

Theoretical Interpretation of ^{31}P NMR Chemical Shifts. I

JOHN H. LETCHER AND JOHN R. VAN WAZER

Monsanto Company, Central Research Department, St. Louis, Missouri

(Received 3 March 1965)

An ASP-LCAO-MO quantum-mechanical calculation of ^{31}P chemical shifts has been made using s , p , and d orbitals and allowing full latitude in the π bonding. This has been accomplished by use of an artfully chosen coordinate notation which allows the chemical-shift expression to be stated in a particularly simple functional form, using a minimum number of hybridization parameters. Numerical examples of the calculations are presented graphically, and they have been applied to experimental data for the symmetrically substituted 1 phosphines, 2 phosphoryl, 3 thiophosphoryl, and 4 selenophosphoryl derivatives, as well as to the 5 phosphonium salts. The calculations show that the ^{31}P chemical shift is primarily sensitive to asymmetric electronic loading and affords a method for estimating the amount of $p_{\pi}-d_{\pi}$ bonding to phosphorus.

INTRODUCTION

DURING the ten-year period that this laboratory has been publishing in the area of ^{31}P nuclear magnetic resonance (NMR) a number of attempts have been made to establish empirical correlations¹ of chemical shifts. In this paper, we are applying the mathematical approach to interpretation of chemical shifts developed by Karplus and Das² using the required matrix elements calculated by Jameson and Gutowsky.³ The only previous theoretical work⁴ on ^{31}P chemical shifts was based on the rationale developed by Saika

and Slichter⁵ for ^{19}F NMR and was applicable only to the phosphine derivatives,



Even as modified in our laboratory,⁶ this previous work was highly empirical and did not contribute much to the understanding of ^{31}P chemical shifts. In this present paper, we are taking account of the s , p , and d orbitals and covering most of phosphorus chemistry treating the compounds in which phosphorus is bonded to both three and four neighboring atoms. The case where phosphorus is bonded to five atoms will be discussed later.

¹ For example, see J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.* **78**, 5715 (1956).

² M. Karplus and T. P. Das, *J. Chem. Phys.* **34**, 1683 (1961).

³ C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.* **40**, 1714 (1964).

⁴ N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.* **78**, 3557 (1956).

⁵ A. Saika and C. P. Slichter, *J. Chem. Phys.* **22**, 26 (1954).

⁶ J. R. Parks, *J. Am. Chem. Soc.* **79**, 757 (1957).

BASIC EQUATIONS

Jameson and Gutowsky³ stated that, if all of the n bonding orbitals ψ_i for $i=1, 2, \dots, n$ are written as linear sums of atomic orbitals

$$\psi_i = \gamma_{x,i} p_x + \gamma_{y,i} p_y + \gamma_{z,i} p_z + \gamma_{z^2,i} d_{z^2} + \gamma_{xz,i} d_{xz} + \gamma_{yz,i} d_{yz} + \gamma_{xy,i} d_{xy} + \gamma_{x^2-y^2,i} d_{x^2-y^2} + s \text{ orbitals} + \text{orbitals on other atoms,} \quad (1)$$

then the elements of the charge-bond-order matrix $p_{\mu\nu}$ were defined as follows, assuming two electrons in each bonding orbital:

$$p_{\mu\nu} = \sum_{i=1}^n 2\gamma_{\mu,i} \gamma_{\nu,i}^* \quad (2)$$

In terms of these elements, the expression for the shielding was given as:

$$\begin{aligned} \sigma_{Av}^{(2)} = & - (2c^2\hbar^2/3\Delta m^2 c^2) \left(\langle 1/r^3 \rangle_p \left[(p_{xx} + p_{yy} + p_{zz}) - \frac{1}{2} (p_{zz}p_{yy} + p_{xx}p_{yy} + p_{xx}p_{zz}) + \frac{1}{2} (p_{yz}p_{zy} + p_{xy}p_{yx} + p_{xz}p_{zx}) \right] \right. \\ & + \langle 1/r^3 \rangle_d \{ 3(p_{z^2,z^2} + p_{xz,xz} + p_{xy,xy} + p_{x^2+y^2,x^2+y^2} + p_{yz,yz}) \\ & - \frac{3}{2} \left(\frac{4}{3} p_{x^2+y^2,x^2+y^2} p_{xy,xy} + p_{z^2,z^2} p_{xz,xz} + p_{z^2,z^2} p_{yz,yz} \right) \\ & - \frac{1}{2} (p_{x^2+y^2,x^2+y^2} p_{xz,xz} + p_{x^2+y^2,x^2+y^2} p_{yz,yz} + p_{xy,xy} p_{yz,yz} + p_{xy,xy} p_{xz,xz} + p_{xz,xz} p_{yz,yz}) \\ & + \frac{3}{2} \left(\frac{4}{3} p_{x^2+y^2,x^2+y^2} p_{xy,x^2+y^2} + p_{z^2,z^2} p_{xz,z^2} + p_{z^2,yz} p_{yz,z^2} \right) \\ & + \frac{1}{2} (p_{x^2+y^2,xz} p_{xz,x^2+y^2} + p_{x^2+y^2,yz} p_{yz,x^2+y^2} + p_{xy,yz} p_{yz,xy} + p_{xy,xz} p_{xz,xy} + p_{xz,yz} p_{yz,xz}) \\ & + (\sqrt{3}/2) \left[(p_{yz,yz} - p_{xz,xz}) (p_{x^2+y^2,z^2} + p_{z^2,x^2+y^2}) + (p_{xy,x^2} + p_{z^2,xy}) (p_{yz,xz} + p_{xz,yz}) \right. \\ & - (p_{z^2,yz} p_{xz,xy} + p_{yz,z^2} p_{xy,xz} + p_{z^2,xz} p_{yz,xy} + p_{xz,z^2} p_{xy,yz}) \\ & \left. + p_{z^2,yz} p_{yz,x^2+y^2} + p_{x^2+y^2,yz} p_{yz,z^2} + p_{x^2+y^2,xz} p_{xz,z^2} + p_{z^2,xz} p_{xz,x^2+y^2} \right] \\ & + \frac{1}{2} \left[p_{x^2+y^2,xz} (2p_{xy,yz} + p_{yz,xy}) + p_{xz,x^2+y^2} (p_{xy,yz} + 2p_{yz,xy}) \right. \\ & \left. - p_{x^2+y^2,yz} (2p_{xy,xz} + p_{xz,xy}) - p_{yz,x^2+y^2} (p_{xy,xz} + 2p_{xz,xy}) + (p_{yz,xz} - p_{xz,yz}) (p_{xy,x^2+y^2} - p_{x^2+y^2,xy}) \right] \}. \quad (3) \end{aligned}$$

The n bonding orbitals used in the derivation of Eq. (3) are eigenfunctions of the Hartree-Fock Hamiltonian operator for the system and therefore they are all mutually orthogonal. In order to calculate $\sigma_{Av}^{(2)}$ using molecular orbitals that depart only slightly from mutual orthogonality, we must return to the equation of Karplus and Das [Eq. (19) of Ref. 2] which states that if the total electronic ground-state wavefunction Ψ_0 is expressed as a Slater determinant

$$\Psi_0 = [(2n)!]^{-1/2} \times | \mathfrak{Z}_1(1) \mathfrak{Z}_2(2) \cdots \mathfrak{Z}_{2n}(2n) |, \quad (4)$$

where

$$\mathfrak{Z}_{2i}(k) = \psi_i(k) \alpha(k) \quad i=1, \dots, n$$

and

$$\mathfrak{Z}_{2i-1}(k) = \psi_i(k) \beta(k);$$

then

$$\sigma^{(2)} = - (e^2/\Delta m^2 c^2) \langle \Psi_0 | \sum_{k,k'} \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \Psi_0 \rangle \quad (5)$$

and

$$\sigma_{Av}^{(2)} = \frac{1}{3} \text{Tr}(\sigma^{(2)}). \quad (6)$$

The validity of the above expression does not depend upon the orthogonality of the molecular orbitals ψ_i .

If we assume that each $S_{ij} \equiv \langle \psi_i | \psi_j \rangle$ is small when $i \neq j$, then the only terms in Eq. (5) yielding significant contributions to $\sigma_{Av}^{(2)}$ over and above those terms that would be predicted under the assumption that $S_{ij} = \delta_{ij}$ for all $i, j=1, \dots, n$ are the ones in which each particle-number permutation term of the left-hand Ψ_0 differs at most by a single permutation from a term of the right-hand Ψ_0 , with the operator scalar product between these terms vanishing when all $S_{ij} = \delta_{ij}$. In other words, terms of order S_{ij}^m where $m \geq 2$ are neglected.

The expression for $\sigma^{(2)}$ can be written as a linear sum over four terms \mathbf{T}_μ , $\mu=1, \dots, 4$. \mathbf{T}_1 and \mathbf{T}_2 are those generated in the double sum over electron numbers k and k' when $k=k'$, the other two when $k \neq k'$. In addition, \mathbf{T}_2 and \mathbf{T}_4 will be those terms that vanish when $S_{ij} \equiv \delta_{ij}$ so that they contain the effect of the nonorthogonality of the molecular orbitals on $\sigma_{Av}^{(2)}$.

When $k=k'$,

$$\langle \Psi_0 | \mathbf{1}_k \mathbf{1}_k / r_k^3 | \Psi_0 \rangle$$

$$= \sum_{i=1}^{2n} \sum_{j=1}^{2n} \langle \mathcal{Z}_i(k) | \mathbf{1}_k \mathbf{1}_k / r_k^3 | \mathcal{Z}_j(k) \rangle \langle \mathcal{Z}_j(k) | \mathcal{Z}_i(k) \rangle \mathcal{N}_{ij}, \quad (7)$$

where $\mathcal{N}_{ij} = -1$ when i and j are unequal and both are odd or both even; it is zero otherwise, unless $i=j$, in which case $\mathcal{N}_{ii} = 1$. We can now say that

$$\mathbf{T}_1 = 2 \sum_{i=1}^{2n} \langle \psi_i | \mathbf{1}_k \mathbf{1}_k / r_k^3 | \psi_i \rangle \quad (8)$$

and

$$\mathbf{T}_2 = 2 \sum_{i=1}^{2n} \sum_{j=1, j \neq i}^{2n} \langle \psi_i | \mathbf{1}_k \mathbf{1}_k / r_k^3 | \psi_j \rangle S_{ij}. \quad (9)$$

The factor of 2 in both of the above expressions comes from summation over the spin states α and β .

