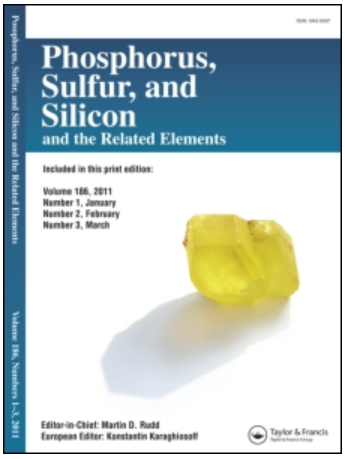

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE ELECTRONIC STRUCTURES OF P(III) COMPOUNDS WITH P-C BONDS

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To cite this Article Magnusson, Eric(1986) 'THE ELECTRONIC STRUCTURES OF P(III) COMPOUNDS WITH P-C BONDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 28: 3, 379 — 394
To link to this Article: DOI: 10.1080/03086648608072830
URL: http://dx.doi.org/10.1080/03086648608072830

Phosphorus and Sulfur, 1986, Vol. 28, pp. 379–394
0308-664X/86/2803-0379/$20.00/0

THE ELECTRONIC STRUCTURES OF P(III) COMPOUNDS WITH P—C BONDS

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A valence theory investigation of substituted phosphines with carbon-containing substituents has been carried out. *Ab initio* molecular orbital calculations at minimal and extended basis set levels were used to determine substituent effects of alkyl and substituted alkyl radicals, unsaturated groups (CN, C_2H, vinyl, allyl), and phenyl and substituted phenyl groups. The interaction of PH_2, PH_3^+ and PH^- groups with alkyl and aryl groups is analyzed and compared with the behaviour of the corresponding nitrogen-containing species. Hyperconjugative interactions are very small and $p\pi$-$p\pi$ and $d\pi$-$p\pi$ conjugation make only a marginal contribution to the P—C interaction in $PH_2 \cdot C_6H_5$. Conjugation is much more important in the charged species $PH_3 \cdot C_6H_5^+$ and $PH \cdot C_6H_5^-$. *d*-Orbitals contribute to the electron distributions of these compounds in a marginal valence role only.

In P(III) compounds, as in other normovalent second row molecules, the nature of the bonding is influenced by three factors: topology, geometry and substitution.[1,2] PH_3 and PH_2^- are characterised by strong σ-bonds which utilize the phosphorus $3p$ orbitals only; the strongly bound $3s$ A.O. is retained, with high occupation, in a nonbonding role. By contrast, high occupation of the central atom s orbital in PH_4^+ is topologically not possible and s and p orbitals mix to perform the bonding role. In explaining responses to geometry change it is useful to inspect the effect of varying the bond angles around phosphorus on the utilization of the $3s_P$ and $3p_P$ orbitals in bonding; it emerges that the $3s$–$3p$ energy difference, not overlap, is the major part of the explanation.[1] Substitution, the third factor, also affects the bonding between phosphorus and its substituents. It is necessary to discriminate the kinds of substituent effects produced on molecules containing second-row elements from the more familiar behaviour of compounds of first-row atoms.

This is a molecular orbital (M.O.) theory investigation of the interrelationships between topology, geometry and substituent type on carbon-containing P(III) compounds. It follows other studies on substitution and hyperconjugation in molecules of second row compounds[3,4] and, in particular, calculations of the separate effects of steric change and substituent type on substituted phosphines.[5] The effects at phosphorus of the following types of substituent are considered here: alkyl groups, C-substituted alkyl groups, unsaturated groups, and phenyl and allyl groups.

METHOD OF CALCULATION

Calculations were performed with the Gaussian 80 suite of programs[6] using extended basis sets (designated 3-21G, 4-31G, and 6-31G) and, where size constraints forced the use of a smaller basis, the STO-3G minimal basis set.[7] All basis sets were supplemented with 5 *d*-functions on the second row atom rather than with 6

d-functions, this type of supplementation being indicated by the symbol "#". The 6-31G## basis is thus the 5 *d*-function equivalent of the Pople group's basis containing polarization functions on all atoms.[7] Use of 5, rather than 6, *d*-functions facilitates the search for the effect of *d* function supplementation. The effective addition of an *s* function in the 6 *d*-function-supplementation recommended by the Pople group[7] leads to marginally lower energies but not to any other significant difference from the results reported here.

The symbol "+" in the 6-31+G and 4-31+G designations refers to the addition of diffuse *s* and *p* functions as recommended for the calculation of anions by Chandrasekhar *et al.*[7(b)]

Molecular geometries were obtained from the literature, or determined by optimization, or estimated, as indicated in the tabulations of results. Particular use has been made of population analysis, especially by subdividing Mulliken gross atomic populations and overlap populations[8] into contributions from the *s*, *p*, and *d* functions of the central atom; the reliability of this kind of analysis has been discussed elsewhere.[9]

RESULTS AND DISCUSSION

The electronic structure of phosphine has frequently been described.[10] Although phosphorus is less electronegative than nitrogen, the *s* electron density at the central atom is higher. The $2s_N$ occupation in NH_3 would be higher if the bond angle were lower than 106.7° but hindrance between H atoms makes this impossible. No other explanation for the high HNH angle in NH_3 need be given than that of the effect of the small core size of a first row atom; there is no need to invoke electron pair repulsion when the H atoms are only ca. 160 pm apart.[1] The core size contrast between first and second row elements has consequences which feature throughout their chemistry but the chief effect is that the *s* A.O.'s of first row atoms are forced into a bonding role while second row atoms generally utilise only *p* A.O.'s for bonding.

Phosphorus, like other second row elements, binds all but the most bulky groups at bond angles in the 90°–100° range. At XPX bond angles in the vicinity of 90° the 3*s* orbital contribution to the H.O.M.O. is anti-bonding, completely offsetting the bonding density terms from the 3*s* contributions to M.O.'s lower down. The result is "*p*-only bonding". The high *s* orbital density contributes strongly to the energy of the molecule because of the low 3*s* orbital energy, but there is no net *s* orbital contribution to bonding.

