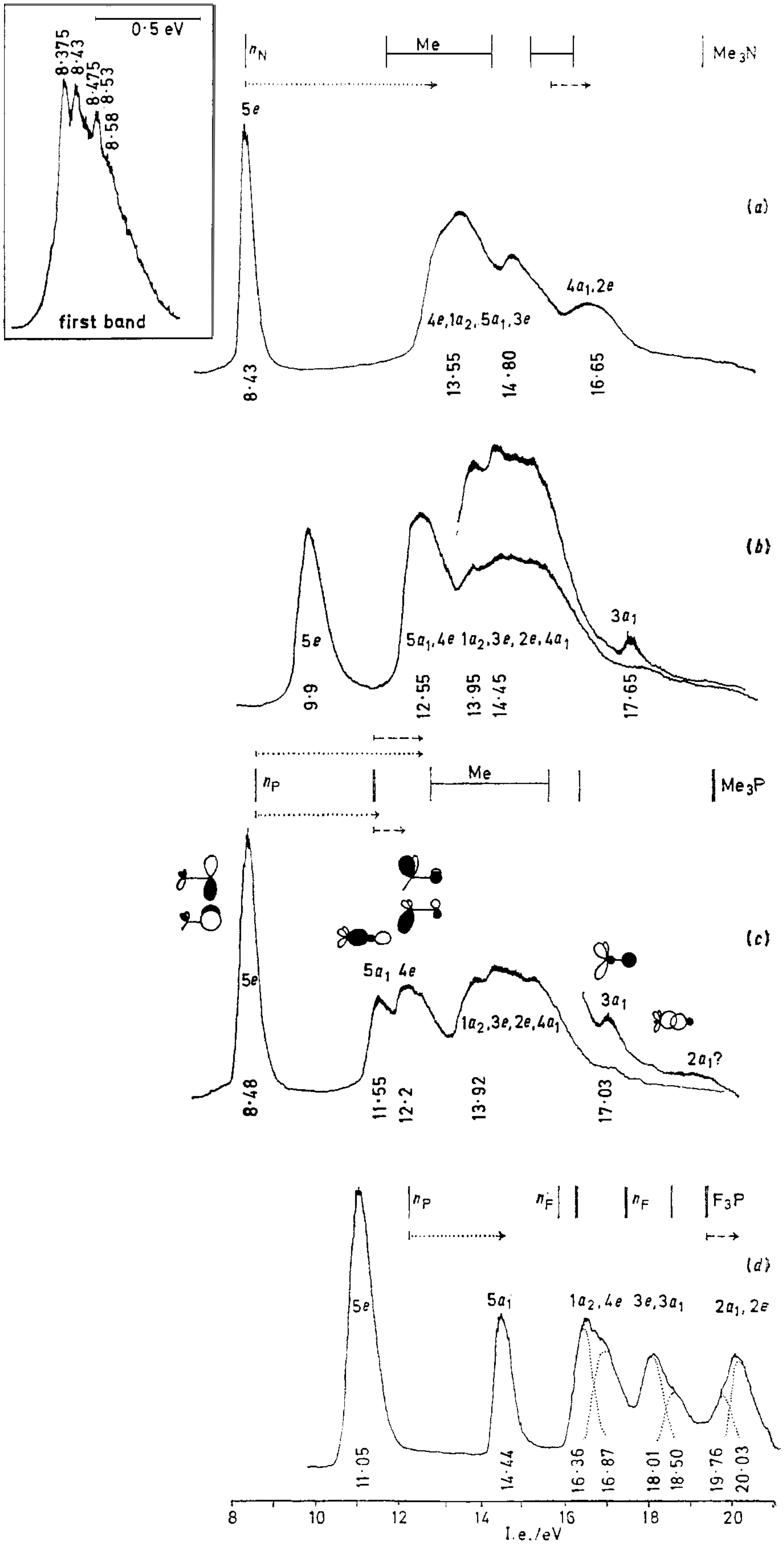
0·5 eV
8·375
8·43
8·475
8·53
8·58
first band
n_N
Me
Me₃N
5e
(a)
4a₁,2e
4e,1a₂,5a₁,3e
8·43
13·55
14·80
16·65
(b)
5e
5a₁,4e 1a₂,3e,2e,4a₁
3a₁
9·9
12·55
13·95
14·45
17·65
n_P
Me
Me₃P
(c)
5e
5a₁ 4e
1a₂,3e,2e,4a₁
3a₁
2a₁?
8·48
11·55
12·2
13·92
17·03
n_P
n_F
n_F
F₃P
(d)
5e
5a₁
1a₂,4e
3e,3a₁
2a₁,2e
11·05
14·44
16·36
16·87
18·01
18·50
19·76
20·03
8
10
12
14
16
18
20
I.e./eV