When $k \neq k'$ we find that

$$\mathbf{T}_3 + \mathbf{T}_4 = \langle \Psi_0 | \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \Psi_0 \rangle,$$

where

$$\mathbf{T}_3 = \sum_{i=1}^{2n} \sum_{j=1, j \neq i}^{2n} \langle \mathcal{Z}_i(k) \mathcal{Z}_j(k') | \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \mathcal{Z}_j(k') \mathcal{Z}_i(k) \rangle - \langle \mathcal{Z}_i(k) \mathcal{Z}_j(k') | \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \mathcal{Z}_i(k') \mathcal{Z}_j(k) \rangle \quad (10)$$

and

$$\mathbf{T}_4 = \sum_{i=1}^{2n} \sum_{j=1, j \neq i}^{2n} \sum_{m=1, m \neq i, m \neq j}^{2n} \langle \mathcal{Z}_i(k) \mathcal{Z}_j(k') | \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \mathcal{Z}_m(k) \mathcal{Z}_i(k') \rangle \langle \mathcal{Z}_j(k'') | \mathcal{Z}_m(k'') \rangle$$

$$+ \langle \mathcal{Z}_i(k) \mathcal{Z}_j(k') | \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \mathcal{Z}_m(k) \mathcal{Z}_j(k') \rangle \langle \mathcal{Z}_i(k'') | \mathcal{Z}_m(k'') \rangle$$

$$- \langle \mathcal{Z}_i(k) \mathcal{Z}_j(k') | \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \mathcal{Z}_i(k) \mathcal{Z}_m(k') \rangle \langle \mathcal{Z}_j(k'') | \mathcal{Z}_m(k'') \rangle$$

$$- \langle \mathcal{Z}_i(k) \mathcal{Z}_j(k') | \mathbf{1}_k \mathbf{1}_{k'} / r_k^3 | \mathcal{Z}_j(k) \mathcal{Z}_m(k') \rangle \langle \mathcal{Z}_i(k'') | \mathcal{Z}_m(k'') \rangle. \quad (11)$$

When S_{ij} is small for $i=j$, $|\mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3| \gg |\mathbf{T}_4|$, and as \mathbf{T}_1 and \mathbf{T}_3 will ultimately yield an expression almost identical to that of Eq. (3) (the above expression for \mathbf{T}_3 has not neglected terms which were dropped by Karplus and Das as being small), \mathbf{T}_2 is the only term needed to correct Eq. (3) for the nonorthogonality of the basis molecular orbitals.

Expanding Eq. (9) in terms of the central-atom (phosphorus) atomic orbitals, φ_ν , we find that

$$\mathbf{T}_2 = 2 \sum_{i=1}^{2n} \sum_{j=1, j \neq i}^{2n} \sum_{\mu=1}^{\alpha} \sum_{\nu=1}^{\alpha} \gamma_{\mu i} \gamma_{\nu j} S_{ij} \langle \varphi_\mu | \mathbf{1}_k \mathbf{1}_k / r_k^3 | \varphi_\nu \rangle \quad (12)$$

and

$$T_2 = \frac{1}{3} \text{Tr}(\mathbf{T}_2) = \frac{1}{3} (T_{2xx} + T_{2yy} + T_{2zz}), \quad (13)$$

where α is the total number of atomic orbitals used for bonding by the central atom

The above matrix elements $\langle \varphi_\mu | l_{k\epsilon} l_{k\epsilon} / r_k^3 | \varphi_\nu \rangle$, $\epsilon = x, y, z$ have been tabulated by Jamison and Gutowsky.³ In all cases of interest here, the magnitude of \mathbf{T}_2 will be much smaller than that of \mathbf{T}_1 ; but, if the S_{ij} terms are sufficiently large, nothing can be said about the relative magnitudes of \mathbf{T}_2 and \mathbf{T}_3 .

Since the NMR chemical shift is determined by the occupation numbers of the atomic orbitals used in the ground-state total electronic wavefunction, this measurement is attributable to the "collective properties"

of the orbital electrons as defined by Dewar.⁷ This author points out that localized two-electron wavefunctions are adequate for representing such time-averaged phenomena, although they may be expected to fail for treating those events (e.g., spectral emission) which depend on the individual electronic configurations.

DEFINITIONS OF WAVEFUNCTIONS USED

In a bond the axis of which forms the z axis in a coordinate system where the origin is defined by the position of the nucleus of the central atom, the σ molecular orbital can use the s , p_z , and d_{z^2} orbitals only; whereas the two perpendicular π orbitals use p_x hybridized with d_{xz} and p_y hybridized with d_{yz} , respectively. In this treatment, δ bonding is neglected. Such δ bonds would use the $d_{x^2-y^2}$ and d_{xy} orbitals. If the bond axis suffers two orthogonal rotations such that the coordinate unit vectors are transformed into a primed set by a rotation of an angle φ about z with a subsequent rotation of $(\pi/2 + \eta)$ about the x' axis, the same orbitals (defined in the primed coordinate system) will be used in each type of molecular orbital. It is known that the three p orbitals defined in the primed system can each be expressed as linear combinations of the three p orbitals in the unprimed system. This is also true of the five d orbitals. Therefore if η and φ

⁷ M. J. S. Dewar, *Tetrahedron* **19**, Suppl. **2**, 89 (1963).

define a bond axis, the atomic orbitals used in this bond are

$$\psi_{\sigma i}(p) = \psi(p_{z'}) = \cos\eta \sin\phi\psi(p_x) + \cos\eta \cos\phi\psi(p_y) - \sin\eta\psi(p_z), \quad (14)$$

$$\begin{aligned} \psi_{\sigma i}(d) = \psi(d_{z'}) = & (1 - \frac{3}{2} \cos^2\eta)\psi(d_{zz}) - (\sqrt{3}/2) \sin 2\eta \sin\phi\psi(d_{xz}) \\ & - (\sqrt{3}/2) \sin 2\eta \cos\phi\psi(d_{yz}) + (\sqrt{3}/2) \cos^2\eta \sin 2\phi\psi(d_{xy}) - (\sqrt{3}/2) \cos^2\eta \cos 2\phi\psi(d_{x^2-y^2}), \end{aligned} \quad (15)$$

$$\psi_{\pi 1i}(p) = \psi(p_{z'}) = \cos\phi\psi(p_x) - \sin\phi\psi(p_y), \quad (16)$$

$$\psi_{\pi 1i}(d) = \psi(d_{z'}) = -\sin\eta \cos\phi\psi(d_{xz}) + \sin\eta \sin\phi\psi(d_{yz}) + \cos\eta \cos 2\phi\psi(d_{xy}) + \cos\eta \sin 2\phi\psi(d_{x^2-y^2}), \quad (17)$$

$$\psi_{\pi 2i}(p) = \psi(p_{y'}) = -\sin\eta \sin\phi\psi(p_x) - \sin\eta \cos\phi\psi(p_y) - \cos\eta\psi(p_z), \quad (18)$$

$$\begin{aligned} \psi_{\pi 2i}(d) = \psi(d_{y'}) = & (\sqrt{3}/2) \sin 2\eta\psi(d_{zz}) - \cos 2\eta \sin\phi\psi(d_{xz}) \\ & - \cos 2\eta \cos\phi\psi(d_{yz}) - \frac{1}{2} \sin 2\eta \sin 2\phi\psi(d_{xy}) + \frac{1}{2} \sin 2\eta \cos 2\phi\psi(d_{x^2-y^2}). \end{aligned} \quad (19)$$

The specific molecular types under study are PZ_3 , PZ_4 , and MPZ_3 , where P represents the element phosphorus; M, a substituent which is often an electron-pair acceptor; and Z, a monofunctional substituent. We therefore wish to characterize the bonding orbitals in which three or four atoms (the substituents) are attached to a central atom.

Confining attention to the MPZ_3 structure, we cause the axis of the M-P bond to form the positive z axis of a Cartesian-coordinate system in which the phosphorus nucleus is the origin. We then complete the geometric specification of the molecule by the definition of four angles, η and φ_i , where $i=1, 2$, and 3 . η is the angle between a P-Z bond axis

and the xy plane, an angle which from symmetry is the same for all three Z substituents; and φ_i is the angle between an arbitrary line through the origin in the xy plane and the projection of the i th P-Z bond axis onto the xy plane. In all of the above molecular types, symmetry dictates that $\varphi_3 = \varphi_2 + \frac{2}{3}\pi = \varphi_1 + \frac{4}{3}\pi$.

It is noted that each molecular orbital is defined in such a way so as to assure the presence of the proper number as well as the proper orientation of each of the required nodal planes in the charge distribution of each molecular orbital. We therefore say that the ground-state wavefunction can be expressed by the following equations:

$$\psi_{\sigma i} = \alpha\psi(s) + \gamma_1\psi_{\sigma i}(p) + \gamma_2\psi_{\sigma i}(d) + \omega_{\sigma i}\psi_{\sigma Z} \quad (\text{on Atom } Z_i), \quad i=1, 2, 3 \quad (20)$$

$$\psi_{\sigma 4} = \beta\psi(s) + \gamma_3\psi_{\sigma 4}(p_z) + \gamma_4\psi_{\sigma 4}(d_{zz}) + \omega_{\sigma 4}\psi_{\sigma M} \quad (\text{on Atom M}), \quad (21)$$

$$\psi_{\pi 1i} = \gamma_5\psi_{\pi 1i}(p) + \gamma_6\psi_{\pi 1i}(d) + \omega_{\pi 1i}\psi_{\pi 1Z} \quad (\text{on Atom } Z_i), \quad (22)$$

$$\psi_{\pi 2i} = \gamma_7\psi_{\pi 2i}(p) + \gamma_8\psi_{\pi 2i}(d) + \omega_{\pi 2i}\psi_{\pi 2Z} \quad (\text{on Atom } Z_i), \quad (23)$$

$$\psi_{\pi 14} = \gamma_9\psi_{\pi 14}(p_x) + \gamma_{10}\psi_{\pi 14}(d_{xz}) + \omega_{\pi 14}\psi_{\pi 1M} \quad (\text{on Atom M}), \quad (24)$$

$$\psi_{\pi 24} = \gamma_{11}\psi_{\pi 24}(p_y) + \gamma_{12}\psi_{\pi 24}(d_{yz}) + \omega_{\pi 24}\psi_{\pi 2M} \quad (\text{on Atom M}). \quad (25)$$

Bonds 1, 2, and 3 are associated with the three Z substituents whereas Bond 4 is associated with the substituent M.