Substitution of Phosphine by Alkyl and Substituted Alkyl Groups

Although methyl substitution of PH_3 leads to a loss of charge from phosphorus (see Table II), the basicity is increased with each methyl group added. This effect may be ascribed to the change in the density profile around the polarisable second row atom and the increase in the bond angle.[4] In the methylamine series, by contrast, the charge flow from the hard nitrogen atom is much smaller, and the change in the density profile is almost negligible. The net effect of interaction between the

σ-acceptor NH_2 group and CH_3 is considerably more destabilizing than the interaction with the weak acceptor PH_2.[3]

Like PH_3, tri-methyl phosphine relies wholly on *p* orbitals for bonding. The energy advantage of the high *s* orbital density is achieved even at the expense of a net negative *s* orbital contribution to bonding. The H.O.M.O. of $P(CH_3)_3$ is about 85% localized on phosphorus and the *s*:*p* ratio of about $sp^{2.0}$ shows it to have marked directional character. (Table II)

Electron population analysis (Mulliken's formula) illustrates the response of the density distribution to methyl substitution; it is stronger around phosphorus than around nitrogen. Below are given the separate contributions of *s* and *p* orbitals to gross atomic populations. The Mulliken gross atomic population of an atom is a composite index, comprising the net atomic density plus one-half of all the overlap densities in which that atom is involved.[8] The part due to the latter, the sum of P—H and P—C (or N—H and N—C) overlap densities, is given in parentheses. (The data are from 3-21G and 3-21G(#) level calculations, respectively, for nitrogen and phosphorus compounds; data from higher level calculations do not depart significantly from the results at this level.[9]) There is controversy about the significance of Mulliken population analysis and the need to confine comment to trends in the charge data, rather than absolute values, should be noted.

PH_3	$3s^{1.77\,(0.00)}\ 3p^{3.31\,(0.95)}$
$PH_2 \cdot CH_3$	$3s^{1.71\,(-0.05)}\ 3p^{3.11\,(0.90)}$
$P(CH_3)_3$	$3s^{1.53\,(-0.20)}\ 3p^{2.72\,(0.83)}$
NH_3	$2s^{1.67\,(0.21)}\ 2p^{4.22\,(0.81)}$
$NH_2 \cdot CH_3$	$2s^{1.66\,(0.16)}\ 2p^{4.13\,(0.78)}$
$N(CH_3)_3$	$2s^{1.69\,(0.08)}\ 2p^{4.00\,(0.75)}$

One of the main differences between phosphorus and nitrogen compounds is the response of the density profile around the central atom to substitution and this makes a sizeable contribution to substitution effects. The effect of substitution on the radial density distribution is readily gauged by observing the population changes in the inner and outer parts with which the valence shell is described in "split valence" basis sets. The results (percentage inner shell occupations) show much greater modification of the valence orbitals for the polarisable second row atom, whether in response to methyl substitution or protonation.

	NH_3	NH_4^+		PH_3	PH_4^+
2*s*	22%	22%	3*s*	45%	52%
2*p*	46%	45%	3*p*	64%	69%
	NMe_3	NMe_3H^+		PMe_3	PMe_3H^+
2*s*	20%	20%	3*s*	51%	65%
2*p*	46%	44%	3*p*	76%	81%

There is a closer match between the energies of the interacting A.O.'s of carbon and phosphorus than those of carbon and nitrogen. The added charge which accompanies protonation worsens the disparity between orbital energies in the nitrogen compounds but produces little change at phosphorus, as σ and π bond order data illustrate:

	$p(\sigma)/p(\pi)$		$p(\sigma)/p(\pi)$
$PH \cdot CH_3^-$	0.53/0.03	$NH \cdot CH_3^-$	0.47/0.17
$PH_2 \cdot CH_3$	0.63/−0.02	$NH_2 \cdot CH_3$	0.49/−0.09
$PH_3 \cdot CH_3^+$	0.58/0.01	$NH_3 \cdot CH_3^+$	0.21/−0.09

Hyperconjugative interaction, expected to be most prominent in the anions, is clearly much less important in methyl-phosphorus compounds than methyl-nitrogen compounds.[4] Relative energy calculations and structural data, as well as π bond orders, attest this fact.[4]

Although absolute energies calculated at the basis set levels used in this study retain major sources of error, the cancellation of errors which occurs in relative energy calculations eliminates many of these. Interaction energies ($\Delta E(CH_3, H)$) for the N—CH_3 and P—CH_3 systems provide some indication of the strength of the N—C and P—C interactions relative to the N—H and P—H interactions by measuring the energy of the processes:

$$YH_2 \cdot CH_3 + H_2 \rightarrow YH_3 + CH_4$$

Substituent interaction energies for P—CH_3 and N—CH_3 interactions in the neutral and charged methyl phosphine and methylamine systems are given below.[3] The 6-31G# # basis was used for the phosphorus-containing species and the 4-31G basis for the nitrogen compounds, in both cases supplemented by diffuse functions for anion calculations (6-31 + G# #, 4-31 + G bases).[7(b)] For accuracy comparable to that obtained from split-valence basis sets on compounds of 1st row elements, calculations on the 2nd row analogues should use *d*-function supplementation (Pietro *et al.*)[7] and should be at a higher basis set level (Magnusson).[9] The 6-31G# # basis used here for the phosphorus compounds is supplemented on all atoms but a reviewer's comment, to the effect that the reaction above is not likely to be well represented even at the Hartree-Fock level, should be noted.

