Chemical Reviews

Volume 69, Number 2 April 1969

THE USE OF OUTER d ORBITALS IN BONDING

K. A. R. MITCHELL

Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

Received April 8, 1968

Contents

I. Introduction

An outstanding problem in the theory of electronic structure concerns the role of d orbitals in the ground states of molecules formed by the typical elements, and this is especially apparent in such molecules as $P(C_6H_5)_5$, SO_2Cl_2, BrF_5, and XeF_6 where the central atom forms more bonds than appears to be allowed by the octet rule. Models have been proposed which give varying prominence to d orbitals in molecules of this type, and the main aim of this review is to assess the usefulness of the theoretical models in current use.

The number of published papers which have commented, either directly or indirectly, on this problem is very large, and consequently this review is restricted in scope to basic underlying principles, with illustrative examples drawn from both theoretical and experimental studies. Special emphasis is given to the elements silicon, phosphorus, and sulfur. This is both because experimental studies useful for discussions of bonding have in the main been more extensive for these elements than for typical elements of the third and later rows of the periodic table, and also because the theoretical basis is further developed. Moreover, it seems probable that models of electronic structure which have proved to be useful for molecules of first-row elements are likely to be more readily adapted for use with molecules of second-row elements than for those of higher row elements.

II. 3d Orbitals and Bonds of Second-Row Atoms

A. MODELS OF ELECTRONIC STRUCTURE

It will be supposed, as is done conventionally, that molecular electronic structure can be described in terms of a model based on atomic orbital functions centered on the constituent atoms. In principle good molecular wave functions can be obtained by using a very large basis set of one-electron wave functions, and these can be complete sets of atomic orbital functions based at the several atomic sites.[1] In practice, unacceptable mathematical complexity forces a limitation on the number of functions in the basis set, and to outline the principle of the usual quantum mechanical methods we shall consider a basis set of the p atomic functions $\xi_1, \xi_2, \ldots, \xi_p$. Where molecular orbital theory is used, the first approximation to a singlet ground state n-electron wave function is the determinant shown in an abbreviated notation in the expression

$$\psi_1 = |\phi_1\bar{\phi}_1 \ldots \phi_\nu\bar{\phi}_\nu| \tag{1}$$

where the normalizing coefficient $(n!)^{-1/2}$ is suppressed, and spin β is denoted by a bar. Electrons are supposed to be assigned to the orbitals $\phi_1, \ldots, \phi_\nu$ according to the prescription that electron 1 is assigned throughout to the first row of the determinant, 2 to the second row, and so on. The determinantal wave function ψ_1 is then totally antisymmetric to electron interchange, and describes a singlet state. $\phi_1, \phi_2, \ldots, \phi_\nu$ are the molecular orbitals of lowest energy and $\nu = n/2$. The molecular orbitals are expressed in terms of the atomic orbital basis functions according to

$$\phi_i = \sum_{j=1}^{p} c_{ij}\xi_j \tag{2}$$

The coefficients c_{ij} may be obtained in various ways depending on the approximations made in minimizing the energy. The more sophisticated, such as the Roothaan self-consistent field (SCF) method,[2] lead to coefficients that give stationary values of the total molecular energy and not only that of the individual orbital. Further improvement can be made by

---

(1) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

(2) C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

allowing interaction between ψ_1 and singlet wave functions belonging to other electron configurations, *i.e.*, other ways of assigning electrons to the available molecular orbitals. The best wave function of this improved type is given in eq 3, where the a's are energy-minimized coefficients, and ψ_2, ψ_3, ... are wave functions with the same symmetry properties as those of ψ_1.

$$\psi = a_1\psi_1 + a_2\psi_2 + \ldots \qquad (3)$$

Recently several reviews have covered theoretical aspects of the electronic structure of small molecules.[1,3–5] In very small molecules configuration interaction can be included, but for more complex molecules, even of first-row elements, the computational effort restricts the calculation to a single configuration. Physically, this means that electron correlation is neglected. Also it is readily appreciated that, even with a single configuration, the larger the basis set the more difficult the evaluation of the molecular integrals, both because they are more numerous and because they get more difficult for the later members of a basis set, which are mathematically more complex. Many molecular calculations are done in a basis set of those atomic orbitals occupied in the free atom (either in ground or low excited states). Two main approaches are available within this approximation. The first is to find the best possible wave functions by using the SCF technique (nonempirical method). In the second, the effect of the approximations is dealt with by parametrizing the calculation by the use of, for example, ionization potentials of spectroscopic transition energies.[1,6–9]