The rotation angles η and φ_i are defined in such a manner that, by symmetry arguments, the twofold decomposition of the orbitals into symmetry types can be shown to make the sum of p_x and $d_{x'z'}$ as well as the sum of p_y and $d_{y'z'}$ equivalent for each of the three P-Z_i bonds. This procedure has the advantage that a minimum number of hybridization parameters are employed to specify fully the bonding orbitals in the molecules.

Using the molecular orbital delineation method proposed here, it is impossible to orthogonalize all of these orbitals by adjustment of relationships between atomic

orbital occupation numbers. Nevertheless, it is felt that the orbital hybridization parameters will assume relationships which lead to orthogonality for as many of these orbitals as possible, in the order of their relative importance as far as bonding is concerned. With this in view, we have forced all σ molecular orbitals to be orthogonal. On this basis, the conditions dictated to the σ -orbital occupation numbers γ_i by the vanishing of their respective scalar products are given by

$$\begin{aligned} \langle \sigma_i | \sigma_j \rangle = & \alpha^2 + \gamma_i^2 (1 - \frac{3}{2} \cos^2\eta) \\ & + \gamma_j^2 (1 - \frac{3}{2} \cos^2\eta + \frac{2}{3} \cos^4\eta) = 0, \\ & i=1, 2, 3 \quad \text{and} \quad j=1, 2, 3; i \neq j \end{aligned} \quad (26)$$

and

$$\langle \sigma_i | \sigma_4 \rangle = \alpha\beta - \gamma_1\gamma_3 \sin\eta + \gamma_2\gamma_4(1 - \frac{3}{2} \cos^2\eta) = 0, \\ i = 1, 2, 3. \quad (27)$$

It is also assumed that the hybridization parameters will attain values such that the σ system will be orthogonal to the π system, leaving a π network in which a degree of delocalization will be present (this is predicted by the finite electronic-transition probabilities from one π orbital to another due to nonvanishing of their respective scalar products) but again, these statistical fluctuations will be averaged out in the NMR measurement. The consequences of the orthogonality of the σ and π systems are discussed later in the section concerned with the effect of π bonding on the chemical shift.

THEORY OF ³¹P CHEMICAL SHIFTS

Expression of the Chemical Shift

We are now in a position to calculate the charge-bond-order matrix. This is done by a relatively simple prescription, e.g., to calculate the p_{xx} , it is necessary only to multiply the number of electrons in each molecular orbital (=2) by the sum of the squares of the normalized coefficients of the p_x atomic orbital in that molecular orbital. This sum extends over all molecular orbitals. As previously stated, the chosen coordinate notation causes such sums generated over the variables ϕ_i to take simple numerical values. For

instance

$$\sum_{i=1}^3 \sin\phi_i = 0, \quad \sum_{i=1}^3 \sin^2\phi_i = \frac{3}{2},$$

etc. When this procedure is followed, it is found that the nonzero elements of the charge-bond-order matrix are

$$p_{xx} = p_{yy} = \frac{3}{2}\gamma_1^2 \cos^2\eta + \frac{3}{2}\gamma_6^2 + \frac{3}{2}\gamma_7^2 \sin^2\eta + \gamma_9^2 \equiv s_1, \quad (28)$$

$$p_{xz} = 3\gamma_1^2 \sin^2\eta + \gamma_3^2 + 3\gamma_7^2 \cos^2\eta \equiv s_2, \quad (29)$$

$$p_{x^2z^2} = \gamma_4^2 + 3\gamma_2^2(1 - \frac{3}{2} \cos^2\eta)^2 + \frac{3}{4}\gamma_8^2 \sin^2 2\eta \equiv t_1, \quad (30)$$

$$p_{xxzz} = p_{yyzz} \\ = \gamma_{10}^2 + \frac{9}{8}\gamma_2^2 \sin^2 2\eta + \frac{3}{2}\gamma_6^2 \sin^2\eta + \frac{3}{2}\gamma_8^2 \cos^2 2\eta \equiv t_2, \quad (31)$$

$$p_{xyxy} = p_{x^2y^2x^2y^2} \\ = \frac{9}{8}\gamma_2^2 \cos^4\eta + \frac{3}{2}\gamma_6^2 \cos^2\eta + \frac{3}{8}\gamma_8^2 \sin^2 2\eta \equiv t_3, \quad (32)$$

$$p_{xxxy} = p_{yyx^2y^2} \\ = \frac{9}{8}\gamma_2^2 \sin 2\eta \cos^2\eta - \frac{3}{4}\gamma_6^2 \sin 2\eta - \frac{3}{4}\gamma_8^2 \cos 2\eta \sin 2\eta \equiv t_4. \quad (33)$$

In obtaining Eqs. (18) and (21), the fact that $\gamma_9^2 = \gamma_{11}^2$ and $\gamma_{10}^2 = \gamma_{12}^2$ was employed. This fact is demonstrated by symmetry arguments in a following section on the π -bond effect.

The NMR chemical shift δ is thus given by the following reduced form of Eq. (3) with the correction for the nonorthogonality of the molecular orbitals.

$$\sigma_{Av}^{(2)} = \delta - \delta_0 = - (2e^2\hbar^2/3\Delta m^2 c^2) \\ \times \{ \langle r^{-3} \rangle_p [2s_1 + s_2 - \frac{1}{2}s_1^2 - s_1s_2 + T_{2p}] + \langle r^{-3} \rangle_d [3t_1 + 6t_2 + 6t_3 - 2t_3^2 - 3t_1t_2 - 2t_2t_3 - \frac{1}{2}t_2^2 - 2t_4^2 + T_{2d}] \}, \quad (34)$$

where δ_0 is a constant determined by the choice of shift-reference sample and T_{2p} and T_{2d} are the contributions to the chemical shift due to nonorthogonality of the basis molecular orbitals. We now define ζ_1 and ζ_2 such that

$$\delta - \delta_0 = [-2e^2\hbar^2/3m^2c^2](1/\Delta) [\langle r^{-3} \rangle_p \zeta_1 + \langle r^{-3} \rangle_d \zeta_2]. \quad (35)$$

The term ζ_1 is determined solely by the p -orbital occupation while ζ_2 is determined by d -orbital occupation only. The first term in the above equation, $-2e^2\hbar^2/3m^2c^2$, contains only atomic constants while the term $1/\Delta$, the reciprocal of the mean excitation energy, should be somewhat different for each different phosphorus molecule. Realizing that this term is a rough measure of the transition energy from the ground state to the first excited singlet state, one should expect on the basis of chemical regularity that it will be about equal for all triply connected phosphorus compounds, and also about equal for all quadruply connected compounds. However, these two values should differ

from each other, due primarily to the presence of the excess negative charge residing in the phosphorus atomic orbitals caused by the full double occupancy of the atomic orbitals in the abortive σ bond (unshared pair) of the triply connected phosphorus. The expectation values of r^{-3} averaged over the p and d phosphorus orbital are impossible to calculate theoretically at this time as molecular phosphorus self-consistent-field (SCF) wavefunctions are unavailable. The value of $\langle r^{-3} \rangle$ could be evaluated from spin-rotation constants⁸ but appropriate data are unavailable. It is true that good SCF wavefunctions exist for the chemically uncombined phosphorus atom. However, such wavefunctions will be highly perturbed when used to characterize phosphorus molecules, due to the strong fields generated by the propinquity to the phosphorus of its substituents. It would, however, be a reasonably fair statement to say that $\langle r^{-3} \rangle_p$ should be constant over molecules of the same type. As the d orbitals are

⁸ W. H. Flygare, J. Chem. Phys. **41**, 793 (1964).

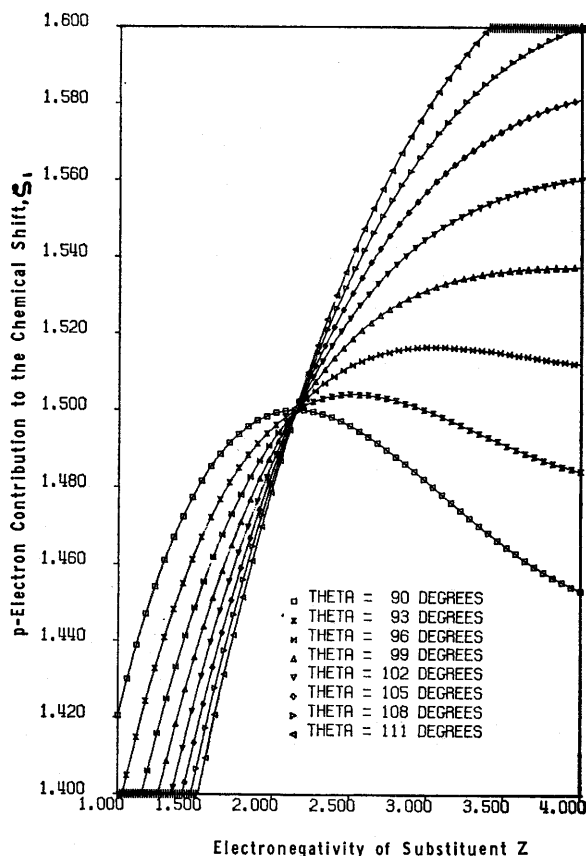


FIG. 1. The contribution, ζ_1 , to the theoretical chemical shift for symmetrically substituted phosphines, PZ_3 , as a function of the electronegativity and the ZPZ bond angle θ , assuming that only s and p orbitals are used in bonding, with effect of the π bonding being omitted. This plot was mechanically produced by the computer.

less shielded from external fields than the p orbitals, the term $\langle r^{-3} \rangle_d$ should have a slight dependency upon the mean value of the charge existing in the phosphorus atomic orbitals, therefore upon the electronegativity of the substituents. However, it is assumed that this effect is negligible. Therefore, we shall describe the ^{31}P chemical shift by the expression

$$\delta - \delta_0 \equiv B(\nu)\zeta_1 + B(\nu)f(\nu)\zeta_2, \quad (36)$$

where B is a function of the phosphorus coordination number ν only, as is

$$f(\nu) \equiv \langle r^{-3} \rangle_d / \langle r^{-3} \rangle_p. \quad (37)$$

A factor which must be taken into account in these calculations is the total charge on the PZ_4 structures, e.g., PR_4^+ , PCl_4^+ , PO_4^{3-} , and PS_4^{3-} . For all of these structures, there are still the required two electrons in each molecular orbital contributing to the valence charge-bond-order matrix so that the charge (due to separation of un-ionized molecules into anions and cations) should be rather well distributed about the

nuclear framework. This situation will change the occupation numbers of the charge-bond-order matrix only inasmuch as the charge shrinks the atomic orbital radial functions. Therefore, if this charge is to have any appreciable effect on the ^{31}P chemical shift, it will be manifest in the mean-excitation potential Δ , and/or the expectation values, $\langle r^{-3} \rangle$, and is expected to show up, if at all, in the term $B(\nu)$.