$\Delta E(CH_3, H)$ (kJ mol^{-1})-substituent interaction energies for methyl amines and phosphines and their ions

$PH \cdot CH_3^-$	−110.7	$NH \cdot CH_3^-$	−135.5
$PH_2 \cdot CH_3$	−77.3	$NH_2 \cdot CH_3$	−127.1
$PH_3 \cdot CH_3^+$	−12.9	$NH_3 \cdot CH_3^+$	−82.7

Interaction energies translate the movements in electron distributions into energy terms but the correspondence between the two is indirect, since there are many variables to affect the total energy when the nature of the donor–acceptor interactions is changing. Relative to the N—H and P—H interactions, all the N—C and P—C interactions are calculated to be destabilizing. According to the thermochemical data,[11] both P—C and N—C bonds are weaker than the bonds to hydrogen, with the N—C bond showing the larger reduction. The interaction energies may be rationalized as resulting from the difference between hydrogen and methyl interactions with the strong σ-acceptor (NH_2) or the weak σ-donor (PH_2). The most noteworthy features of the results are the absence of significant hyperconjugative stabilization in $PH \cdot CH_3^-$ (which makes $PH_2 \cdot CH_3$ so much less acidic than $NH_2 \cdot CH_3$) and the destabilization of the N—C bond in $NH_3 \cdot CH_3^+$ (which makes $NH_2 \cdot CH_3$ so much less basic than $PH_2 \cdot CH_3$).

Compared with the effect on amine donor properties, alkyl substitution in phosphines produces a much larger range of basicities, a fact which explains the very different effects of different phosphines in metal complexation.[12] The methyl and phenyl phosphines, $PH_n(CH_3)_{3-n}$ and $PH_n(C_6H_5)_{3-n}$, are notable for the size of the substituent effect on proton affinity, the enhancement across the methyl series being 153 kJ m^{-1} and across the phenyl series 167 kJ m^{-1}, compared with 87 kJ

m^{-1} and 49 kJ m^{-1} for the corresponding nitrogen compounds.[12] No such contrast between 1st and 2nd row compounds is found for the ionization energies of these compounds.

The Effect of Bond Angle Constraint on Electron Distribution

The electronic consequences of exchanging the methyl group for other alkyl groups in these compounds are almost entirely due to the bond angle changes necessary to accommodate the bulkier groups. They are concentrated in the H.O.M.O. and lead to the well-known increases in proton affinity and decreases in ionization energy found for phosphines substituted with larger alkyl groups.[2,9]

Because the optimum geometries for PH_3 and substituted phosphines depend on steric factors,[1] the effect of bulky groups in widening the bond angles around phosphorus may be estimated from the deformation potential curve for PMe_3. (See the energy data in Table I.) It has been estimated elsewhere the half of the proton affinity (P.A.) change produced by methyl substitution is attributable to the bond widening and half to the electronic effect of the CH_3 attachment.[4] Substitution of the phenyl for the methyl group produces changes entirely accounted for by the steric effect of the large group.

The $P(CH_3)_3$ data show that a 5° increase in the CPC bond angle increases the calculated energy of proton addition by 11 kJ mol^{-1}, and decreases the H.O.M.O. energy by 0.9 eV. It is in the H.O.M.O. that the effects of steric changes are concentrated. In contrast, the 6e M.O.'s (the major P—C bonding orbitals) change only by 0.1 eV and the P—C bond order moves only from 0.488 to 0.492.

The very minor response shown by the bond order to geometry change result emphasizes the fact that P—C bonding is not governed by the familiar relationship

TABLE I

Energy and population analysis data for $P(CH_3)_3$ over the bond angle range CPC = 90°–120° [a]

CPC = 90°		101.5°	109.5°	120°
Overlap densities:				
$p(s)$	−0.143	−0.128	−0.073	0.176
$p(p)$	0.572	0.545	0.515	0.385
$p(d)$	0.066	0.061	0.064	0.053
Atomic charges:				
$q(3s)$	1.606	1.532	1.487	1.293
$q(3p)$	2.664	2.699	2.841	3.316
$q(3d)$	0.136	0.129	0.134	0.111
q_P	14.247	14.270	14.300	14.556
Energies:				
ϵ_{HOMO} (eV)	−9.61	−8.59	−7.68	−6.21
E_{Total}	−457.19558	−457.23776	−457.21277	−457.15530

[a] 3-21G(#) level calculations. The P—C distance is held constant at the optimized value. The minimum energy conformation has ∠(CPC) = 101.5°, r(P—C) = 187.7 pm, CH_3 group at the standard geometry of J. A. Pople and M. S. Gordon.[34]

between *sp* ratio and bond angle but by all the terms in the molecular energy expression, including the energies contributed by the non-bonding 3*s* electrons. Electron distribution data for tri-methyl phosphine over the CPC bond angle range 90°–120° is also presented in Table I; it is noteworthy that the 3*s* density is still high at angles near optimum.

Judging by the usual reduction in ionization energy (I.E.) that follows widening of the CPC bond angle in alkyl phosphines, the 8.28 eV ionization energy of tri-ethyl phosphine would suggest a larger bond angle; the ionization energy of tri-methyl phosphine is 8.60 eV.[13] The geometry of PEt_3 is not known experimentally but it may be inferred from the following observations. If hindrance between methyl groups were all that mattered, the CPC bond angle could be as low as it is in PMe_3, 99.1°. However, the configuration which minimizes contact between C_2H_5 groups (each C—C axis coplanar with the threefold axis of the molecule) brings β-carbon hydrogen atoms within 260 pm of phosphorus. The contact is short enough to drive a rotation of the methyl groups around the P—C bonds, changing the CPC angle by about 1°, as suggested by the ionization energy evidence.