The usefulness of these procedures is well established for molecules of first-row elements and may, for instance, be illustrated by the theory of the electronic structure of the conjugated carbocyclic hydrocarbons and related molecules.[1,10,11] Moreover, analyses of SCF wave functions have shown that the familiar pictorial concepts of quantum chemistry, such as localized two-electron bonds, nonbonding electron pairs, and hybridization, can often be rationalized in this form of molecular orbital theory.[12–14] The difficulties begin when it is assumed that models using simple bases of atomic orbital functions are also applicable to molecules of second-row elements. To illustrate the point, one can consider PF_5. According to a conventional view, the first step is to promote the phosphorus atom from its ground configuration $3s^23p^3$ into the pentacovalent excited configuration $3s3p^33d$. Then molecular orbitals are formed by linear combination (eq 2) of the fluorine bonding orbitals with those of phosphorus, giving to each orbital the properties it had in the free atom. It is now found that the 3d orbital is so diffuse that its overlap with the bond orbital of a fluorine is too small to make a significant contribution to molecular binding.[15] This suggests either 3d-orbital involvement is negligible, or the properties of 3d orbitals are so modified in the molecular environment that bonding becomes feasible. Before considering the latter, it is useful to discuss more fully 3d orbitals in free atoms.

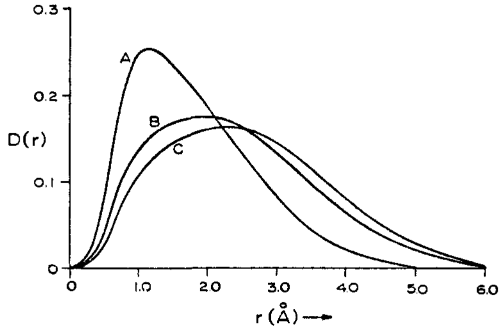

Figure 1. 3d orbital distribution functions for the sulfur configuration $3s3p^33d^2$: (A) in the ^7F term, (B) in the "state" of average energy, (C) in the ^1S term.

B. 3d ORBITALS IN FREE ATOMS

The usefulness of theoretical models which emphasize 3d-orbital contributions to the electronic structure of compounds containing second-row elements in the higher covalence states depends closely on the energy and form of the 3d radial functions. Atomic SCF calculations have been reported for the ^7F and ^3I terms of the sulfur $3s3p^33d^2$ configuration and also for the ^5D term of the $3s^23p^33d$ configuration;[16] these particular terms are represented by a single determinantal wave function. This work showed that 3d orbital distribution functions may vary widely from those given by Slater's rules[17] for hydrogenic functions of the type

$$R(r) = Nr^2e^{-\alpha r} \qquad (4)$$

where N is a normalization constant and α the orbital exponent. SCF calculations are complex for terms described by multideterminantal functions, and a convenient alternative is to use analytical one-electron wave functions of sufficient flexibility. Craig and Thirunamachandran[18,19] have explored this possibility and shown that sulfur SCF 3d orbitals may to a good approximation be represented by a linear combination of two functions of the type in eq 4 belonging to different values of exponent α. This approach allowed investigation of other terms of the $3s3p^33d^2$ configuration of sulfur, and in particular those of high energy. It has become clear that the properties of 3d orbitals vary sensitively in the various terms of the atomic configuration; while in the ^7F term lying at the low energy end of the term manifold the radial maximum is at 1.18 Å, it is at 2.33 Å in one of the ^1S terms lying at the high-energy end. Appropriate probability distribution functions D(r), defined by eq 5, are illustrated in Figure 1.

$$D(r) = r^2R^2(r) \qquad (5)$$

---

(3) D. M. Bishop, *Advan. Quantum Chem.*, 3, 25 (1967).

(4) R. K. Nesbet, *ibid.*, 3, 1 (1967).

(5) R. G. Parr in "Molecular Orbitals in Chemistry, Physics, and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 21.

(6) W. Moffitt, *Proc. Roy. Soc.* (London), A210, 245 (1951).

(7) R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 466 (1953).

(8) R. Pariser and R. G. Parr, *ibid.*, 21, 767 (1953).

(9) J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953).

(10) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co. Ltd., London, 1963.

(11) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966.

(12) D. Peters, *J. Chem. Soc.*, 2003 (1963).

(13) D. Peters, *ibid.*, 2015 (1963).