Effect of Sigma Bonds

Through energy-minimization arguments, it can be shown that σ bonds will use s and p orbitals primarily. Therefore, in order to determine the elements of the charge-bond-order matrix, it is necessary to obtain an expression that relates a physical observable to a function of the orbital occupation numbers. We resort to the Coulson-modified⁹ Pauling definition of electronegativity χ , which states that the average amount of charge residing in the atomic orbitals of one atom of a two-atom bond is given by the expression

$$h_A = 1.0 + 0.16(\chi_P - \chi_A) + 0.035(\chi_P - \chi_A)^2. \quad (38)$$

We now make the statement that the average amount of charge residing in the phosphorus atomic orbitals due to one P-Z σ bond is given by $(\alpha^2 + \gamma_1^2 + \gamma_2^2)$. Likewise, the average amount of charge residing in the phosphorus atomic orbitals from those electrons in the M-P σ bond is given by $(\beta^2 + \gamma_3^2 + \gamma_4^2)$. If the electronegativity differences $(\chi_P - \chi_A)$, are known, and this information is coupled with the two orthogonality requirements [Eqs. (16) and (17)], we still have two degrees of freedom in the specification of the σ -orbital occupation numbers. If we say, however, that s and p orbitals are used exclusively, $\gamma_2^2 = \gamma_4^2 = 0$, then the occupation numbers α , β , γ_1 , and γ_3 are uniquely determined. These as a rule will all be functions of the bond angle, η . In the triply connected phosphorus compounds, h_M equals 2, which expresses the fact that the two electrons in the abortive σ bond (unshared electron pair) reside exclusively in phosphorus atomic orbitals.

Figure 1 expresses the calculated values of ζ_1 as a function of the electronegativity of the substituent Z , and it also shows the effect of varying the ZPZ bond angle¹⁰ θ . ζ_1 is calculated assuming neither π bonding nor configuration interaction, which is the mixing of p and d (plus, perhaps, higher molecular orbitals) in a given molecular-bonding type. The amount of configuration interaction is generally small, as can simply be seen by comparing overlap integrals between an s

⁹ C. A. Coulson, *Valence* (Oxford University Press, London, 1963), corrected 2nd ed., p. 141.

¹⁰ The bond angle η employed in our mathematics is related to the ZPZ bond angle θ customarily used in x-ray diffraction work by the relationship

$$\eta = \arccos[(2/\sqrt{3}) \sin \frac{1}{2}\theta].$$

orbital of the Z substituent and either the p_x or d_{x^2} orbitals of the phosphorus. The σ system would preferentially use s and p orbitals; while in π bonding the overlap of the d_{xz} orbital with a p_x orbital on the Z substituent should, in general, be larger than a p_x - p_x overlap.

In the PZ_4 molecules, the four substituents are identical, therefore $\gamma_1 = \gamma_3$, $\gamma_2 = \gamma_4$, and $\alpha = \beta$. The bond angle is fixed, as the molecule is tetrahedral ($\cos^2 \eta = \frac{8}{9}$). Figure 2 shows the calculated values of ζ_1 as a function of the electronegativity of the Z substituent.

Figures 3, 4, and 5 show the calculated values for the MPZ_3 molecular type of ζ_1 as a function of the electronegativity of the Z substituent, the electronegativity of the M substituent and the bond angle θ . Again, these plots demonstrate the contribution to the chemical shift of only the σ electrons.

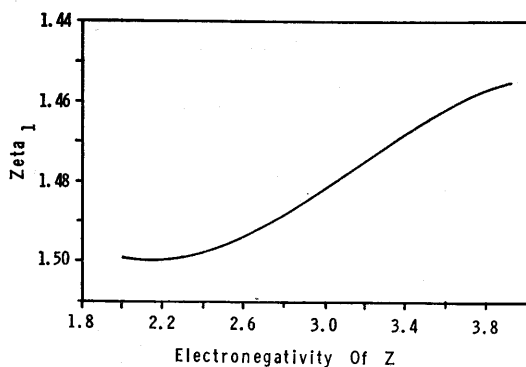


FIG. 2. The contribution, ζ_1 , to the theoretical chemical shift for the totally symmetrical quadruply connected phosphorus compounds (molecules of the type PZ_4) as a function of the electronegativity of the substituent Z. The molecules are all tetrahedral, and it is assumed that only s and p orbitals are used, with the effect of the π bonding being omitted.

Figure 6 shows ζ_1 and ζ_2 calculated for several given substituent electronegativities under conditions where configuration interaction is allowed in the PZ_4 molecular type.

Pi-Bond Effect

When it is assumed that σ bonds use s and p orbitals only, orthogonality suggests the use of only the d orbitals in the π bonds. If some d character is allowed in the σ system, orthogonality automatically requires the use of a definite proportion of p character in the π system. Confinement of the σ system to s and p orbitals will be justified later by regularities that occur between experimental data and the theoretical shifts calculated on the assumption of no d character in the σ bonds. We therefore employ the phosphorus d orbitals primarily in the treatment of π bonding.

When this is done, all σ molecular orbitals can be forced to be mutually orthogonal using only s and p

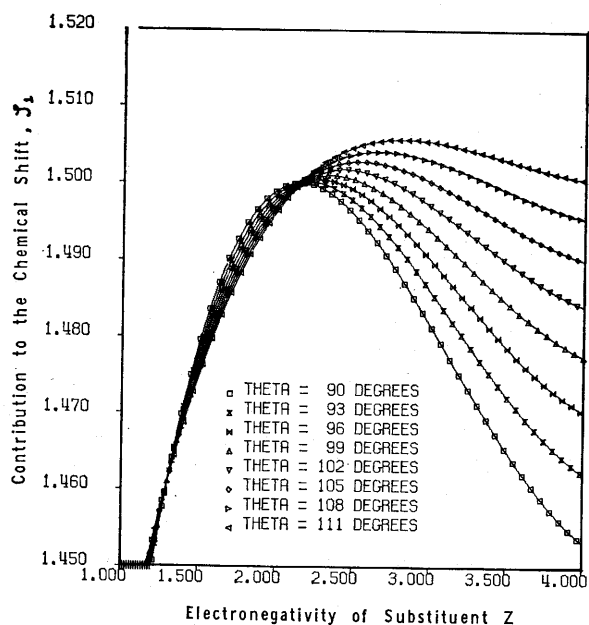


FIG. 3. The contribution, ζ_1 , to the theoretical chemical shift for molecules of the form MPZ_3 as a function of the electronegativity of the Z substituent and the ZPZ bond angle θ . It is assumed that only s and p orbitals are used, with the effect of the π bonding being omitted. The electronegativity of the M substituent is 1.3. This plot was mechanically produced by the computer.

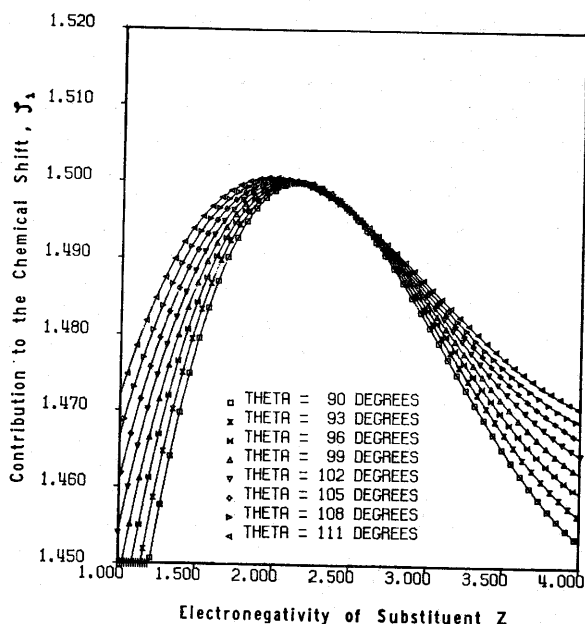


FIG. 4. The contribution, ζ_1 , to the theoretical chemical shift for molecules of the form MPZ_3 as a function of the electronegativity of the Z substituent and the ZPZ bond angle θ . It is assumed that only s and p orbitals are used, with the effect of the π bonding being omitted. The electronegativity of the M substituent is 2.8. This plot was mechanically produced by the computer.

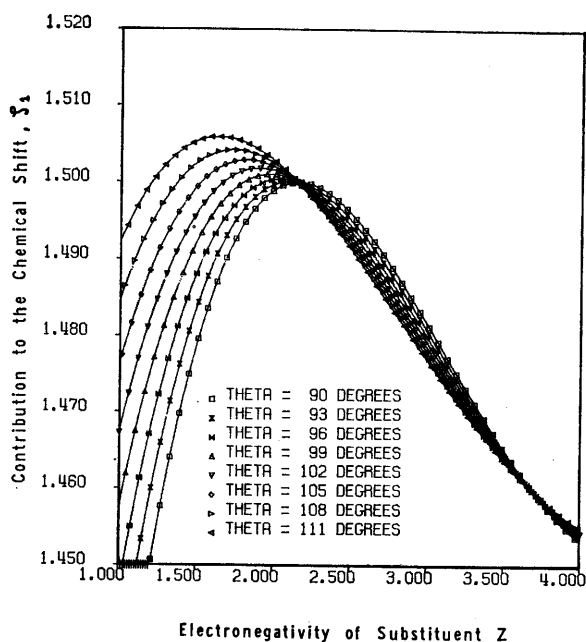


FIG. 5. The contribution, ζ_1 , to the theoretical chemical shift for molecules of the form MPZ_3 as a function of the electronegativity of the Z substituent and the ZPZ bond angle θ . It is assumed that only s and p orbitals are used, with the effect of the π bonding being omitted. The electronegativity of the M substituent is 3.7. This plot was mechanically produced by the computer.

orbitals (i.e., $T_{2p} \equiv 0$) and all σ molecular orbitals will be orthogonal to all π orbitals. This leaves a degree of delocalization within the π network; but, in all experimental cases studied, the occupation of the phosphorus d_π orbitals is small. This is dictated by the fact that, if a given π two-electron bond never donates more than 0.24 electrons to the phosphorus d_π orbitals, so then at no time can the normalized γ_π^2 be greater than 0.12 so that no S_{ij} computed from the π molecular orbitals will exceed 0.06. This justifies the use of Eqs. (12) and (13) to correct for nonorthogonality of the π wavefunctions. In the experimental case showing the most π bonding, S_{ij} is found to be no greater than 0.06 for all i and j , with $i=j$. For all of the experimental cases, T_{2d} was found to contribute less than 1% of those terms constituting Eq. (3), that the slight non-orthogonality of the basis molecular orbitals can, for the purposes considered here, be ignored. In the application to experimental data, the nonorthogonality was first ignored. Then an elaborate computer study of the effect of added terms which were both first and second order in S_{ij} was carried out. This showed that these added terms were insignificant.