There are large differences between the bonding in phosphines with other saturated carbon-containing substituents. Charge distributions vary a great deal but there is relatively little change in electron density at phosphorus. (Table II) *d* Functions make a small contribution to the wave functions of these compounds, chiefly in the uppermost *e* orbital. Inspection of the wave functions shows that *d* functions improve the directional properties of the phosphorus 3*p* A.O.'s which overlap with the carbon 2*p* orbitals. Phosphorus 3*s* orbitals are unavailable for this task in M.O.'s of *e* symmetry. Minimal basis set calculations exaggerate the degree of *d* function involvement[9] because the supplemental functions tend to compensate for deficiencies in the *s*, *p* basis, but at extended basis set levels this error largely disappears. At the 3-21G level *d* functions increase the P—C bond order from 0.442 to 0.478 and provide for charge flow back to phosphorus from carbon (ca. 0.15 *e*) and optimum P—C bond lengths are reduced by about 5 pm.

If the H.O.M.O.'s of a series of phosphines were completely localized on phosphorus the H.O.M.O. energies would be expected to move as the relative $3s_P$ and $3p_P$ contributions move, rising as the 3*p* A.O. contribution rises, falling whenever the more stable 3*s* A.O. becomes more important. Less than complete localization should impose a secondary alteration on this pattern, the actual shift depending on the kind of interaction included and whether the H.O.M.O. is mixed with bonding or anti-bonding orbitals from other parts of the molecule. This line of reasoning provides a suitable rationalization for the I.E. trend displayed by the carbon-substituent phosphines.

Taking tri-methyl phosphine as the basis of comparison, the saturated substituents, none of which vary very much in degree of localization, cause the I.E.'s to move as follows:

(a) $P(C_2H_5)_3$ – a small destabilization of the H.O.M.O. (0.2 eV) accompanies the drop in the *s*-orbital contribution from 0.58 *e* to 0.54 *e* and the corresponding rise for the *p*-orbital (1.14 *e* to 1.16 *e*) occasioned by the sterically-driven angle change.

(b) $P(CH_2CN)_3$ – in spite of the small drop in both the 3*s* contribution (0.58 *e* to 0.54 *e*) and the 3*p* contributions (1.14 *e* to 1.09 *e*) there is a large drop in H.O.M.O.

TABLE II

Energy and population results of calculations on substituted phosphines.[a]

Molecule	$r(P\text{-}X)$ (pm)	XPX Angle	E_{total} (Hartrees)	ε_{HOMO} (eV)	P.A. (kJ mol^{-1})	HOMO Utilisation (s/p) and % localisation.[b]	q_P	$3s, 3p, 3d$ contributions to gross atomic population, (s, p, d contributions to $P\text{-}X$ population).
PH_3	141.5	93.5°	−338.68430	−8.19	970	(0.38/0.56) 90%	14.79	$3s^{1.68\,(0.00)}, 3p^{3.01\,(0.57)}, 3d^{0.19\,(0.09)}$
$P(CH_3)_3$	184.3	99.1°	−454.44578	−6.86	1222	(0.58/1.14) 74%	14.64	$3s^{1.54\,(0.00)}, 3p^{2.84\,(0.55)}, 3d^{0.23\,(0.11)}$
$P(C_2H_5)_3$	185.0	100.0°	−570.18654	−6.70	1236	(0.54/1.16) 76%	14.66	$3s^{1.64\,(0.00)}, 3p^{2.87\,(0.53)}, 3d^{0.24\,(0.11)}$
$P(CH_2CN)_3$	187.0	98.2°	−726.08780	−8.91	951	(0.54/1.09) 74%	14.56	$3s^{1.68\,(-0.01)}, 3p^{2.74\,(0.52)}, 3d^{0.24\,(0.11)}$
$P(CF_3)_3$	194.0	99.8°	−1331.56941	−8.69	920	(0.30/0.14) 67%	14.70	$3s^{1.71\,(-0.02)}, 3p^{2.87\,(0.48)}, 3d^{0.20\,(0.09)}$
$P(C_6H_5)_3$	183.0	103°	−1018.95982	−5.96	1212	(0.37/0.73) 47%	14.66	$3s^{1.62\,(0.02)}, 3p^{2.88\,(0.56)}, 3d^{0.14\,(0.12)}$
$P(C_2H)_3$	175.0	106.9°	−562.91180	−7.32	1039	(0.55/0.73) 59%	14.57	$3s^{1.57\,(0.01)}, 3p^{2.79\,(0.59)}, 3d^{0.30\,(0.15)}$
$P(CN)_3$	179.0	93.5°	−610.36937	−10.49	715	(0.56/0.62) 56%	14.45	$3s^{1.65\,(-0.03)}, 3p^{2.62\,(0.57)}, 3d^{0.28\,(0.14)}$

[a] STO-3G* basis set calculations at experimental geometries: PH_3: K. Kuchitsu, *J. Mol. Spectrosc.*, **7**, 399 (1961); $P(CH_3)_3$: L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960); $P(CH_2CN)_3$: O. Dahl and S. Larsen, *J. Chem. Res.*, **396**, 4645 (1979); $P(CF_3)_3$: H. J. M. Bowen, *Trans. Farad, Soc.*, **50**, 463 (1954); $P(C_6H_5)_3$: J. J. Daly, *J. Chem. Soc.*, 3799 (1964); $P(C_2H)_3$: J. Kroon, J. B. Hulscher and A. F. Peerdeman, *J. Mol. Struct.*, **7**, 217 (1971); $P(CN)_3$: K. Emerson and D. Brotton, *Acta Cryst.*, **17**, 1134 (1964).

[b] Orbital utilisation is calculated as the sum of the squares of the (s/p) orbital coefficients in the HOMO; degree of localisation as the sum of squares of the phosphorus orbital coefficients as a percentage of the total sum of squares of coefficients of all contributing orbitals in the HOMO.

energy. It is due to the substitution of C—H bonding interactions in the H.O.M.O. for the antibonding contributions in $P(CH_3)_3$.

(c) $P(CF_3)_3$ – the $3s$ contribution drops considerably (0.58 e to 0.30 e) but the H.O.M.O. is stabilised by 1.8 eV by this substituent. The effect is produced by the introduction of a $2p_F$ contribution to the H.O.M.O.