FIGURE 1

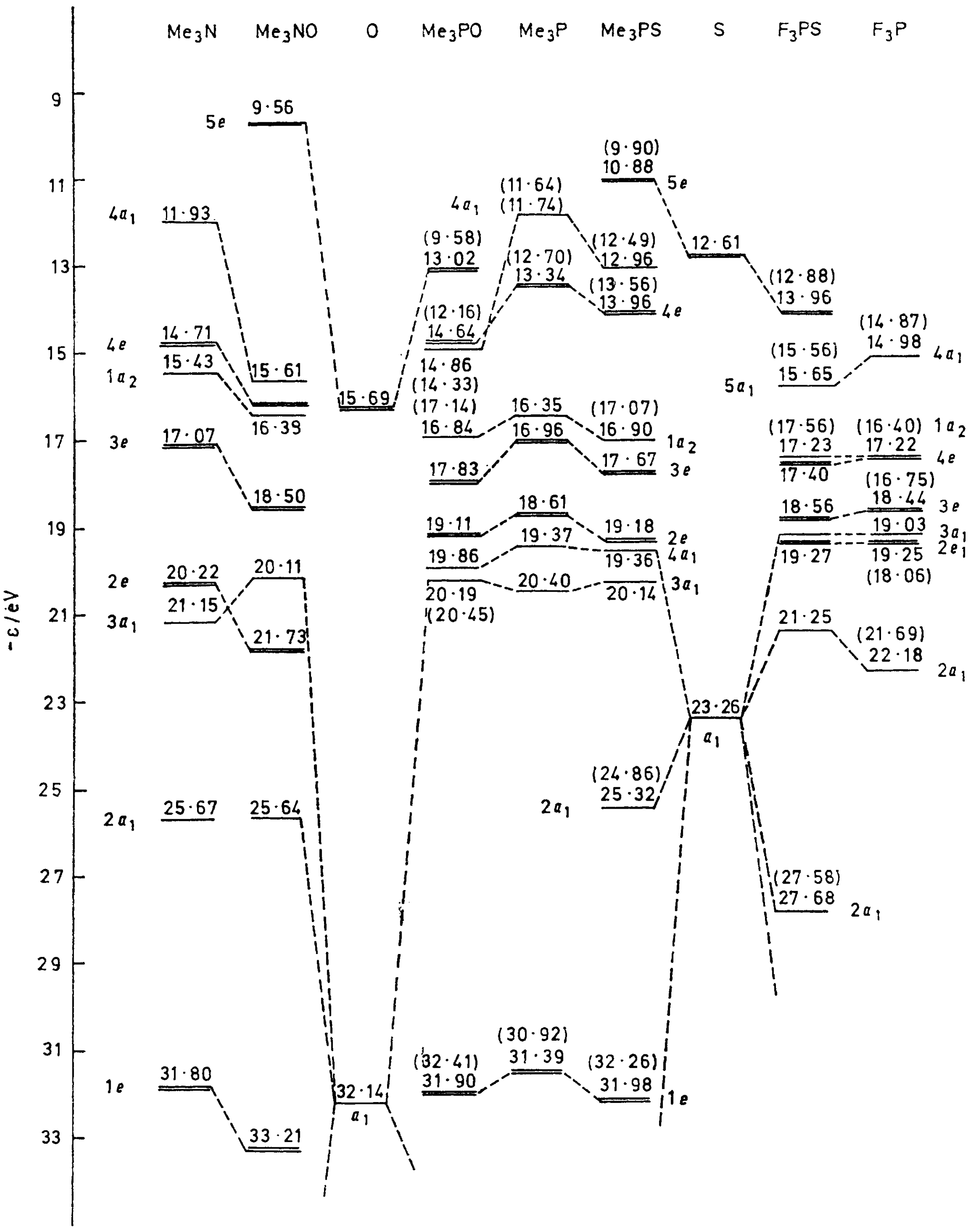

FIGURE 2 Correlation of CNDO eigenvalues of R_3EX and R_3E molecules and singlet X atoms (R = Me or F; E = N or P; X = O or S). Values in parentheses refer to calculations without *d* orbitals in the basis set

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Caption to Figure 1

FIGURE 1 P.e. spectra of Me_3NO (*a*), Me_3PO (*b*), Me_3PS (*c*), and F_3PS (*d*) and the p.e. energies of the parent molecules Me_3N,[1] Me_3P,[1] and F_3P.[16,18,19] Composite p.e. bands of R_3E are reproduced as their half-widths drawn as solid lines. The stabilization of the original E–R σ-bonding orbitals of R_3E (4*e* or 2*e*) is shown by broken arrows; lone-pair orbital stabilization ($n_E \rightarrow \sigma_{E-X}$) is indicated by dotted arrows. M.o. pictures refer to 5*e*, 5a_1, 4*e*, 3a_1, and 2a_1 CNDO eigenfunctions of Me_3PS

Restrictions were made with respect to the weaker and less polar P–S bond compared to P–O.[9] In contrast to alkylamine oxides, (c) and (d) appeared to give a better fit to the photoelectron (p.e.) spectroscopic [12] and structural [15] peculiarities of the F_3NO molecule. Symmetry properties of R_3EX compounds require a cylindrical E–X bonding type as suggested by (a), (b), or (d) and no fundamental differences in P–X and N–X bonding are expected. The satisfactory agreement between calculated and experimental ionization potentials (i.p.s) has encouraged the discussion of p.e. band shifts on co-ordination in terms of σ donation, π back donation,[14a,16] and even the Lewis acidities of the acceptors X.[17]

In order to examine the various effects of changing substituents R, central atoms E, and acceptors X on the co-ordinate bond, we have studied a series of representative, isoelectronic, and isostructural compounds, R_3EX, by p.e. spectroscopy and semiempirical calculations.