(14) K. Ruedenberg in "Modern Quantum Chemistry," Part 1, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, p 85.

(15) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E Sutton, *J. Chem. Soc.*, 332 (1954).

(16) D. W. J. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, 40, 3733 (1964).

(17) J. C. Slater, *Phys. Rev.*, 36, 57 (1930).

(18) D. P. Craig and T. Thirunamachandran, *J. Chem. Phys.*, 43, 4183 (1965).

(19) D. P. Craig and T. Thirunamachandran, *ibid.*, 45, 3355 (1966).

The question is whether either of these extremes is appropriate to hexavalent sulfur in a molecule, for example, SF_6. The alternative is to use the properties of the d orbitals in the atomic valence state.

"Valence state" is a concept that has proved useful for discussions of bonding in first-row elements[20] and usually refers to a state of random spin, although, within the valence-bond method, this concept may be defined in relation to various molecular models. In the first, valence state belongs to a single atomic configuration, for example, the $3s3p^33d^2$ configuration of sulfur, and then involves many terms of this configuration. The perfectly paired sp^3d^2 valence state gives inequivalent bonds. This is clearly unrealistic for SF_6, which has O_h symmetry,[21] but bond equivalence may be secured by resonance. Alternatively, the valence state may be defined for equivalent octahedral hybrids, in which case the valence state is multiconfigurational.

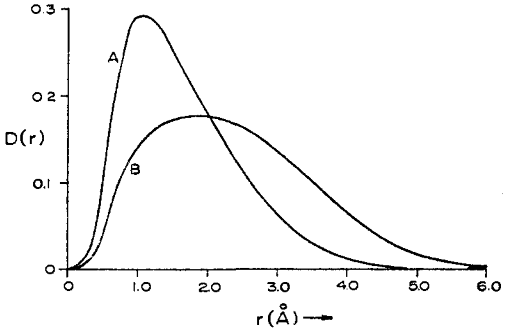

Figure 2. 3d orbital distribution functions for sulfur valence states: (A) for equivalent octahedral hybrid orbitals, (B) for the single configuration $3s3p^33d^2$.

The scarcity of atomic spectroscopic data makes the estimation of valence-state energies much more difficult for second-row elements than for first-row elements. For example, the expression for the octahedral hybrid valence state of sulfur requires knowledge of 18 terms belonging to the sp^3d^2 configuration,[19] but in fact no terms of this configuration have been identified in the atomic spectrum. Nonempirical methods are therefore needed for deriving valence-state energies, and this has encouraged Craig and Thirunamachandran to propose another model for the valence state.[22] This has been termed the resonance valence state and corresponds to a state of maximum spin multiplicity; resonance among different pairing schemes maintains bond equivalence required by molecular symmetry. This approach has still to be explored in detail, but one immediate advantage derives from the simple expressions for valence states; in many examples the resonance valence state corresponds to the lowest term of the valence configuration, and this is found for sulfur in SF_6. For many examples the resonance valence-state energy should be directly available from measured spectral term values.

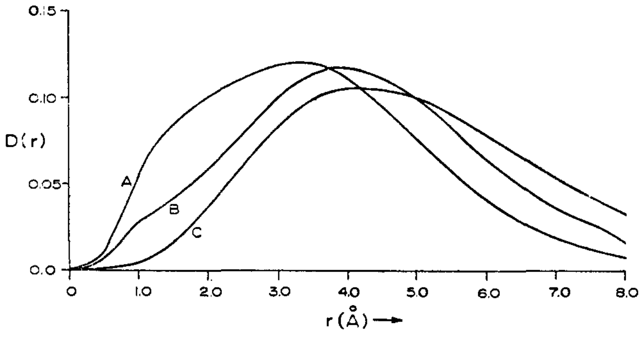

Figure 3. 3d orbital distribution functions in d^1 configurations: (A) in the ^6D term of $P(sp^3d)$, (B) in the ^5D term of $S(s^2p^3d)$, (C) in the ^2D term of $Al(s^2d)$.

