Photoelectron Spectra of Group 5 Compounds. Part V.[1] Phosphorus Halides, $R_2P(X)Y$ and $RP(X)Y_2$ (R = Me or F; X = O, S, or Se; Y = Cl or Br)

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A complete assignment of the He(I) p.e. spectra of the isoelectronic title compounds is given. A comparison with analogous C_{3v} compounds R_3PX and Y_3PX, with corresponding phosphine halides R_2PY and RPY_2, and with similar molecules like $Me_2P(X)H$ has been utilized instead of molecular-orbital (m.o.) calculations. A qualitative ' composite-molecule ' m.o. model is derived for substituent group orbitals n_Y and Me, and is applied to n_Y band characterization.

DESPITE the low molecular symmetry (C_s), and without the use of large-scale molecular-orbital (m.o.) calculations, the He(I) photoelectron (p.e.) spectra of the phosphorus halides $Me_2P(O)Cl$, $Me_2P(S)Cl$, $Me_2P(Se)Cl$, $Me_2P(S)Br$, $F_2P(S)Br$, and $MeP(O)Cl_2$, $MeP(S)Cl_2$, $MeP(Se)Cl_2$, $MeP(S)Br_2$, and $FP(S)Br_2$ can be completely assigned in a quite empirical way, providing sufficient comparative p.e. data are available. The following possibilities of comparison are utilized here: (*i*) isoelectronic molecules of higher symmetry, R_3PX and Y_3PX (Y = halogeno); (*ii*) corresponding phosphines R_nPY_{3-n}; and (*iii*) hydrogen compounds $R_2P(X)H$ to establish halogen-substituent effects in phosphine complexes. These approaches should give a consistent picture of the electronic structures and the relative ionization potentials (i.p.s) of the above compounds.

RESULTS AND DISCUSSION

The He(I) p.e. spectra of the phosphorus halides studied are shown in Figures 1—3. The correlation with the i.p.s of the parent phosphines RPY_2 [2,3] and R_2PY [2-4] is displayed separately within Figures 1 and 2 and drawn as background spectra in Figure 3 as broken lines. Bands are labelled according to our qualitative m.o. model and to C_s symmetry. Vertical ionization energies (i.e.s) of the series $R_nP(X)Y_{3-n}$ and of the halogenated phosphines are summarized in the Table.

The first p.e. band of $R_nP(X)Y_{3-n}$ compounds is assigned to orbitals exhibiting predominant lone-pair character on X (' n_X ') in each case and obviously parallels the trend in the sum of the substituent group