The contrast between substitution by CH_3 and CF_3 is instructive. Fairly close matching of the phosphorus $3p$ and carbon $2p$ A.O.'s near the top of the valence shell prevents much variation in $3p_P$ utilization. Both substituents remove charge from phosphorus but CF_3 substitution increases the I.E. and CH_3 substitution reduces it. The change in the atomic charge between $P(CF_3)_3$ and $P(CH_3)_3$ is ten times smaller for phosphorus ($0.060e$) than for carbon ($0.65e$).

The utilisation of phosphorus orbitals is the most important factor in the comparison of CH_3 and CF_3 bonding. The relative closeness of the $3s$ orbital of phosphorus to the fluorine $3p$ orbitals ensures its involvement in low-lying M.O.'s of $P(CF_3)_3$. Consequently, there is much less $3s_P$ character in the n_P orbital in CF_3-substituted phosphines, $3s$ utilization dropping by 0.5 e from PH_3 to $P(CF_3)_3$ compared with the much smaller drop (0.2 e) from PH_3 to $P(CH_3)_3$. Replacing the s character in tri-methyl phosphine are anti-bonding arrangements of C and H orbitals and, in $P(CF_3)_3$, non-bonding $2p_F$ orbitals. This explains why the H.O.M.O. is lower than that of PH_3 in one molecule and higher in the other. The calculated charge distributions for the $PH_n(CF_3)_{3-n}$ and $PH_n(CH_3)_{3-n}$ series compounds show the same feature developing across each of the series.

Substitution by Unsaturated Groups

Figure 1 provides a comparison between the phosphines with saturated substituents ($X = CH_3, CH_2CN, CF_3$) and with unsaturated groups ($X = C_6H_5, CN, C_2H$). Note

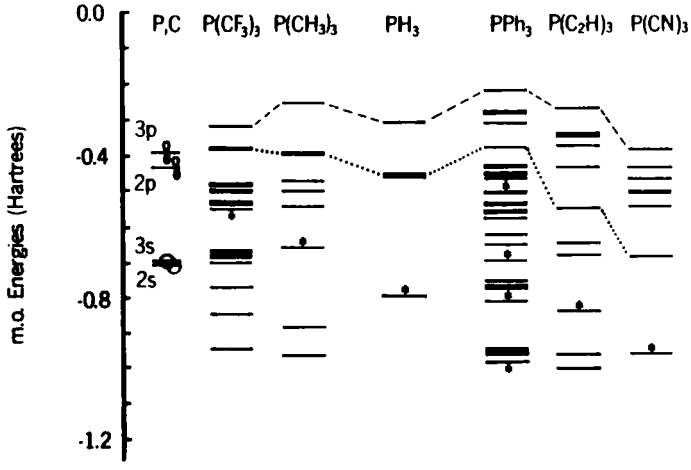


FIGURE 1 Valence shell M.O. energy levels of substituted phosphines with P—C bonds. Dashed lines connect the HOMO's, dotted lines connect the pairs of M.O.'s most closely related to the PH_3 e-type M.O.'s (the main P—X bonding M.O.'s utilizing $3p_P$ and $2p_C$ atomic orbitals) and asterisks identify the M.O.'s in which $3s_P$ character is mainly concentrated.

the large changes in the energy of the H.O.M.O. and the P—C bonding *e*-type M.O.'s. $p\pi$–$p\pi$ and $p\pi$–$d\pi$ interactions allow the latter groups to attract more charge away from phosphorus, increase P—C bond orders, and reduce the localisation of the H.O.M.O. by mixing with substituent π-type M.O.'s.

Calculation suggests that the C_6H_5, CN, and C_2H groups gain electronic charge from phosphorus by conjugative transfer, the extent of which plays an important part in determining the donor behaviour of these phosphines.

The contribution of *d*-functions to the electronic structure of $P(CN)_3$ is revealed by comparison between calculations with and without *d*-function supplementation. Coupled with the strong π acceptor character of the CN group, the existence of a degree of π coupling via phosphorus explains the strong π acid properties of $P(CN)_3$.[15]

Continuing the rationalization of energy movements in the H.O.M.O. in response to substitution, it is seen that the unsaturated substituents produce major changes in the degree of localisation of the H.O.M.O. As before, the comparison is with $P(CH_3)_3$.

(d) $P(C_6H_5)_3$ – populations of both $3s_P$ and $3p_P$ drop sharply, due to the introduction of ring orbitals with which they interact in antibonding fashion. The H.O.M.O. energy rises by 0.9 eV.

(e) $P(C_2H)_3$ – acetylenic π-orbitals are mixed with the phosphorus orbitals at the expense of the $3p_P$ contribution. The H.O.M.O. energy accordingly drops by 0.5 eV.

(f) $P(CN)_3$ – the large infusion of C—N π-bonding character accounts for the drop in H.O.M.O. localisation and consequent stabilisation by 2 eV.

Phenyl phosphines

Substitution in the phenyl ring of phenyl phosphines has a strong effect on proton affinity and ionization energy, raising the question of possible conjugative transfer of the electronic effect to phosphorus.[16–22] Many research groups have offered

TABLE III

Energy and population analysis data for $P(CN)_3$ [a]

Basis set:	3-21G	3-21G(#)
Overlap densities:		
$p(s)$	−0.295	−0.279
$p(p)$	0.415	0.455
$p(d)$	—	0.086
Atomic charges:		
$q(3s)$	1.340	1.319
$q(3p)$	2.086	2.317
$q(3d)$	—	0.199
q_P	13.258	13.664
Energies:		
E_{Total} (Hartree)	−614.3355	−614.3983
ε_{HOMO} (eV)	−12.57	−12.55

[a] The $P(CN)_3$ geometry (experimental) for the calculations was: r(P—C) = 178.0 pm, r(C—N) = 115.0 pm, ∠(CPC) = 93.5°. Data from K. Emerson and D. Brotton.[35]