RESULTS AND DISCUSSION

The He(I) p.e. spectra of Me_3NO, Me_3PO, Me_3PS, and F_3PS shown in Figure 1 are assigned by comparison with the p.e. data of the free bases (Me_3E [1] and F_3P [16,18,19]) and molecular-orbital (m.o.) calculations (Figure 2). Numerical values of the vertical i.p.s of the resolved p.e. band maxima of R_3EX are included in Figure 1. Here, too, the vertical i.p.s of the parent phosphines and trimethylamine are inserted. (Composite bands are approximated by showing their half-widths as horizontal solid lines.) Bands are labelled and numbered according to the C_{3v} point group and to valence orbitals, respectively.

A common feature of the spectra is the overall stabilization of R_3E energies on co-ordination. This is in accordance with the simple picture of donor–acceptor bond formation according to bonding types (a) or (b), and is due to charge migration from $(R_3)E$ to X. The known p.e. spectra of halides Y_3PX [14,19] were interpreted correspondingly, and their assignments were supported by *ab initio* calculations.[3-9] In contrast to F_3NO [19a] R_3E band stabilization is also valid for Me_3NO.

The dotted arrows in Figure 1 indicate the shifts of the original lone-pair orbitals n_E ($4a_1$) on formation of the dative bond σ_{E-X} (σ donation). The E–X σ-bonding orbital is attributed to the $5a_1$ bands of R_3EX (Figure 1), in agreement with corresponding experimental and *ab initio* results for Y_3P–Y_3PX pairs (Y = halogeno), except for Cl_3PO.[8] The *p*-type E–X σ-bonding m.o. ($5a_1$) has contributions from n_X lone-pair orbitals as well as *R* orbitals due to symmetry (a_1) and energy effects [i.e. (p_X) $\longleftrightarrow$ i.e. (p_R) where i.e. = ionization energy]. The character of the three highest a_1 orbitals is illustrated in Figure 1 with CNDO eigenfunctions of Me_3PS.