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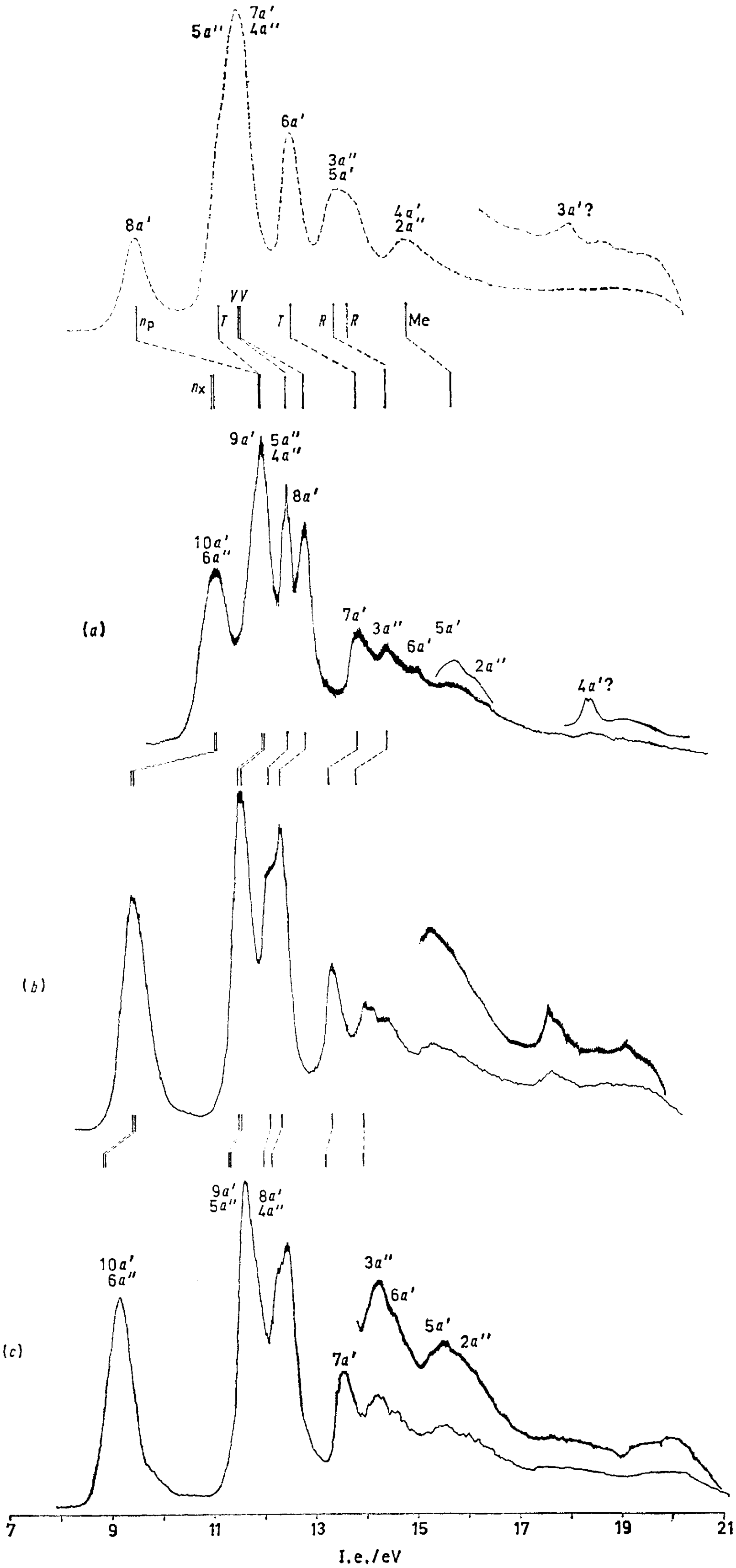

FIGURE 1 P.e. spectra of MeP(O)Cl$_2$ (*a*), MeP(S)Cl$_2$ (*b*), and MeP(Se)Cl$_2$ (*c*) assigned according to a qualitative m.o. model (see text) and to C_s symmetry. The assigned p.e. spectrum of MePCl$_2$ [2,3] (- - - - -) is included for correlation. Vertical i.p.s are summarized in the Table

(R and Y) electronegativities within a series $R_nP(X)Y_{3-n}$ (*e.g.* X = S, Figure 2). The actual degeneracy of the two n_X lone-pair orbitals in C_{3v} persists throughout the series ($5e \rightarrow 10a',6a''$). Half-widths of n_X bands of C_{3v} and C_s analogues are approximately the same.

Considering the mixed halides $MeP(X)Y_2$ and $Me_2P(X)Y$ (Y = Cl or Br), the energy range beyond the n_X bands may be further subdivided into n_Y (sharper intense bands, 11—13.5 eV) and Me regions (broad featureless bands, *ca.* 14—16.5 eV) * joined by bands due to orbitals possessing large P–R, P–Y, and P–X σ-bonding contributions. Mixing of n_Y and P–Me bands is reduced on going from Cl to Br due to an increased energy gap, $\alpha_{Br} < \alpha_{Cl} < \alpha_{Me},\alpha_{P\text{-}Me}$. Chlorine and Br lone-pair orbitals ionize more readily than Me group orbitals, while the order is reversed on replacing Cl, Br, or Me by F: $\alpha_{Br} < \alpha_{Cl} < \alpha_{Me},\alpha_{P\text{-}Me} \leqslant \alpha_F$, see, for example, Figure 2. n_{Br} Band splitting is favoured due to smaller interaction parameters β_P and β_{Br} compared to the chlorides and thus facilitates the assignments.