All of the molecular forms presently under discussion possess at least C_{3v} symmetry. This means that a rotation of $2\pi/3$ about the M-P bond axis will preserve the form of all wavefunctions. Let us now consider the two orthogonal π orbitals in the M-P bond. As a rotation of $2\pi/3$ will not give identical wavefunctions and as symmetry requires that these rotated wave-

functions be equivalent to the original ones, the initial π orbitals of Types 1 and 2 (the perpendicular ones in a given bond) must be equivalent. That is to say that $\gamma_9^2 = \gamma_{11}^2$ and $\gamma_{10}^2 = \gamma_{12}^2$. By the same argument it can readily be seen that the Type-1 π orbitals must be equivalent for all three P-Z_i bonds and that it is also true for the Type 2; but it does not require that orbitals of Types 1 and 2 be equivalent to each other in a P-Z_i bond. It is shown later, however, that nonequivalence of these orbitals has little effect on the chemical shift so, for convenience, we take them to be equivalent, thus, $\gamma_6^2 = \gamma_8^2$.

For molecules of the type PZ_3 , $\gamma_{10}^2 = \gamma_{12}^2 = \gamma_9^2 = \gamma_{11}^2 = 0$, as there can be no π interaction from a nonexistent substituent. For molecules of the type MPZ_3 , $\gamma_{10}^2 = \gamma_{12}^2$, which equals a value which is not necessarily zero; and again we set $\gamma_6^2 = \gamma_8^2$ for the sake of convenience. For molecules of the type PZ_4 , all π orbitals in all

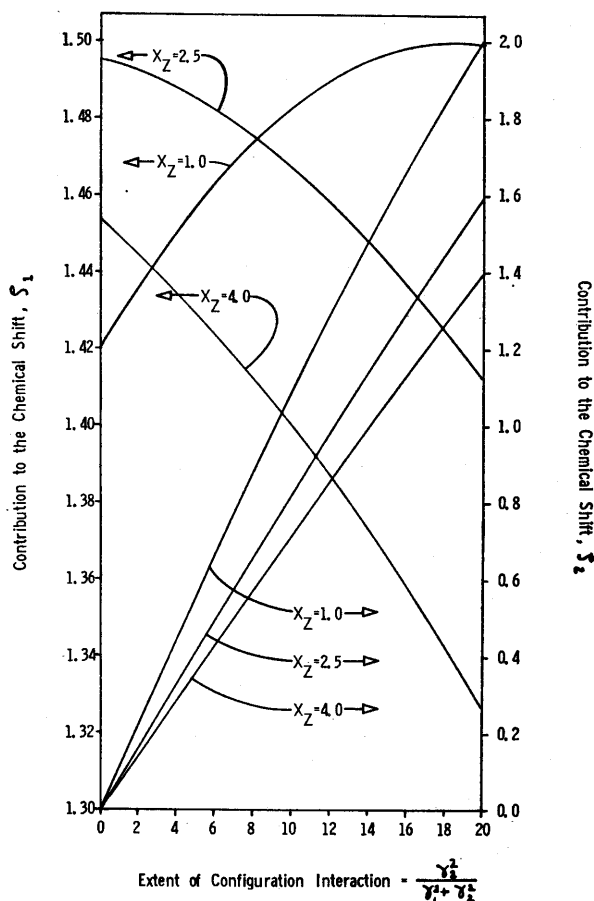


FIG. 6. The plot, as a function of the relative amount of d character in each bond, of the contributions to the chemical shift, ζ_1 and ζ_2 , due only to σ electrons in the tetrahedrally symmetric molecules of the type PZ_4 in which s , p , and d orbitals are used in σ bonding. This is to say, the extent of configuration interaction is determined by the relative amount of d character used in the σ bond—an amount which is expressed by the ratio of the number of d electrons to the sum of the number of p and d electrons [$\gamma_d^2 / (\gamma_p^2 + \gamma_d^2)$] used in each σ bond.

bonds are equivalent, therefore the condition $\gamma_6^2 = \gamma_8^2$ is no longer simply a convenience but is a requirement of symmetry. When $\gamma_6^2 = 0.1$, approximately 0.6, 0.6, and 0.8 electrons have been transferred by all of the Z_i substituents to the phosphorus atomic orbitals for the molecular types PZ_3 , MPZ_3 , and PZ_4 , respectively. When, in the MPZ_3 structure, $\gamma_{10}^2 = 0.1$, approximately 0.2 electrons have been transferred to the phosphorus from the substituent M.

In terms of these occupation numbers, the π contribution, ζ_2 , computed both with and without the term T_{2a} to the chemical shift for each molecular type was calculated. The dependence of ζ_2 upon γ_6^2 and γ_{10}^2 exhibited approximately the behavior

$$\zeta_2 = A_1(\theta)\gamma_6^2 + A_2(\theta)\gamma_{10}^2, \quad (39)$$

where the functions of the bond angle $A_1(\theta)$ and $A_2(\theta)$ are tabulated in Table I for each molecular type. One

TABLE I. Values of $A_1(\theta)$ and $A_2(\theta)$ for each molecular type as a function of bond angle.

Bond angle (θ)	PZ_3		PZ_4		MPZ_3	
	A_1	A_2			A_1	A_2
90°	16.87	0.0	16.87	5.01
100°	16.77	0.0	16.77	5.13
			A_1	A_2		
110	16.76	0.0	16.53 ^a	5.51 ^a	16.76	5.29
120°	16.99	0.0	16.99	5.50

^a This value corresponds to the tetrahedral angle ($\theta \approx 109.5^\circ$).

must remember that in the PZ_3 compounds $\gamma_{10}^2 \equiv 0$, and in the PZ_4 compounds the bond angle is the tetrahedral angle ($\theta \approx 109.5^\circ$) only and $\gamma_6^2 \equiv \gamma_{10}^2$. Figure 7 is a plot of the exact calculated values of ζ_2 for the PZ_4 molecule. These are compared with the straight line dictated by the above equation. In no instance was there a greater deviation from the linear relation between γ_6^2 and ζ_2 at constant bond angle than is shown in this plot.

It is of interest to test the assumption that, in the structure types other than PZ_4 , $\gamma_6^2 = \gamma_8^2$. Values of ζ_2 were calculated at many bond angles holding invariant (but then allowing it to assume different values) the total amount of π interaction from each Z substituent ($\gamma_6^2 + \gamma_8^2 = \text{constant}$) but allowing γ_6^2 to have the magnitude of $k\gamma_8^2$, where $k = 0.8, 0.9, 1.0, 1.1, \text{ and } 1.2$. It can readily be seen from Table II that in each case the effect on the value of ζ_2 of asymmetric loading of each π orbital is indeed small, as is the effect of bond angle. It would seem that the π contribution to the chemical shift is not only approximately a linear func-

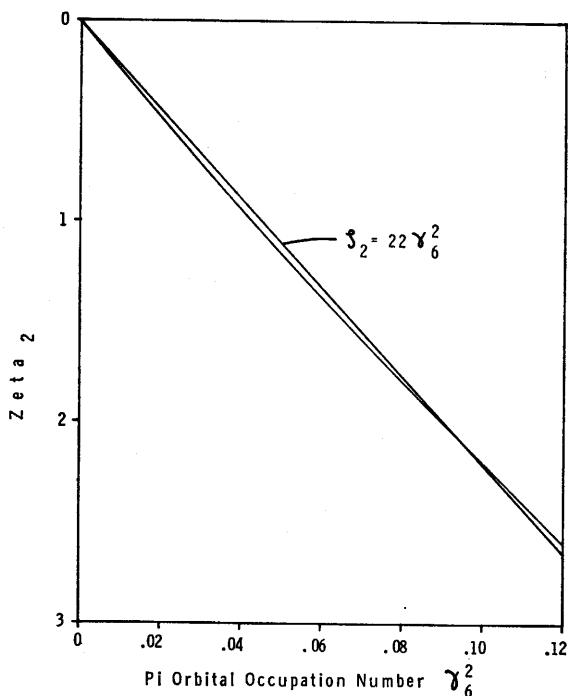


FIG. 7. Calculated values of the contribution to the chemical shift, ζ_2 , as a function of the π orbital occupation number, γ_6^2 , in molecules of the type PZ_4 . Also plotted is the straight line predicted by Eq. (29) in the text.

tion of the total amount of π interaction, but also that each Z_i substituent produces approximately an additive and independent contribution to ζ_2 .

In π -bond-vs-no-bond resonance, the electrons of the σ system exhibit a finite probability of being found in a nonorthogonal (to the σ system) π orbital. Although this phenomenon does not show up explicitly in the LCAO-MO formalism, it may be expressed therein by allowing a certain amount of $p_\pi - p_\pi$ bonding while reducing equivalently the number of electrons in the σ orbitals. Simple calculations have demonstrated that withdrawing some electronic charge from the p_σ atomic orbitals and donating it directly to the p_π atomic orbitals leads to no change in the calculated chemical

TABLE II. Values of $A_1(\theta)$ and $A_2(\theta)$ for the MPZ_3 molecular type as a function of the asymmetry of occupation k of the two π orbitals in each P-Z bond.

$k = \gamma_6^2 / (\gamma_6^2 + \gamma_8^2)^a$	MPZ_3	
	A_1	A_2
	$\theta = 104^\circ$	
0.40	16.69	5.23
0.45	16.72	5.21
0.50	16.75	5.18
0.55	16.77	5.16
0.60	16.78	5.14

^a γ_6^2 and γ_8^2 are the occupation numbers of the two π orbitals in each P-Z bond.