Recently, 3d orbital radial functions have been estimated in the various valence states for hexacovalent sulfur.[19,22] For the valence state of the sp^3d^2 configuration the 3d functions have radial maxima at 1.98 Å. This is greater than most bond distances for hexavalent sulfur, but these orbitals are not as diffuse as that with the Slater exponent[17] of 0.55, which has a radial maximum at 2.89 Å. However, in the valence state for equivalent octahedral hybrids the 3d orbitals are more compact with radial maxima at 1.08 Å. This value is well within the bond length distance in SF_6 and is much closer to the positions of the principal radial maxima for 3s and 3p orbitals. Probability distribution functions for 3d orbitals in sulfur valence states are shown in Figure 2. The 3d radial function for the resonance valence state of octahedral hexacovalent sulfur is that reported in Figure 1 for the ^7F term of the sp^3d^2 configuration.[22]

On grounds of orbital size, therefore, it seems likely that 3d orbitals in valence states for SF_6 are suitable for participation in bond formation, but so far we have not mentioned the energy involved in forming the valence state. The SCF calculation indicated that the ^7F term is about 24.5 eV above the s^2p^4 ground state.[16] Promotion to valence states with random spin have been estimated[23] to be greater and probably in excess of 30 eV. It is difficult to envisage a convincing theory of bonding using 3d orbitals when promotion energies are of this magnitude. Certainly configuration interaction must reduce the promotion energy, but it seems unlikely that this is sufficient by itself.

The relationship between orbital size and orbital energy is not in general a simple one, although within the term manifold of a single configuration 3d orbital size does increase with increasing term energy. For a multiconfigurational valence state, on the other hand, there is no similar correspondence. Consequently, the observation already quoted that sulfur 3d orbitals are more compact in the octahedral hybrid valence state than in the sp^3d^2 valence state does not imply that the former have lower energy than the latter.[19] Other configurations contribute to the octahedral valence state, and in some, like sp^2d^3, s^2d^4, and p^3d^3, the 3d orbitals experience reduced screening of the nucleus, so making the radial forms more compact.

Investigations of d orbitals in d^1 configurations show a contrast with those in the sulfur sp^3d^2 configuration. The Hartree-Fock calculation[16] for the ^5D term of the sulfur s^2p^3d configuration showed the distance of maximum probability to be 3.4 Å, and this represents a distance of more than twice the bond length in, for example, SF_4. The ^5D term is calculated to be 7.2 eV above the sulfur s^2p^4 ^3P ground state,[16]

---

(20) C. A. Coulson, "Valence," Oxford University Press, London, 1961.

(21) J. Gaunt, *Trans. Faraday Soc.*, 49, 1122 (1953).

(22) D. P. Craig and T. Thirunamachandran, *Proc. Roy. Soc.* (London), A303, 233 (1968).

(23) G. L. Bendazzoli and G. Zauli, *J. Chem. Soc.*, 6827 (1965).

and compares with the 8.4 eV observed.[24] The diffuse nature of the 3d orbital in this state is consistent with the ^5D term being only 1.9 eV below the ionization limit.[24] Likewise, d orbitals in the sp^3d configuration of phosphorus[25] and the s^2d configuration of aluminum[26] are diffuse. Some representative radial distribution functions are illustrated in Figure 3.

In summary, the main objections to 3d-orbital participation in bonds of second-row elements are: (1) the diffuse nature of free atom 3d orbitals in d^1 configurations; (2) the large promotion energies in relation to the energy gain on bond formation. These difficulties have led some authors to suggest 3d orbitals are not significantly involved in bond formation for high covalence states, and others to propose that 3d orbital properties may be sufficiently modified by the molecular environment to allow bond formation. These suggestions are developed and compared in the following sections.

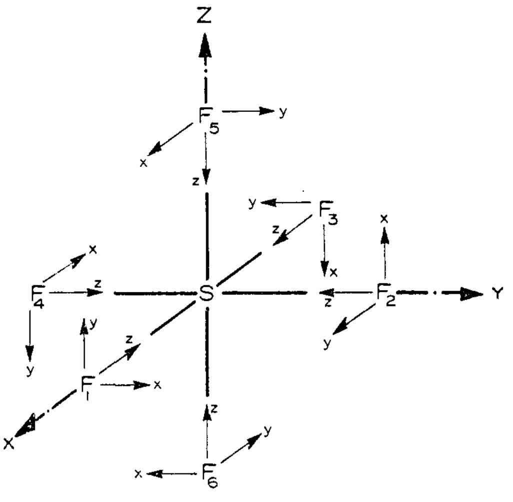

Figure 4. Axes in octahedral SF_6.