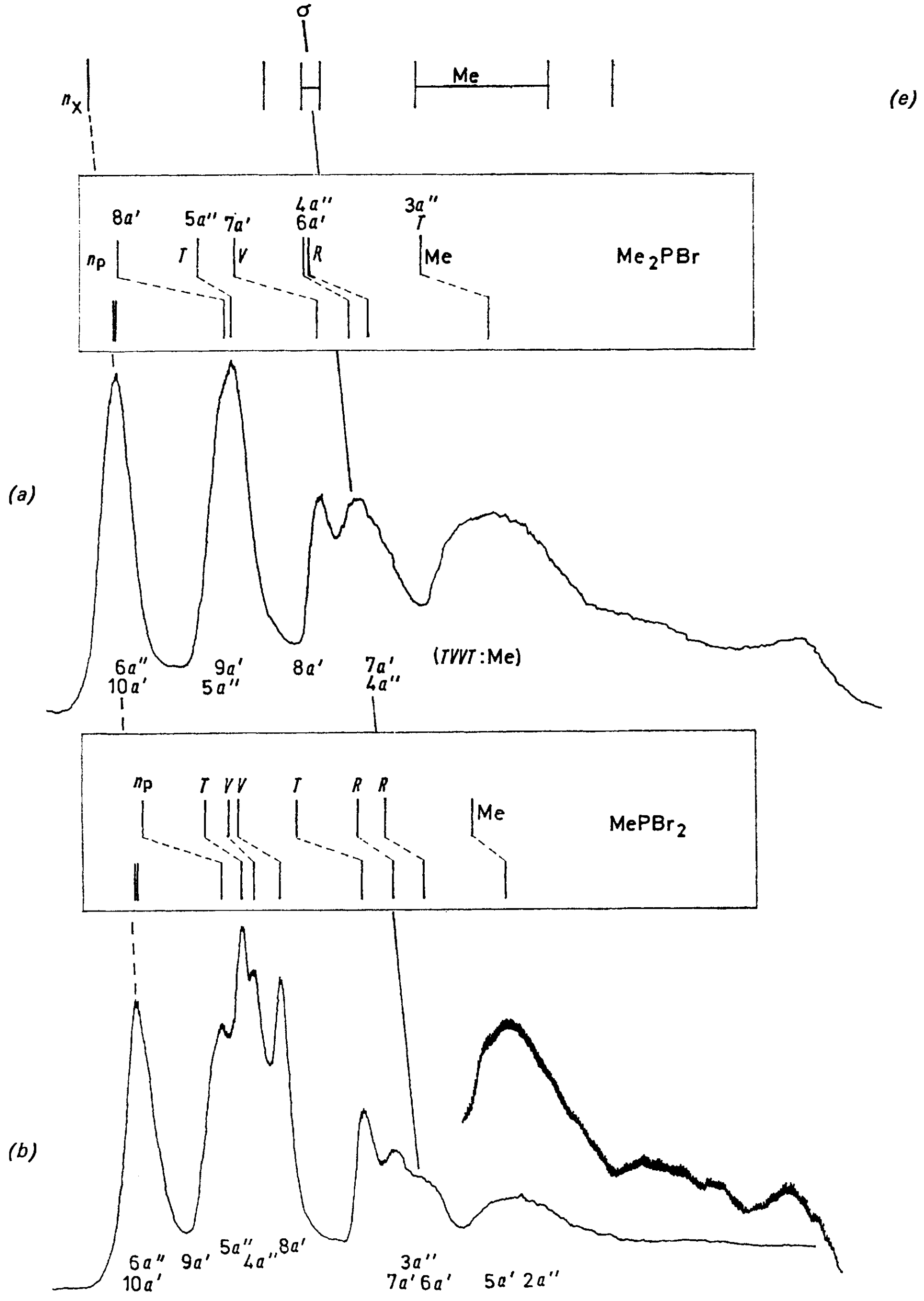

FIGURE 2

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* 1 eV ≈ 1.60×10^{-19} J.