TABLE IV

Calculated total energies and substituent interaction energies of *p*-substituted phenyl phosphines and phosphonium ions with with comparative data on nitrogen-containing species[a, b]

X	Phosphines (Amines) $E_{Total}(B)$ (Hartrees)	$\Delta E(X,H)(B)$ (kJ mol^{-1})		Phosphonium ions (Anilinium ions) $E_{Total}(BH^+)$ (Hartrees)	$\Delta E(X,H)(BH^+)$ (KJ mol − 1)	
OCH_3	−677.85798	15.3	(−6.3)	−678.29189	30.8	(11.7)
F	−662.90437	−0.1	(3.3)	−663.32986	−6.7	(−8.3)
Cl	−1019.46453	3.8	—	−1019.88610	−13.0	—
CH_3	−604.02836	−0.3	(−2.1)	−604.45973	8.5	(8.3)
H	−565.44467	—	—	−565.87266	—	—
CN	−655.99852	2.4	(5.9)	−656.41179	−36.2	(−37.7)
NO_2	−766.13800	3.9	(9.2)	−766.54707	−45.8	(−52.7)

[a] Calculations were at STO-3G* basis set level. The bond lengths and bond angles adopted (estimated) for $PH_2 \cdot C_6H_5$ are ∠(HPH) = 93.5°, ∠(HPC) = 97.5°, *r*(P—H) = 141.5 pm, *r*(P—C) = 183.0 pm. For $PH_3 \cdot C_6H_5^+$ the same bond lengths were employed and a regular tetrahedral arrangement around P adopted. Substituents were attached at standard bond distances and bond angles.[34]

[b] Data, from Pross and Radom,[36] for substituted anilines and anilinium ions are given in parentheses.

answers. Arguing from photoelectron spectroscopy, Schweig and co-workers[20] and Weiner *et al.*[18] say not, but Debies and Rabalais point to features of the photo-electron spectroscopy not included in the earlier analysis and disagree.[21] Numerous NMR investigations have been carried out, some workers interpreting the results to mean that phosphorus-phenyl conjugation is absent,[19,23,24,28] and some the opposite.[22,25-27] The variety of conclusions is partly due to the marginal nature of the interaction. The situation is the same for spectroscopic measurements of aryl phosphines.[29]

To resolve the question of P—C conjugation, two kinds of calculations have been performed–minimal basis set calculations of the effect of para-substitution on phenyl phosphine (STO-3G* calculations on $R \cdot C_6H_4 \cdot PH_2$ and $R \cdot C_6H_4 \cdot PH_3^+$ for R = H, CH_3, CH_3O, F, Cl, CN, and NO_2; estimated PH_nC geometries, standard geometries for $R \cdot C_6H_4$) and extended basis set calculations on $PH_2 \cdot C_6H_5$, $PH_3 \cdot C_6H_5^+$ and $PH \cdot C_6H_5^-$ (3-21G(#) basis set; estimated PH_nC geometries, standard geometries for C_6H_5). The results are set out in Tables IV and V and Figure 2. Both sets of calculations assume an orientation in which the HPH bisector is perpendicular to the benzene ring plane and π interaction between the phenyl group and the phosphorus lone pair orbital is at a maximum. Experimental geometries for these compounds are not known and the calculated quantities must be expected to change if geometries are changed, especially for different PH_2-ring plane orientations. For the aryl-dialkyl phosphines, the phosphorus lone pair is said to be orthogonal to the π orbitals of the ring.[31]

The results of extended basis set calculations for $PH_2 \cdot Ph$, $PH_3 \cdot Ph^+$ and $PH \cdot Ph^-$ suggest moderate phosphorus-phenyl conjugation in the charged species and small but not insignificant conjugation in the neutral compound. Bond orders (σ and π) and interaction energies (kJ mol^{-1}) for the three species, calculated at 3-21G(#) level, are given in Table V. (Note that the geometrical parameters of the PH_2, PH_3^+ and PH^- groups, to which calculated energies are sensitive, were not optimized in these calculations.) Charge distribution data, which are not expected to

TABLE V

Energy and population analysis data for phenyl phosphine, aniline and the anions and cations

	E_{Total} (Hartrees)	$\Delta E(C_6H_5, H)$ (kJ mol^{-1})	P—C and N—C Bond Orders $p(\sigma)/p(\pi)$
$PH_2 \cdot C_6H_5$	−569.00257	−122.2	0.456/0.023
$PH_3 \cdot C_6H_5$	−569.26046	−154.9	0.605/0.075
$PH \cdot C_6H_5^-$	−568.42221	−27.2	0.390/0.116
$NH_2 \cdot C_6H_5$	−284.13962	−72.3	0.513/0.038
$NH_3 \cdot C_6H_5^+$	−284.50051	−74.3	0.204/− 0.052
$NH \cdot C_6H_5$	−283.44132	27.2	0.651/0.326

[a] 3-21G level calculations for nitrogen compounds, 3-21G(#) level for phosphorus compounds.
[b] Interaction energies $\Delta E(C_6H_5, H)$ refer to the processes:

$$Y \cdot C_6H_5 + H_2 \rightarrow YH + C_6H_6.$$

[c] Geometries (non-optimized) for the phosphorus compounds: r(P—C) = 183.0 pm, r(P—H) = 141.5 pm throughout. In $PH_2 \cdot C_6H_5$ ∠(XPC) = 101°, ∠(XPH) = 46.75°; in $PH_3 \cdot C_6H_5^+$ ∠(XPC) = 107.5°; in $PH \cdot C_6H_5$ ∠(HPC) = 100° with the P—H bond lying in the benzene ring plane. Estimates based on experimental data for PH_3 and $P(C_6H_5)_3$.[37] Geometries for the nitrogen compounds were based on the experimental data for aniline.[38]