Assuming a singlet state for the acceptors X during complex formation according to simple Lewis structures, their orbitals transform as *e* (p_X) and a_1 (s_X). On co-ordination the a_1 orbital of X is involved mainly in *s*-type E–X σ bonding and ionizes at higher energies. The degenerate lone-pair orbitals, n_X, undergo hyperconjugative interaction with the E–R σ-bonding m.o.s of R_3E (4*e* or 2*e*, respectively), thus producing RE–X π-antibonding (5*e*) and RE–X π-bonding m.o.s (4*e* or 2*e*, respectively), if E–X p_π–d_π feedback is ignored. The corresponding 5*e* and 4*e* CNDO eigenfunctions are portrayed in Figure 1 for the case of Me_3PS. The broken arrows (Figure 1) indicate the shifts of the degenerate E–R σ-bonding orbitals of R_3E on co-ordination, including the main π-back-donation effects. From calculations, the degenerate E–Y and N–Me σ-bonding orbitals are assigned to the 2*e* orbitals of R_3E, as is commonly accepted (Me_3N [1,20a] and Y_3P [19]), whereas the P–Me σ m.o.s are mainly attributed to the 4*e* orbital of Me_3P.[1,20b,*] For the alkyl derivatives this approach is supported by experimental evidence, since bands due to orbitals containing a large amount of central-atom character are expected to be separated from those due to Me. This is fulfilled for the second band of Me_3P (4*e*, **11.34** eV) and the third band of Me_3N (2*e*, **15.7** eV).†

If the central atoms are allowed to have *d* character, 5*e* correlates with the bonding combination of the acceptor *e* orbital and the first virtual 5*e* orbital of R_3E which is believed to have appreciable *d* character.[3] No decision can be made from p.e. spectra as to whether the 5*e* m.o.s of R_3EX are destabilized by suitable empty orbitals on the central atom (*e.g.* *d* and σ_{E-R}*). RE–X π-bonding character might be reflected in the greater half-width of the first band of Me_3PO (5*e*) compared to Me_3PS, or its rather high ionization energy in relation to the amine oxide ‡ (Figure 1). A consistent interpretation can still be given by neglecting *d*-orbital effects, since the 5*e* energies parallel the relative p_X valence ionization potentials (v.i.p.s) as well as E–X distances and X electronegativities within the series R_3PX [X = O or S (Se [21])]. Furthermore, an analogous trend in half-widths of n_X bands was found in the furan

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* It has been pointed out already (*e.g.* refs. 6 and 8) that E–R σ bonding is delocalized over a number of orbitals. A qualitative m.o. model based on the D_{3h} point group (see *e.g.* refs. 19*a* and 12*b*) shows that 4*e* and 2*e* orbitals (*e'* in D_{3h}) should mix, whereas 3*e* (*e''* in D_{3h}; substituent group orbitals orientated perpendicular to the R_3 plane) should be less affected. Although this approach appears to be rather artificial on adaption to C_{3v} systems, it is supported, for example, by the various spin-orbit splittings of degenerate n_Y orbitals of Y_3E and Y_3EX compounds (*e.g.* ref. 14) due to the differing steric arrangements of substituent group orbitals (*cf.* K. Wittel and R. Manne, *Theor. Chim. Acta*, 1974, **33**, 347 and refs. therein).

† 1 eV ≈ 1.60×10^{-19} J.

‡ Complex vibrational fine structure was observed in the first band of Me_3NO (5*e*, Figure 1) which could be caused either by two overlapping progressions or by Jahn–Teller distortion.

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series $(CH_2)_4X$ (X = O to Te)[22] and was discussed in terms of increased hyperconjugation on going from the Te to the O derivative.