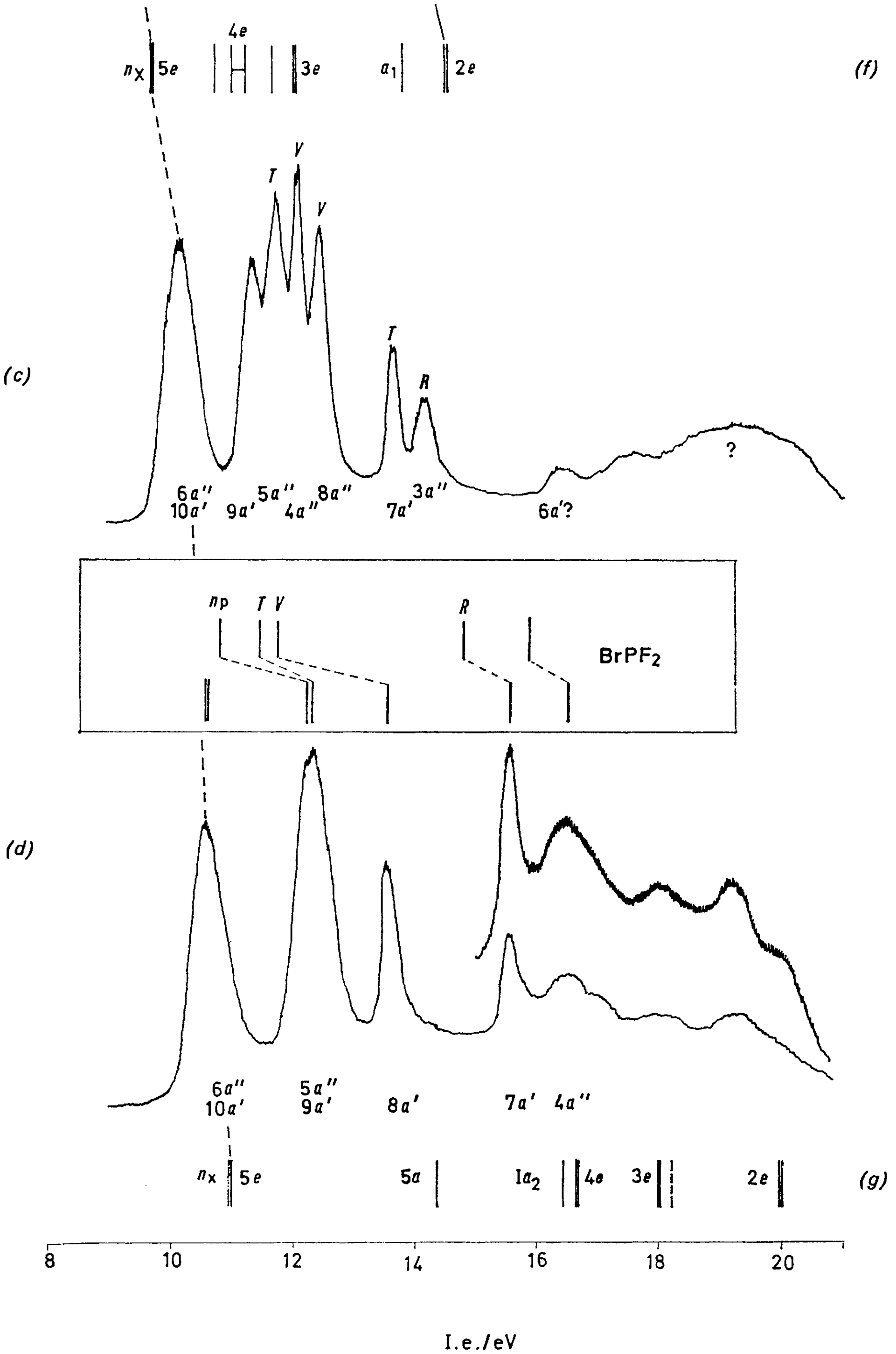

FIGURE 2 P.e. spectra of the series Me$_2$P(S)Br (*a*), MeP(S)Br$_2$ (*b*), Br$_2$P(S)F (*c*), and BrP(S)F$_2$ (*d*) assigned according to a qualitative m.o. model (see text) and to C_s symmetry. Correlation with p.e. data of the corresponding phosphines MePBr$_2$,[2] F$_2$PBr,[4] and Me$_2$PBr [2] is given in the insets. Vertical i.p.s. of C_{3v} analogues Me$_3$PS (*e*), Br$_3$PS (*f*), and F$_3$PS (*g*) are drawn schematically