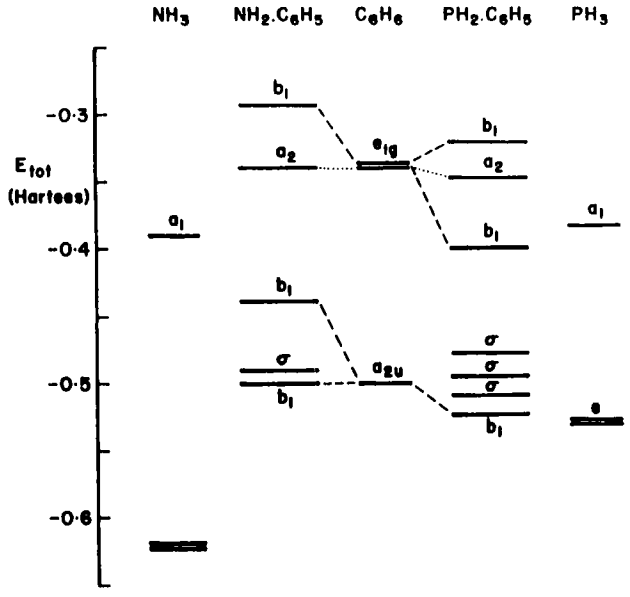
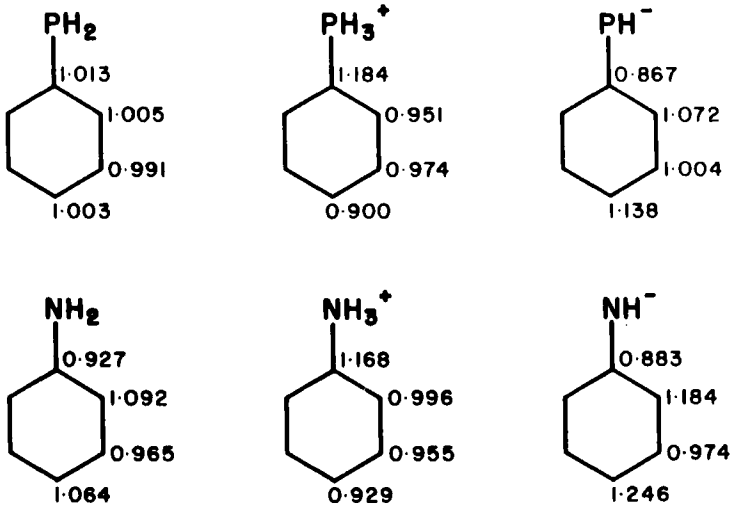


FIGURE 2 Upper M.O. energy levels of phenyl phosphine and aniline, showing the tendency of the NH_2 group to interact with the lower π-type M.O. of the ring. The PH_2 group interacts more strongly with one of the upper π M.O.'s.



be very sensitive to small geometry changes around phosphorus, are presented in the chart above. In contrast to the π-donor character of NH_2, PH_2 is calculated to have only a very small effect on the charge distribution in the ring π orbitals.

The relative energy results show how the charge on Y affects the energy of the process $Y \cdot C_6H_5 + H_2 \rightarrow YH + C_6H_6$ (Y = PH_2, PH_3^+, PH^- and NH_2, NH_3^+, NH^- groups). The P-aryl interactions are destabilizing for PH_2, PH_3^+, NH_2, and NH_3^+ but the $p\pi$–$p\pi$ component in the PH^--aryl and NH^--aryl cases is sufficient

to produce a positive $\Delta E(C_6H_5, H)$ result, contrasting with the PH^--alkyl and NH^--alkyl cases, where the interaction is strongly destabilizing. The magnitude of the interaction energies is surprisingly high for the phosphorus-containing compounds, $\Delta E(X, H)$ results for other substituents being generally lower for second row than for first row compounds.[3]

Although the P—C overlap density varies only from 0.48 ($PH_2 \cdot Ph$) to 0.51 ($PH_3 \cdot Ph^+$) to 0.68 ($PH \cdot Ph^-$), the interaction energies span a range of 280 kJ mol^{-1}. The N—C bond interaction energies are much less sensitive to charge, covering a range of only 100 kJ mol^{-1}, in spite of the much heavier dependence of bond order on charge. N—P overlap densities vary by almost 100% in each direction from the value for the neutral compound: 0.55 ($NH_2 \cdot Ph$), 0.15 ($NH_3 \cdot Ph^+$), 0.98 ($NH \cdot Ph^-$).

The effect of the PH_2 group on the π electrons of the ring is noticeable but small, as expected for such small values of the $p\pi$–$p\pi$ and $d\pi$–$p\pi$ overlap densities. By contrast, the results show much stronger phosphorus-ring conjugation in the charged species (particularly the PH^- compound), as is so strongly suggested by the NMR results on PH_3R^+ and PHR^- compounds.[19,22-28] Nevertheless, the dominance of σ interactions ensures that the overall phosphorus–phenyl bond interactions are still unfavourable. At minimal basis level the barrier to rotation about the P—C bond is only 3.4 kJ mol^{-1} (Table VI), only about 10% of the barrier calculated for aniline with the same data. Recently reported I.E. results are in agreement with these conclusions.[33]

In the comparison between phosphorus—phenyl species and the analogous nitrogen-containing compounds the second row compounds differ from the nitrogen compounds in two important respects. Higher bond angles forced on the nitrogen compounds by steric factors force a high degree of *sp* mixing in the N—H and N—C bonding and keep the $2s_N$ electron density lower than the 3*s* density of

TABLE VI

Conformational dependence of calculated total energies of phenyl, vinyl and allyl substituted phosphines[a]

Molecule	α	ε_{HOMO} (eV)	E_{Total} (Hartrees)
$PH_2 \cdot C_6H_5$	0°	6.69	−565.44467
	45°	6.94	−565.44398
	90°	7.47	−565.44340
$P(CH_3)_2 \cdot C_2H_3$	0°	6.20	−491.74801
	22.5°	6.03	−491.74802
	45°	5.77	−491.74781
	67.5°	5.58	−491.74819
	90°	5.53	−491.74506
$P(CH_3)_2 \cdot C_3H_5$	0°	6.18	−530.35225
	22.5°	6.18	−530.35394
	45°	6.18	−530.35614
	67.5°	6.17	−530.35700
	90°	6.16	−530.35557