TABLE III. Experimental data and resulting π bonding for the symmetrically substituted phosphines.

Molecule	Electro- negativity χ_Z	Bond angle θ	Chemical shift (ppm) δ	Estimated number of π electrons per P atom		
				From ^{31}P NMR ^b	From the bond distance ^c	
				$S+S$	H	
PH_3	2.20	93.5°	240	0.000	0.3	0.3
$\text{P}(\text{CN})_3$	2.52	(97) ^a	142 136	0.007
$\text{P}(\text{CH}_3)_3$	2.60	100	62	0.000	0.3	0.0
$\text{P}(\text{C}_6\text{H}_5)_3$	2.70	(102)	6	0.000
PF_3	3.93	100	-97	0.011	0.9	0.6
PCl_3	3.15	101	-219	0.302	0.0	0.3
PBr_3	2.94	102	-227	0.340	0.0	0.0
PI_3	2.65	102	-178	0.420	0.9	0.6
$\text{P}[\text{N}(\text{CH}_3)_2]_3$	3.10	(102)	-123	0.018
P_4O_6	3.51	99	-113	0.200	0.3	0.2
$\text{P}(\text{OCH}_3)_3$	3.55	(100)	-141	0.148
P_4S_3	2.60	100	-72	0.318	0.2	0.2
$\text{P}(\text{SCH}_3)_3$	2.60	(102)	-124	0.350

^a Values in parentheses estimated *a priori* by J.R.V.W. on the basis of chemical regularities.

^b Assuming the value of 0.2 in P_4O_6 and normalizing each of the other values to be consistent.

^c Values taken from Ref. 14 where $S+S$ and H refer to values obtained from slightly different ways of handling the correction for ionic character.

shift according to our equations. However, if the entire σ orbital suffers the loss of this fractional unit of charge by donation to a nonorthogonal p_π orbital, there will be a change in the calculated value of ζ_1 . The magnitude of this change is given in Fig. 8.

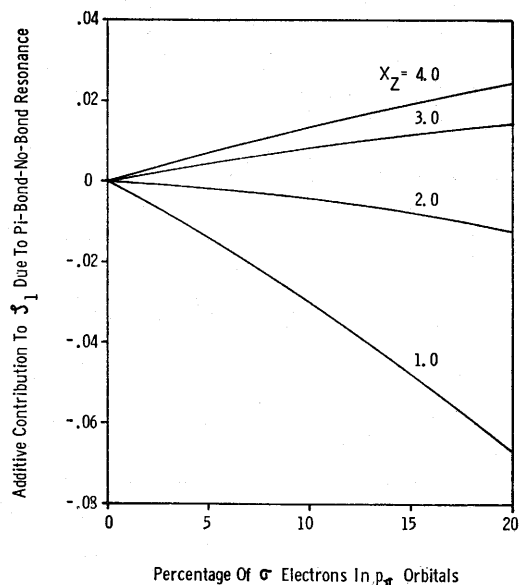


FIG. 8. The additive contribution to ζ_1 due to π -bond-no-bond resonance as a function of the fraction of σ electrons elevated to nonorthogonal p_π orbitals.

APPLICATION TO EXPERIMENTAL DATA

Symmetrically Substituted Phosphines

The experimental data for the compounds of the type PZ_3 are presented in the first four columns of Table III. Some of the group electronegativities given in this table differ from the usual mean values appearing in published tabulations.¹¹ The variations from the mean were based on a questionable correlation¹² of electronegativity of a given group with the difference between the methyl and methylene resonances in the proton NMR spectrum of the ethyl derivative of that group. In the case of substituents where these proton NMR data were not available, an estimation was made on the basis of the Taft¹³ and Hammett¹⁴ σ parameters.

From the bond angles¹⁵ and electronegativities, the values of ζ_1 were calculated on the assumption of the σ bonding being based completely on the use of s and p orbitals. These values are plotted versus the observed ^{31}P chemical shift as referenced to 85% phosphoric acid

¹¹ M. L. Huggins, *J. Am. Chem. Soc.* **75**, 4123 (1953).

¹² B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.* **77**, 3977 (1955).

¹³ R. W. Taft, *Steric Effects in Organic Chemistry*, edited by M. S. Newman (John Wiley & Sons, New York, 1956), pp. 590-619.

¹⁴ H. H. Jaffé, *Chem. Rev.* **53**, 191 (1953).

¹⁵ H. J. M. Bowen, J. Donohue, D. G. Jenkin, O. Kennard, P. J. Wheatley, and D. H. Whiffen, *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Special Publication No. 11 (The Chemical Society, London, 1958).

in Fig. 9, from which it can be seen that a straight line drawn through the points for the PH_3 and $\text{P}(\text{CH}_3)_3$ molecules passes through a number of other points. Neither PH_3 nor $\text{P}(\text{CH}_3)_3$ should exhibit π bonding and, furthermore, the bond angle for the PH_3 is well established. Moreover, the point for PF_3 , which we think might have no π bonding, also lies on this line; so we conclude that the line truly corresponds to the chemical shifts of molecular structures in which phosphorus π orbitals are not involved. It seems reasonable to assume that, if there were configuration interactions, they would be different for the various molecules lying on the line, since the substituents of these PZ_3 molecules correspond to a wide range of electronegativities.

We therefore conclude that in Eq. (26) the constant $B(\nu) = -7719$ ppm for $\nu = 3$, and δ_0 in this same equation has the value of $+11828$ ppm when 85% phosphoric acid is employed as the reference standard for chemical shifts reported in parts per million of the magnetic field.

According to the calculations of this paper as applied to the data of Table I, the utilization of the phosphorus π orbitals should cause the respective points in Fig. 9 to always appear above the line corresponding to no π bonding; and it should be noted that all of the points which are not lying on this line do appear above it.

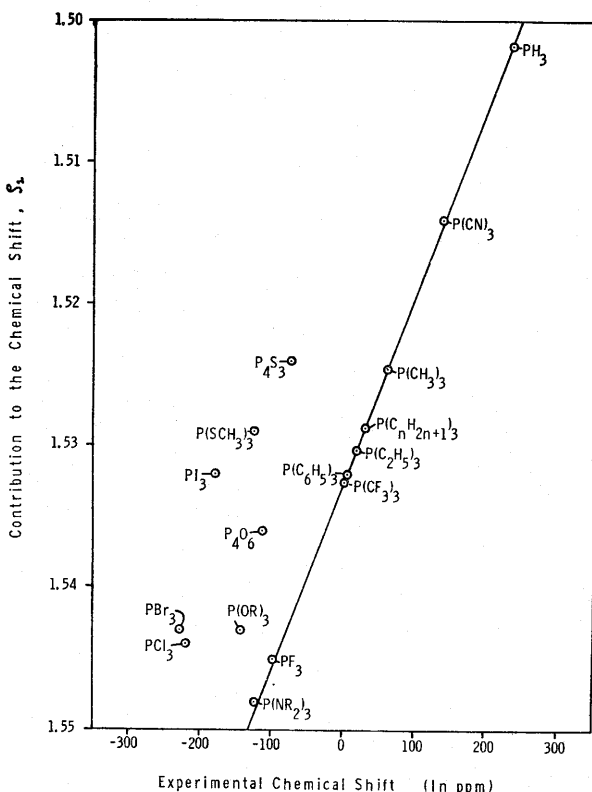


FIG. 9. The p -orbital contribution, ζ_1 , to the ^{31}P chemical shift as a function of the observed chemical shift referenced to 85% H_3PO_4 for the symmetrically substituted phosphines, PZ_3 .

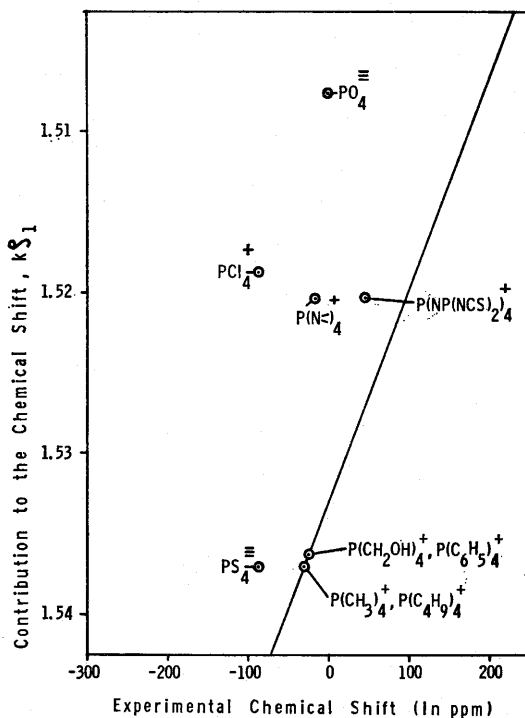


FIG. 10. The p -orbital contribution, $k\zeta_1$, to the ^{31}P chemical shift (where $k=1.028947$) as a function of the observed chemical shift referenced to 85% H_3PO_4 for the tetrahedrally symmetrical compounds of the form PZ_4 .

From the distance these points are removed from the line, one can calculate the relative amount of π interaction for the respective structures. The parameter $f(\nu)$ was evaluated from our earlier work¹⁶ by assuming that there are 0.20 π electrons per phosphorus atom in the P_4O_6 structure; so that $f(3) = 0.058$. The amount of π bonding obtained on this assumption is shown in the fifth column of Table III, where it can be compared with equivalent values¹⁶ for the π bonding as estimated from bond-distance data, which were further correlated with values obtained from thermodynamic data. In view of the unsettled state of treatment of $p_\pi-d_\pi$ bonding, the qualitative agreement between the values given in the last three columns of Table III is gratifying.

Total Symmetrical Tetrahedral Structures

The cations of phosphonium salts as well as the orthophosphate and orthothiophosphate anions consist of a phosphorus atom tetrahedrally surrounded by four substituent atoms. The data for these PZ_4 -type molecules are presented in Fig. 10 where the straight line of Fig. 9 is caused to run through the points for the tetraalkyl and aryl phosphonium salts by a change of slope of about 3%. This gives us the value of $B(4) = -7940$ ppm, which is 3% larger than $B(3)$. Again, as in Fig. 9, the points in Fig. 10 which are not on the line all lie

¹⁶ J. R. Van Wazer, J. Am. Chem. Soc. **78**, 5709 (1956).

TABLE IV. Data and resulting π bonding for the PZ_4 type of molecules.