Within the series MeP(X)Cl$_2$ and Me$_2$P(X)Cl (X = O, S, or Se; Table), a marked low-energy shift of the first band only takes place for the transition X = O→S (second to third period); n_{Se} is less shifted relative to n_S and thus reflects the trend in p_X valence ionization potentials (v.i.p.s). An equivalent destabilization of i.p.s due to orbitals with predominant s_{R-P-X} character was observed in the high-energy range: MeP(O)Cl$_2$,

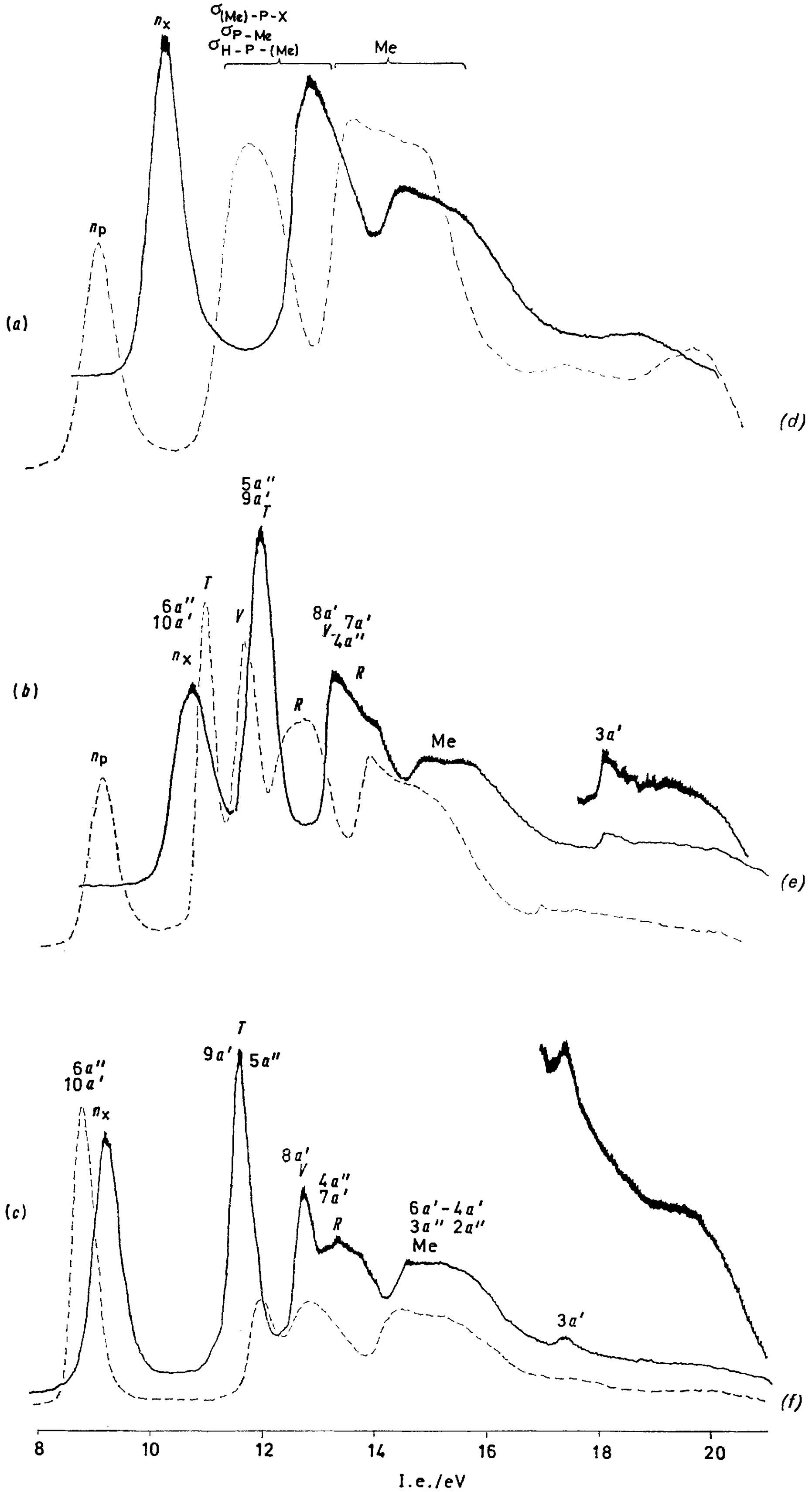

FIGURE 3 P.e. spectra of $Me_2P(O)H$ (*a*), $Me_2P(O)Cl$ (*b*), and $Me_2P(S)Cl$ (*c*) (full lines), and the corresponding Me_2PH, (*d*) Me_2PCl (*e*), and $Me_2P(S)H$ (*f*) (broken lines) assigned according to C_s molecular symmetry and to a qualitative m.o. model (see text)

18.83; $MeP(S)Cl_2$, 17.9; $Me_2P(O)Cl$, 18.12; and $Me_2P(S)Cl$, 17.39 eV (Figures 1—3). A more detailed analysis was prevented by the low band intensities.

The phosphorus halides discussed here belong to series of isoelectronic and isostructural molecules which are limited by the C_{3v} members R_3PX and Y_3PX. They all possess 16 occupied valence orbitals which