Neither the spectrum of Me_3NO nor the calculations (Figures 1 and 2) show any fundamental differences from Me_3PO. The same is true for F_3PX. The lower first i.p. (Me_3NO, 8.43; Me_3PO, 9.95 eV) may be a consequence of enhanced hyperconjugative *e*–*e* orbital interaction due to a smaller E–X bond distance and/or a strong inductive effect. This is compatible with the relatively larger average stabilization of *R* levels (Figure 1), with Δa_2 data from CNDO calculations (Figure 2) and with p.e. band shifts of analogous phosphine and amine complexes suggesting greater inductive effects on N-bonding.[23] The average stabilization of *R* levels (n_Y, Me) is *ca.* 0.75 eV in Me_3NO, *ca.* 0.5 eV in Me_3PX, and *ca.* 0.4 eV in R_3PS (most clearly in the latter case due to band separation), while E–R σ-bonding orbitals are shifted to greater extents.

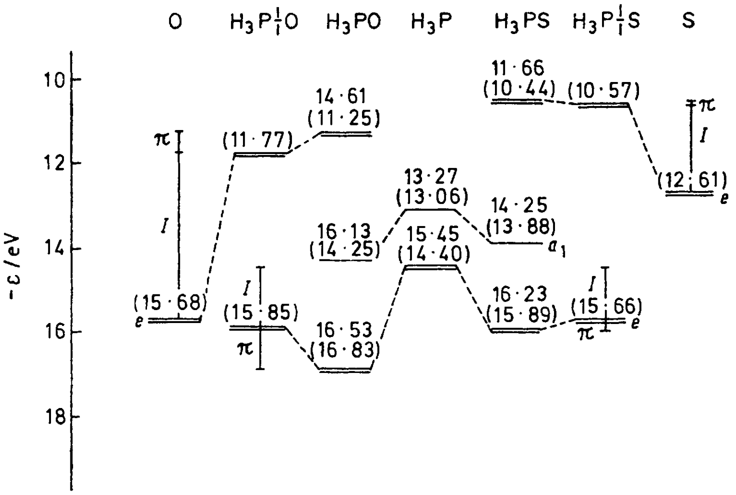

FIGURE 3 Inductive (*I*) and hyperconjugative (π) effects on co-ordination $R_3E + X \rightarrow R_3EX$, simulated by CNDO eigenvalues in a ' composite-molecule ' model. Values in parentheses refer to calculations without *d* orbitals in the basis set

All R_3E and R_3EX molecules contain a unique a_2 orbital. Although entirely located in the R_3 skeleton due to symmetry, its energy changes with charge transfer to (or from) X and thus is a quantitative measure of the inductive effect (neglecting geometry changes on co-ordination). The inductive lowering Δa_2 is most obvious in the p.e. spectra of Y_3P and Y_3PX, where $1a_2$ bands are better resolved (Cl_3P and Cl_3PO, 0.70;[14,19a] Cl_3P and Cl_3PS, 0.32;[14,19a] F_3P and F_3PS, 0.47 eV), and is assumed to parallel the average stabilization of Me levels of Me_3E. A simple electrostatic model considering electron-density distribution[21] shows that the inductive stabilization for *e* and a_1 orbitals is of course not the same as Δa_2. Thus the inductive contributions to shifts $\Delta 4e$ or $\Delta 2e$ remain undetermined (Figure 1), and neither hyperconjugative destabilization nor p_π–d_π back donation concerning 5*e* can be deduced from the p.e. spectra of R_3E and R_3EX.

Although no conclusions about inductive and hyperconjugative interactions can be drawn from the experimental evidence, a ' composite-molecule ' approach based on the method of Baird[24] may be helpful in gaining some insight into the dimensions of formal inductive (*I*) and pseudo-π effects during the hypothetical reaction $R_3E + X \longrightarrow R_3EX$. Figure 3 shows the stepwise coupling procedure for *e* orbitals of the moieties R_3E and X which has been simulated by CNDO eigenvalues of H_3P, O and S (singlet states), H_3PX, and their fictitious fragments.[24] Hydrogen derivatives were taken for clarity, although the inductive *R* standard $1a_2$ is missing here. (This omission is not serious, since the relative Δa_2 values from Figure 2 should still hold.) Figure 3 can give an impression of the complexity of the inductive and hyperconjugative perturbations on co-ordination. An analogous approach is shown for the present compounds in Figure 2.