Molecule	Chemical shift (ppm) δ	Estimated number of π electrons per P atom		
		From ^{31}P NMR ^a	From the bond distances ^b	
			S+S	H
$\text{P}(\text{C}_6\text{H}_5)_4^+$	-32	0
PS_4^{3-}	-87	0.395	0.3	0.7
$\text{P}(\text{N}=\text{O})_4^+$	-17	0.805	0.6	0.6
$\text{P}(\text{Cl}_4)^+$	-86	1.4	0.0	0.4
PO_4^{3-} in H_3PO_4	0	1.4	1.5	1.4

^a Assuming 1.4 π electrons/P in PO_4^{3-} .

^b Values taken from Ref. 16 where S+S and H refer to values obtained from slightly different ways of handling the correction for ionic character.

above it, so that their distance from this line can be interpreted in terms of π bonding. On the assumption based on Ref. 16 that there 1.4 π electrons per phosphorus atom in the PO_4^{3-} anion, $f(4)$ is thereby set equal to 0.0175. The resulting calculated values for the number of π bonds per phosphorus atom are given in Table IV, where these values can be compared with the equivalent ones estimated from bond-distance data. The amounts of π character in the P-Z bonds, as presented in Table IV, appear reasonable so that some faith may be placed in the values of $B(4)$ and $f(4)$, which may be used in treating the more difficult situation corresponding to molecules of the MPZ_3 type if we assume that $B(4)$ is unaffected by the fact that some PZ_4 structures are anions while others are cations. Since it was possible to obtain rational results by including the triply charged anions in the same grouping which contains the cations, it seems reasonable to conclude that $B(4)$ has not been affected by the total charge of the PZ_4 structures. This conclusion is somewhat substantiated by the near equivalence of $B(3)$ and $B(4)$.

Other Structures of Quadruply Connected Phosphorus

The largest amount of data for structures of the type MPZ_3 are to be found for M = oxygen, sulfur, and, to a lesser extent, selenium. Knowing $B(4)$ and $f(4)$, we are still faced with the problem of two adjustable parameters—the ZPZ bond angle θ and the number of π electrons per phosphorus—one of which must be established in order that the other may be calculated from the chemical shift. Unfortunately, there is a paucity of data on the bond angles, and the few values that are available have large standard deviations (several degrees). Indeed in the x-ray table,¹⁵ these particular structure determinations are graded in the class of lowest accuracy with respect to the bond lengths, which, by the way, are far easier to measure precisely than are the bond angles.

Because neither the bond angle nor the number of π electrons per phosphorus can be established *a priori*, the chemical shifts given for the compounds of the type MPZ_3 in Table V are presented in Figs. 11, 12, and 13 in terms of the total number of π electrons per phosphorus as a function of the bond angle θ , according to the mathematical treatment of this paper. These curves were obtained from graphs similar to those shown as Figs. 3-5, using the previously established values of $B(4) = -7940$ ppm and $f(4) = 0.0175$. It is interesting to note that the variation in the amount of π bonding with bond angle for the OPZ_3 compounds shown in Fig. 11 is inappreciable and that this is also true for about half of the SPZ_3 compounds of Fig. 12 and half of the SePZ_3 compounds of Fig. 13.

For most of the molecular structures covered by Figs. 11-13, it is to be expected that the bond angle would not be far from tetrahedral so that, in spite of the lack of accurate knowledge concerning the value of θ , the number of π bonds per phosphorus atom may be estimated to within an error of about 0.1 unit from the ^{31}P chemical-shift data and the values of the electronegativities used. These values for π bonding from the ^{31}P NMR data are compared with our previous estimates¹⁶ from bond distance and thermodynamic data in Table V. Although the ^{31}P chemical shifts are quite different and appear in different order for the OPZ_3 ,

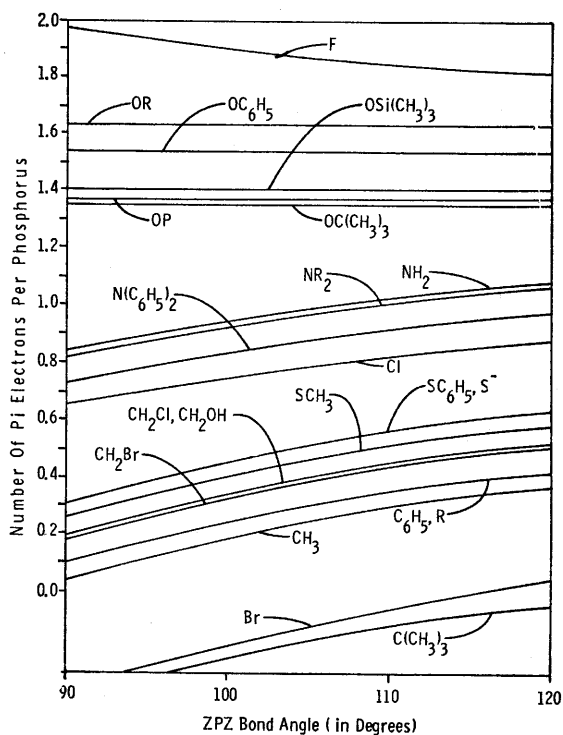


FIG. 11. Calculated variation of the total number of electrons donated from the oxygen and the three other substituents to the π orbitals of the phosphorus atom plotted vs the ZPZ bond angle in the symmetrically substituted phosphoryls, OPZ_3 . The electronegativity of oxygen is taken to be 3.55 and Pauling-type electronegativities are used for each substituent.

TABLE V. Reported data and resulting π bonding for the MPZ_3 type of molecules.

Substituent Z	Electro- negativity χ_Z	Observed chemical shift (ppm)			π bonds/P estimated from Figs. 11-13		
		OPZ ₃	SPZ ₃	SePZ ₃	OPZ ₃	SPZ ₃	SePZ ₃
Br	2.94	103	112	n.a.	0.00	-0.11	...
C(CH ₃) ₃	2.55	+41	-41	-31	-0.07	0.00	-0.14
C ₆ H ₅	2.70	-24	-43	n.a.	0.40	0.18	...
CH ₃	2.60	-36	-59	n.a.	0.35	0.21	...
CH ₂ Cl	2.70	-38	n.a.	n.a.	0.50
CH ₂ Br	2.65	-43	n.a.	n.a.	0.48
R	2.58	-45	-48	-46	0.40	0.11	0.03
CH ₂ OH	2.65	-46	n.a.	n.a.	0.50
SC ₆ H ₅	2.65	-55	-92	n.a.	0.61	0.50	...
SR	2.60	-61	-93	-76	0.56	0.44	0.25
SCH ₃	2.60	-66	-98	-82	0.56	0.47	0.30
S ⁻	2.55	-86	-87	n.a.	0.61	0.32	...
Cl	3.15	-2	-34	n.a.	0.86	0.67	...
N(C ₆ H ₅) ₂	3.15	-2	n.a.	n.a.	0.96
NH ₂	3.12	-22	-61	n.a.	1.06	0.78	...
NR ₂	3.10	-24	-78	n.a.	1.04	0.90	...
N(CH ₃) ₂	3.10	-23	-82	-84	1.03	0.93	0.76
OP	3.51	+45	-16	n.a.	1.38	0.83	...
OC(CH ₃) ₃	3.54	+13	-41	-31	1.36	0.99	0.81
OSi(CH ₃) ₃	3.55	+27	n.a.	n.a.	1.41
O ⁻	3.50	+0	-34	n.a.	1.40	0.97	...
OC ₆ H ₅	3.57	+18	-53	-58	1.54	1.22	0.98
OR	3.55	+1	-68	-73	1.63	1.28	1.11
OCH ₃	3.55	+1	-73	-78	1.63	1.31	1.15
F	3.93	+36	n.a.	n.a.	1.82

SPZ₃, and SePZ₃ sets of compounds, it is encouraging to note that an ordering of the Z substituents with respect to the π bonds per phosphorus forms the expected regular pattern, as shown in Table V.

For the usual type of M substituent (i.e., oxygen, sulfur, selenium, carbon, nitrogen, etc.) in molecules having the MPZ_3 symmetry, the total π bonding per phosphorus is rather sensitive to the exact electronegativity difference between the phosphorus and the Z substituent. Numerically it turns out that, for an increase in the difference of an 0.1 electronegativity unit, 0.12 to 0.15 π electron/P are added.

It should be noted that the formalism employed in this study gives the total number of π electrons per phosphorus atom without reference to their distribution among different bonds. In compounds of the MPZ_3 type, there will, of course, be a difference in the amount of π character in the M-P bond as compared to the P-Z bond, with the π orbitals being restricted completely to the M-P bond in those cases shown in Figs. 11-13 where Z stands for an alkyl group (and probably also for an aryl group). However, in the other compounds, π character is expected in all four bonds,¹⁶ contrary to the assumption recently made by Wagner in another quantum-mechanical treatment¹⁷ of phosphoryl compounds.

There is no *a priori* reason that phosphorus cannot donate electrons to p_π or d_π orbitals of its substituents,

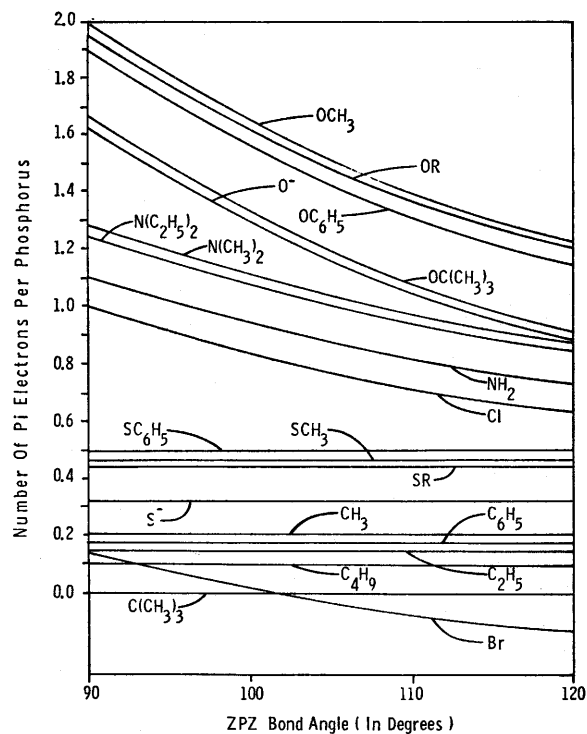


FIG. 12. Calculated variation of the total number of electrons donated from the sulfur and the three other substituents to the π orbitals of the phosphorus atom plotted vs the ZPZ bond angle in the symmetrically substituted thiophosphoryls, SPZ₃. The electronegativity of sulfur is taken to be 2.60 and Pauling-type electronegativities are used for each substituent.