transform as a' (10) and a'' (6) under C_s symmetry. The number of visible p.e. bands in the He(I) section can therefore be estimated by comparison with the known C_{3v} analogues: 12 i.p.s Me_3PO,[1] Cl_3PO,[5] Cl_3PS;[5] 13 i.p.s Me_3PS;[1] 14(?) i.p.s Br_3PS.[5] Furthermore, the arguments in the preceding paper,[1] which were derived from the co-ordination of the parent phosphines, should be valid for the mixed species too. On co-ordination all original R_2PY [2-4] and RPY_2 [2,3] energies are appreciably stabilized by the strong electron-withdrawing effect of the acceptors X and partially by hyperconjugation. Orbitals possessing P–X σ-bonding contributions (a_1 in C_{3v}, a' in C_s) should be affected more than levels of a'' representations. Here, too, the downward shift of a' orbitals is counteracted by the s-orbital v.i.p.s of the acceptor, s_X.

TABLE

P.e. band maxima i.p.$_n$/eV of phosphorus halides $R_nP(X)Y_{3-n}$ (R = Me or F; X = O, S, or Se; Y = Cl or Br; n = 0—3), hydrogen derivatives, $Me_2P(X)H$, and phosphines $MePY_2$, Me_2PY, and F_2PBr.[4] *T*, *V*, and *R* refer to the qualitative m.o. model (see text)