[a] Supplemented STO-3G calculations. At $\alpha = 0°$ the phenyl, vinyl and allyl groups lie in the plane which bisects the P—C or P—H bonds. α is the angle of rotation around the P-phenyl, P-vinyl and C—C single bonds, in $PH_2 \cdot C_6H_5$, $PMe_2 \cdot C_2H_3$ and $PMe_2 \cdot C_3H_5$, respectively.

phosphorus, in spite of the lower electronegativity of the latter. Secondly, the stability of the nitrogen $2p$ A.O. induces it to interact mainly with the lowest π M.O. of the ring system (the a_{2u} M.O. of benzene) whereas the interaction in phenyl phosphine is mainly with one of the upper e_{1g} M.O.'s of C_6H_6 (see Figure 2). As the charge distribution data show, the effect of attachment of phosphorus on the density distribution in the ring is qualitatively different from the effect of attaching nitrogen, not just a milder version of it.

Chief interest in Figure 2 centres on the upper group of M.O. levels which are due to the splitting of the doubly degenerate e_{1g} levels of benzene by interaction with PX_2. One only of the e_{1g} orbitals interacts, producing a pair of levels, one stabilized and one destabilized, to an extent which depends on the relative orientation of the PX_2 group and the ring. The same situation occurs in $P(C_6H_5)_3$ where the group of 7 orbitals (in the range -5.96 to -8.45 eV) accounts for the phosphorus lone pair and the three pairs of e_{1g} benzene orbitals contributed by the three rings. The order, from the H.O.M.O. downwards, is a_1, e, e, a_1, a_1. The middle three M.O.'s (e, e, a_1) are all very close to the energy of the unperturbed e_{1g} benzene M.O. at -7.66 eV; three of these can be deemed to be the three noninteracting members of the pairs of e_{1g} benzene orbitals and two the pair of e orbitals at the middle of the set of four resulting from interaction of the n_P orbital with three of the e_{1g} orbitals. This interaction also produces the a_1 levels, one raised and one lowered.

Modro has used NMR measurements on phenyl phosphines to calculate substituent parameters for various phosphorus-containing groups.[23] Results for the PMe_2 group obtained from ^{13}C and ^{19}F NMR measurements yield $\sigma_I = 0.04$ and $\sigma_R = 0.02$. The PF_2 values are very different ($\sigma_I = 0.16$ and $\sigma_R = 0.37$), reflecting the important modifying effect of the fluorine atoms. Wuyts et al., from ^{13}C NMR measurements, give $\sigma_R = 0.22$ for the PPh_3^+ group.[25]

A major topic in the discussion of conjugation with phosphorus is the involvement of d orbitals. The d orbital occupations in $PH_2 \cdot Ph$ and $PH_3 \cdot Ph^+$ are calculated at minimal basis set level to be ca. 0.2 e and 0.3 e respectively, but recalculation at 3.21G(#) level yields the following d function population data:

	$PH_2 \cdot Ph$	$PH \cdot Ph^-$	$PH_3 \cdot Ph^+$
Gross atomic population	0.138	0.083	0.181
$d\pi$–$p\pi$ overlap population	0.011	0.007	0.021

These values are typical of compounds with P—C bonds and indicate a role for d functions intermediate between polarization (minor adjustment to the density in the bonding region) and actual valence utilization of d orbitals. Inspection of the wave function shows the functions to be involved in P—C and P—H σ-bonding, not in π-type interactions. This is also true of $PF_2 \cdot Ph$, where the total d function density is more than doubled, a typical result for compounds with P—F or P—O bonds.[9]

Hyperconjugation: vinyl and allyl phosphines

Schweig *et al.* have argued that hyperconjugation is more important in phosphines than direct conjugation with π electron systems, citing the P—C bonding orbitals as the main source of the interaction with the unsaturated system.[20] Calculations at supplemented minimal basis level on the vinyl and allyl phosphines, $C_3H_4 \cdot P(CH_3)_2$ and $C_2H_3 \cdot P(CH_3)_2$, broadly support the conclusions but not the explanations

given. (See Table VI) The π interactions are weak and at this level it is hard to separate hyperconjugative effects from steric effects. The M.O.'s of the vinyl and allyl compounds seem to be equally affected by the change from the eclipsed to the perpendicular conformation (rotation around the P—C bond in vinyl phosphine, around the C—C single bond in allyl phosphine). The energy preferences in the vinyl case (more stable in the eclipsed than in the perpendicular geometry) are probably due to steric hindrance, one C_{methyl}—C_{vinyl} distance being within 300 pm.

CONCLUSIONS

The electron distribution around phosphorus is softer and more polarizable than found for nitrogen in similar environments, and P—C interactions are characteristic of the second row element, not merely weaker copies of N—C interactions. Analysis of wave functions calculated for phosphorus(III)-carbon compounds explain why stabilizing/destabilizing interactions are usually greater for P—C than for N—C bonds, the reverse of the usual order for donor–acceptor interactions with 1st and 2nd row elements.

Calculation shows more charge flow from P following substitution and a much more profound substituent effect on the density profile of the central element than in N—C compounds. Both conjugative and hyperconjugative interactions are weaker in the 2nd row compounds, the higher energy phosphorus orbitals tending to mix with higher-lying M.O.'s of the attached groups than in the corresponding nitrogen compounds, but P—C interaction energies are still significant, particularly in PHR^- and PH_3R^+ species.

p-Only bonding in P(III) molecules is prevalent. It is to be associated with the low CPC bond angles possible around the large second row core and the consequent high non-bonding *s* orbital densities. *d* Orbitals are calculated to perform in a marginal valence role only.

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