¹⁷ E. L. Wagner, J. Am. Chem. Soc. **85**, 161 (1963).

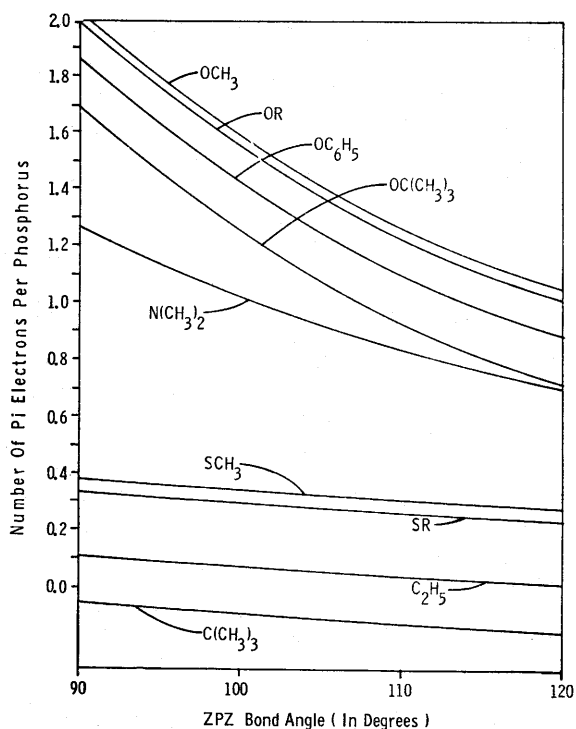


FIG. 13. Calculated variation of the total number of electrons donated from the selenium and the three other substituents to the π orbitals of the phosphorus atom plotted vs the ZPZ bond angle in the symmetrically substituted selenophosphoryls, SePZ_3 . The electronegativity of selenium is taken to be 2.50, and Pauling-type electronegativities are used for each substituent.

so that the number of π bonds per phosphorus atom may be negative. In Fig. 11, the curves for OPBr_3 and $\text{OP}[\text{C}(\text{CH}_3)_3]_3$ go into the negative region of π bonds/P as does the curve for SPBr_3 in Fig. 12. The case of tritertiarybutylphosphine oxide, $\text{OP}[\text{C}(\text{CH}_3)_3]_3$, is probably explained completely on the basis of steric hindrance since a CPC bond angle of 115° is not unreasonable and, from electrostatic considerations, it would seem that such a large bond angle should greatly inhibit the π -electron feedback from the oxygen. In the case of the phosphoryl and thiophosphoryl bromides, it would be possible to envisage the situation where the oxygen or sulfur atoms were feeding electrons into the d_π orbitals of the phosphorus while the phosphorus was, in turn, feeding electrons into p_π or d_π orbitals of bromine, with the latter process outweighing the former. However, we do not think that this is the situation, and we are tempted to assign the low range of these curves to hyperconjugation (defined as electron delocalization due to slight deviations from orthogonality of the bonding orbitals) and/or small errors in the electronegativities.

Since the vertical positioning of the curves in Figs. 11–13 are quite sensitive to the values of the electronegativities employed in the calculations, it is not unreasonable to expect minor adjustments in the

amount of π bonds/P when more accurate electronegativity values or their equivalent become available. In particular, the use of a group electronegativity for the phosphorus atom would lead to a small vertical transposition of the entire set of curves in a given figure. Thus the electronegativity (with respect to the Z substituents) of a phosphorus in the phosphoryl group should be somewhat different from that of a phosphorus in the thio- or selenophosphoryl groups; and, likewise changing the Z substituents should cause a small change in the effective electronegativity of the phosphorus with respect to the M substituent.

DISCUSSION

For the symmetrically substituted compounds based on triply connected phosphorus, the bond angle is the major parameter affecting the ^{31}P chemical shift, with the amount of π bonding also being important. The strong dependence on bond angle of the ^{31}P shift of these compounds is clearly attributable to the electrodynamic properties of the abortive bond. As shown in Fig. 1, the effect of changing the bond angle on the σ -bond contribution to the chemical shift decreases as the electronegativity of the substituent approaches that of phosphorus. This follows from the fact that the electronic distribution in the phosphorus atomic orbitals more closely approximates that of atomic phosphorus under these conditions. In the hypothetical case where the substituents have either extremely high or extremely low electronegativities such that the phosphorus is completely ionized so as to have the rare-gas configuration of neon or argon, respectively, the function ζ_1 would be zero. Therefore, ζ_1 must maximize at intermediate values, as shown in Fig. 1.

For those compounds based on quadruply connected phosphorus, the electronegativity and amount of π bonding essentially determine the shift. In Figs. 3 through 5, the complete insensitivity of ζ_1 to bond angle when the substituents have an electronegativity equal to that of phosphorus has the same explanation as the one given above for Fig. 1. Likewise, the explanation for the appearance of maxima in these figures is similar to that given for Fig. 1 except that, in the two extremes, the phosphorus will be present in the form of a hypothetical ionized MP diatomic molecule, the bonding orbitals of which must be added (subtracted) from the rare-gas configuration attributed to the phosphorus. Furthermore, the curves corresponding to different bond angles in Figures 3–5 can be seen to cross not only at the electronegativity corresponding to phosphorus but also at the electronegativity equal to that of the M substituent. This second crossover point will, of course, correspond to the respective point on the curve of Fig. 2. Although Fig. 2 was calculated for the tetrahedral bond angle, the assumption of other bond angles would give exactly the same curve since the phosphorus p orbitals in PZ_4 cannot be subjected

to asymmetric occupation by changes in hybridization due to variation in bond angle.

The observed chemical shifts cover a much wider range for the compounds based on triply connected as compared to those based on quadruply connected phosphorus. This is due to the fact that the σ -bond contribution to the chemical shift is attributable to the asymmetric loading as well as the total occupation of the phosphorus atomic orbitals. In the class of PZ_3 molecules, there are large changes in asymmetry which overpower the effect of changes in total occupation of the phosphorus atomic orbitals. For the PZ_4 and MPZ_3 class of compounds, there is little opportunity for asymmetric loading so that the chemical shift is dominated by changes in total occupation of the phosphorus orbitals when going from one molecule to another.

The relationships of this paper do not follow from a simple picture such as the often stated misconception that increasing the electron-donating power of the substituents will cause an increase in the shielding. Nearly ten years ago, we pointed out¹ that the ^{31}P chemical shift of "the phosphonic acids and the phosphonates offers a direct way to measure the relative electron-donating ability of organic radicals, ... [with] the stronger electron-donating groups cause[ing] the lesser shielding of the phosphorus nucleus." This effect, which has been treated by others as an anomalous reversal is expected behavior, follows directly from the equations of this paper! The phosphonate anions, RPO_3^- , fall in the class of the MPZ_3 compounds, where Z is fixed and M represents a series of organic radicals of which, in all cases, a carbon atom is bonded to the phosphorus. The underlying calculations are equivalent to keeping the electronegativity of substituent Z constant and equal to that of oxygen, holding the bond angle approximately constant, and varying the electronegativity of substituent M, as is done when going from Figs. 4 to 5. In general, the mathematical treatment given here for MPZ_3 compounds offers a precise way of establishing relative electronegativities for the various organic groups.

The mathematical scheme employed here will shortly be extended¹⁸ to compounds of the type PZ_5 and may also be used to treat compounds of the type PZ_6 . The case of mixed substituents (i.e., employing different groups in the Z locations of various classes of phosphorus compounds) is also being treated¹⁸ quantita-

tively on the basis of the arguments presented in this paper.

In treating the ^{31}P chemical-shift data, the "ionic character" of the σ bonds has been handled in terms of electronegativities by use of Eq. (28). If this treatment is superseded by a more satisfactory one, the necessary mathematics for calculating new values of ξ_1 has been presented herein. Likewise better values of ξ_1 and ξ_2 may be obtained from these mathematics if a scheme is developed to predict in a reasonable manner the extent of configuration interactions. Incorporation of hyperconjugation into our mathematical scheme is also feasible and is discussed elsewhere.¹⁸

The ratio of the expectation value of r^{-3} for the $3d$ to that of the $3p$ orbitals of phosphorus is given by $f(\nu)$. Values for this ratio may be crudely estimated from ratios of the respective spin-orbit coupling constants¹⁹ obtained from spectral data where the J - J coupling is small or nonexistent. Thus, $f(\nu)$ is evaluated to be 0.0121 from the P_{III} atomic spectrum and 0.0085 from the P_{V} spectrum. These values are quite close to $f(3) = 0.058$ and $f(4) = 0.017$ obtained from the above treatment of the ^{31}P chemical-shift data on the basis of the amount of π bonding calculated from bond-length shortening for P_4O_6 and PO_4^{3-} , respectively. We feel that the molecular orbital delineation method presented here could be used profitably in treating not only other experimental parameters but also the NMR chemical shifts of nuclei other than phosphorus.

The mathematical calculations were run on the IBM-7040 high-speed electronic digital computer in the Monsanto Computing Center and many of the results (exemplified by Figs. 1, 3-5) were plotted directly for use by a Calcomp autoplottter. The computer programs were written by one of us (J.H.L.).

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Professor M. J. S. Dewar, Professor Lindsay Helmholtz, Professor Bernard Goodman, and Professor Eugene Feenberg for helpful discussions on this material.

¹⁸ J. H. Letcher and J. R. Van Wazer, *Topics in Phosphorus Chemistry* edited by M. Grayson and E. J. Griffith, (Interscience Publishers, Inc., New York, 1966), Vol. 4, Chaps. 2 and 3.

¹⁹ For example, see B. R. Judd and I. Lindgren, *Phys. Rev.* **122**, 1802 (1961). For P_{III} in the $3s^23p^1$ configuration, the spin-orbit coupling constant, ξ_{so} equals 559.6 cm^{-1} and, in the $3s^23d^1$ configuration, ξ_{so} equals 11.3 cm^{-1} . For P_{V} in the $3p$ configuration, ξ_{so} equals 794.6 cm^{-1} ; and in the $3d$ configuration, $\xi_{so} = 11.2 \text{ cm}^{-1}$. In all cases, the respective spectral lines were well separated from others with which J - J coupling could occur. The values were taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std., Circ. No. 467, **1**, 163-80 (1949).