Compound	I.p.$_1$	I.p.$_2$	I.p.$_3$	I.p.$_4$	I.p.$_5$	I.p.$_6$	I.p.$_7$	I.p.$_8$
$MeP(O)Cl_2$	11.43	12.33 *T*	12.82 *V*	13.17 *V*	14.23 *T*	14.75 *R*	15.23 ?*R*	16.15
$MeP(S)Cl_2$	9.73	11.89 *T*	12.47 *V*	12.65 *V*	13.66 *T*	14.32 *R*	15.6	17.9
$MeP(Se)Cl_2$	9.16	11.64 *T*	12.47 *V*	13.6 *T*	14.25 *R*	15.62	19.94	
$MeP(S)Br_2$	9.53	10.86	11.17 *T*	11.37 *V*	11.78 *V*	13.08 *T*	13.54 *R*	15.35
$FP(S)Br_2$	10.23	11.41	11.81 *T*	12.14 *V*	12.51 *V*	13.71 *T*	14.22 *R*	
$Me_2P(O)Cl$	10.77	12.0 *T*	13.28 *V*	14.12 *R*	15.0	15.53	18.12	
$Me_2P(S)Cl$	9.12	11.53 *T*	12.69 *V*	13.5 *R*	14.55	15.54	17.39	19.2
$Me_2P(Se)Cl$	8.64	11.31 *T*	12.57 *V*	13.67 *R*	14.08	19.6		
$Me_2P(S)Br$	8.18	10.96 *T*	12.4 *V*	12.9 *R*				
$F_2P(S)Br$	10.58	12.33 *T*	13.55 *V*	15.6 ?*R*	16.53	16.95?	18.05	19.22 ?
$Me_2P(O)H$	10.32	13.87	14.57	18.67				
$Me_2P(S)H$	8.78	11.98	12.78	14.4	15.3	19.7		
Me_3PS [1]	8.48	11.55	12.2	13.92	17.03			
Br_3PS [5]	9.89	10.92	11.20/ 11.42	11.83	12.0	13.96	14.68	
F_3PS [1]	11.08	14.46	16.50	18.05	20.0			
$MePCl_2$ [2,3]	9.86	11.89 *TVV*	12.91 *T*	14.0 *R*	15.06	18.58		
Me_2PCl [2,3]	9.15	11.0 *T*	11.74 *V*	12.72 *R*	13.9	15.3	16.98	
$MePBr_2$ [2]	9.66	10.59 *T*	11.00 *V*	11.16 *V*	12.08 *T*	13.05 *R*	13.45 *R*	14.83
Me_2PBr [2]	9.24	10.47 *T*	11.06 *V*	12.20 *R*	14.0			
F_2PBr [4]	10.86	11.51 *T*	11.8 *V*	14.85	15.9			

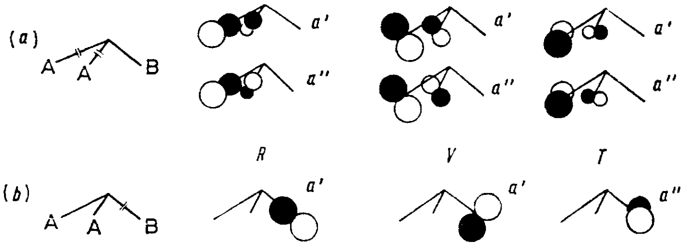

FIGURE 4 Substituent group orbitals for two (*a*) or one (*b*) decoupled substituents (A_2 and B) in A_2PB phosphines (A = Me, B = Y; A = Y, B = Me) based on a 'composite-molecule' approach (see text)

A comparison of the corresponding phosphines and phosphorus halides allows the co-ordination and hyperconjugative effects (interaction with central atomic orbitals, α_{P-X} and α_{P-R}) on n_Y levels to be assessed. Especially well isolated and non-degenerate n_{Br} bands (Figure 2) are suitable for examination. Since the original molecular geometry of the phosphines only changes slightly on complex formation, the same m.o. models should be appropriate for both the phosphines and the halides. As can be seen in Figures 1—3, n_Y orbitals are not stabilized to the same extent. This observation provides the basis of a qualitative m.o. model from which a probable ordering of n_Y energies should emerge. For dichlorophosphines [3,6] p.e. assignments were made by neglecting n_Y ordering because of band overlap.

As we reported previously,[2] isoelectronic substituent p-type group orbitals, *e.g.* those of the Y and Me groups, can be differentiated with respect to their steric arrangement, symmetry, and their degree of interaction. Pure substituent group orbitals A and B in compounds as APB_2 or A_2PB (A = Me or Y; B = Y or Me) may be classified according to their radial (*R*), horizontal (*T*, tangential), and vertical (*V*) orientations relative to the

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[6] A. H. Cowley, M. J. S. Dewar, and D. W. Goodman, *J. Amer. Chem. Soc.*, 1975, **97**, 3653.