In order to study the effect of σ transfer, indicated by the dotted arrows in Figure 1, the a_1–a_1 interactions have to be analyzed. The transformation of the orginal n_E lone-pair orbitals on complex formation has already been mentioned. The *p*-type E–X σ-bonding orbitals correlating with n_E have been assigned to the $5a_1$ bands in each case. These bands are separated only for R_3PS. The σ_{P-O} level is expected to coincide with σ_{P-Me} energies (12.5 eV) according to *ab initio*[3] and CNDO eigenvalues (Figure 2). The σ_{N-O} energy is obscured by the Me bands centred at 13.6 eV (Figure 1), but is assigned to the low-energy shoulder of this band in agreement with our CNDO eigenvalues (Figure 2).

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Although the lengths of the arrows could reflect the expected σ-donation abilities as predicted by theory, Figure 1 and particularly Figure 2 show the remarkable influence of the relative s v.i.p.s of the acceptors X on all original a_1 orbitals of the free bases. Even though the s_X orbital interferes mainly with $3a_1$ (the $3a_1$ orbital of F_3P, *e.g.* at 18.57 eV, remaining nearly constant in F_3PS, $4a_1$ at *ca.* 18.50 eV) and less with $4a_1$ (n_E) due to energy effects, the rather small $n \rightarrow \sigma$ shifts for sulphur and borane complexes do not necessarily mean weak σ donation ($\Delta n_E \rightarrow 5a_1$: Me_3P and Me_3PO, *ca.* 3.95; Me_3P and Me_3PS, 2.96; Me_3P and $Me_3P{\cdot}BH_3$, *ca.* 2.0;[21] Me_3N and Me_3NO, *ca.* 4.65; Me_3N and $Me_3N{\cdot}BH_3$, 2.86;[16] F_3P and F_3PO, 3.4;[19] F_3P and F_3PS, 2.15 eV). The shifts reflect the effect of nearby s_S or B_sH_3 orbitals (a_1) that counteract the inductive stabilization on complex formation. The remarkable amount of s_X character, even in the $5a_1$ m.o., as a function of the $s_X \leftrightarrow n_E$ energy gap is confirmed by *ab initio* calculations (*e.g.* F_3PO, 14; F_3PS, 20%)[4] and our CNDO results.[21]

Obviously, concepts such as ' σ donation ' or ' π back donation ' cannot be substantiated by p.e. spectroscopy and their application therefore seems vague and only relative. In contrast, theoretical studies can be used to determine differing bond orders or charge effects as suggested by the models (a)—(d) of the E–X co-ordinate bonding which were mentioned in the Introduction. For comparison, CNDO and EHMO bond orders, net atomic charges, experimental stretching force constants, and observed and calculated dipole moments of the present compounds (and partially of their parent bases R_3E) are summarized in Supplementary Publication No. SUP 21743 (2 pp.).* The sequence of CNDO bond orders calculated without d orbitals[25] for analogous C_{3v} phosphine and amine complexes[21] is: ${}_{H}B{-}P_F < S{-}P_{Me} \approx {}_{H}B{-}P_{Me} < O{-}N_{Me} \approx {}_{H}B{-}N_{Me} \leqslant S{-}P_F \approx S{-}P_{Cl} < O{-}P_{Me} \approx O{-}N_F < P{-}P_{Cl} = O{-}P_F$. Apart from reversals in the order due to the inclusion of d orbitals with respect to N–X and P–X, the sequence is well reproduced by results of Choplin and Kaufmann[10] for comparative data.

EXPERIMENTAL

The He(I) (584 Å) spectra were recorded on a Perkin-Elmer PES 16 spectrometer. Calibration was with argon and xenon. The estimated error in the ionization potentials is ±30—40 meV. The resolution ranged between 25 and 40 meV.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975 Index issue (items less than 10 pp. are supplied as full-size copies)

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