bond axes (Figure 4). When coupling two A substituents and central atomic orbitals P–B (' composite-molecule ' approach) as in Figure 4(*a*), both radially oriented m.o.s (*R*) change significantly in energy, since they are involved in σ bonding. Four typical substituent orbitals then remain when considering two decoupled A and B moieties. For C_s symmetry, and based on their different steric interactions, the qualitative model yields the energy sequence: $T(a'') < V(a'') < V(a') < T(a')$. Application of the above principles to R_2PMe or R_2PY phosphines or their complexes (taking into account one decoupled Me with respect to Y) leads to an analogous model [Figure 4(*b*)]. The initial degeneracy of *T* and *V* orbitals is lifted on uniting with R_2P by a stronger hyperconjugative interaction of the *V* m.o. with central atomic orbitals of R_2P (n_P or σ_{P-X}). The resulting ordering $T(a'') < V(a')$ of n_Y is evident in all p.e. spectra of R_2EY compounds (E = N to Sb),[2,3] but is not as apparent in the monomethyl derivatives R_2EMe. Here *T* and *V* orbitals of the methyl group overlap strongly. The same is true for the four *T* and *V* methyl group orbitals of Me_2PY compounds (Figures 2—4).

From these models differing n_Y shifts are expected due to the degree of interaction between n_Y and the central atomic orbitals σ_{P-X}, σ_{P-Me}, and σ_{P-Y}, which is additionally governed by the energy separation $\sigma_Y \longleftrightarrow \alpha_X$ and the inductive perturbation. Figure 4(*a*) shows that *V* orbitals should obviously be less affected than *T* orbitals when effective mixing with *R* orbitals occurs. Within the n_Y band set for dihalogenophosphines the $V(a'')$ m.o. can be regarded as an ' internal-inductive standard.' It exhibits the smallest interatomic interactions and is thus the least stabilized of the original n_Y peaks. [For assignments see Figures 1 and 2; these assumptions are defined exactly only for planar R–P–Y skeletons (C_{2v}), where *R* and *T* orbitals transform as a_1 or b_2, while *V* orbitals transform as $1a_2$ and one substituent b_1 m.o., *cf.* ref. 1.] The σ-bonding *R* orbitals transforming as a' and a'' remain almost degenerate within the series $R_nP(X)Y_{3-n}$. Their average i.p.s show a linear regression (solid line in Figure 2, indicated ' σ ') and can be estimated from the positions of the e(P–R) levels in R_3PX (R = Me,[1] $4e$; R = Y,[1,5] $2e$), which are presumed to have similar α_R and β_{P-R} parameters.

Considering the symmetrical R_3PX molecules,[1] we assigned those orbitals which exhibited the main *p*-type P–X σ-bonding character to the highest-occupied a_1 orbitals in each case. Due to the lower symmetry, we have not assigned an analogous m.o. in Figures 1—3, since the $8a'$ and $6a'$ i.p.s of $MePY_2$,[2,3] $8a'$ and $7a'$ respectively of Me_2PY [2,3] (F_2PBr [4]), are significantly affected on co-ordination [see $9a'$ and $7a'$ bands of $MeP(X)Y_2$ in Figures 1 and 2 and $9a'$ and $8a'$ of $R_2P(X)Y$ in Figures 2 and 3; the correlation was made by respecting the non-crossing rule concerning a'–a' lines].

As we previously pointed out,[1] co-ordination is paralleled by an overall inductive stabilization of the corresponding phosphine energies. A similar effect occurs on substituting H by Y in $Me_2P(X)H$.* This effect is suggested to be small, because the i.p.s from the Me_2P fragment remain nearly constant [$Me_2P(S)H \longrightarrow Me_2P(S)Cl$, Figure 3], whereas Me_2P bands are much more stabilized on co-ordination [$Me_2PCl \longrightarrow Me_2P(O)Cl$, $Me_2PH \longrightarrow Me_2P(O)H$; Figure 3].

The p.e. spectra of phosphorus halides discussed above can be easily assigned despite their C_s symmetry. Although it seems hazardous to adapt m.o. models which were derived and defined for analogous symmetric-top molecules to species of low molecular symmetry, p.e. spectral assignment for the present compounds has been successful using this approximation. The n_Y band pattern, in particular, is a challenge to this C_s–C_{2v} model. Together with a comparison with analogous phosphorus(III) compounds, this approach implies the complete p.e. band assignment of the phosphorus halides.

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* The p.e. band pattern of $Me_2P(O)H$ and $Me_2P(S)H$ (Figure 3) suggests the absence of possible ' enol ' isomers Me_2P–X–H.