There is no doubt that the development of accurate wave functions using a large basis set of atomic orbitals according to the method outlined section II.A will eventually confirm contributions by 3d orbitals, and indeed by other orbitals with higher principal quantum number. This is expected, since even for molecules of first-row atoms, for example, HF, inclusion of 3d orbitals in the basis set leads to a significant lowering of energy.[27] The question that is relevant to present discussion really concerns the degree of 3d-orbital participation in relation to the contributions by 3s and 3p orbitals.

C. THE MOLECULAR ORBITAL THEORY OF SF_6

The O_h molecular symmetry of SF_6 makes it a convenient example for illustrating bonding principles, and in particular for comparing the models which involve differing degrees of 3d-orbital participation. The principles we discuss for SF_6 apply with small modification to related molecules with lower molecular symmetries.

Table I

Symmetry Orbitals for Octahedral SF_6

Representation	*Sulfur orbital*	*Fluorine orbitals*	
		σ	π
a_{1g}	3s	$z_1 + z_2 + z_3 + z_4 + z_5 + z_6$	
t_{1u}	$3p_x$	$z_1 - z_3$	$y_2 + x_5 - x_4 - y_6$
	$3p_y$	$z_2 - z_4$	$x_1 + y_5 - y_3 - x_6$
	$3p_z$	$z_5 - z_6$	$y_1 + x_2 - x_3 - y_4$
e_g	$3d_{x^2-y^2}$	$z_1 - z_2 + z_3 - z_4$	
	$3d_{z^2}$	$2z_5 + 2z_6 - z_1 - z_2 - z_3 - z_4$	
t_{2g}	$3d_{xy}$		$x_1 + y_2 + y_3 + x_4$
	$3d_{xz}$		$y_1 + x_5 + x_3 + y_6$
	$3d_{yz}$		$x_2 + y_5 + y_4 + x_6$
t_{1g}			$x_1 - y_2 + y_3 - x_4$
			$y_1 - x_5 + x_3 - y_6$
			$x_2 - y_5 + y_4 - x_6$
t_{2u}			$y_2 - x_5 - x_4 + y_6$
			$x_1 - y_5 - y_3 + x_6$
			$y_1 - x_2 - x_3 + y_4$

It is supposed that molecular orbitals are formed from the valence-shell orbitals of the sulfur and fluorine atoms. The axes used are indicated in Figure 4, and the symmetry-determined combinations of ligand orbitals are specified in Table I. Four atomic orbitals are included at each fluorine. We consider these to be the two hybrids formed by the 2s and $2p_z$ orbitals, and the $2p_x$ and $2p_y$ orbitals. This conveniently allows us to designate by z (Table I) the hybrids directed at the sulfur atom; the outward directed hybrids can, in a first approximation, be considered to contain lone pairs. The fluorine atomic orbitals designated by x and y (Table I) represent $2p_x$ and $2p_y$.

On this basis, there are 6 electrons from the sulfur atom and 5 from each fluorine atom, giving a total of 36 electrons to be accommodated in molecular orbitals. To start with, we follow Rundle[28] and ignore participation by 3d orbitals. Then the e_g and t_{2g} molecular orbitals, as well as those of the t_{1g} and t_{2u} representations, are completely determined by symmetry, and together these can accommodate 22 electrons. Another 6 electrons are accommodated in the relatively weak bonding molecular orbitals of t_{1u} symmetry that are formed between the sulfur 3p orbitals and π combinations of fluorine orbitals, so leaving 8 electrons for the four strongly bonding molecular orbitals (symmetries a_{1g} and t_{1u}). These bonding molecular orbitals are delocalized with a net electron drift to the fluorine atoms.

Although this model illustrates that the stability of SF_6 can be interpreted without recourse to 3d-orbital participation, it can only be considered to be an initial proposal since such simple molecular orbital theory predicts stability for some molecular species that have not so far been synthesized (for example, H_3 with respect to three isolated hydrogen atoms[29]). Its significance must therefore be determined through further theoretical and experimental studies.

With participation by 3d orbitals, the two molecular orbitals of symmetry e_g become bonding, and there are then

---

(24) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, Vol. I, U. S. Government Printing Office, Washington, D. C., 1949.

(25) G. S. Chandler and T. Thirunamachandran, *J. Chem. Phys.*, 47, 1192 (1967).

(26) M. Synek, *Phys. Rev.*, 131, 1572 (1963).

(27) E. Clementi, *J. Chem. Phys.*, 36, 33 (1962).

(28) R. E. Rundle, *Survey Progr. Chem.*, 1, 81 (1963).

(29) J. N. Bradley, *Trans. Faraday Soc.*, 60, 1353 (1964).

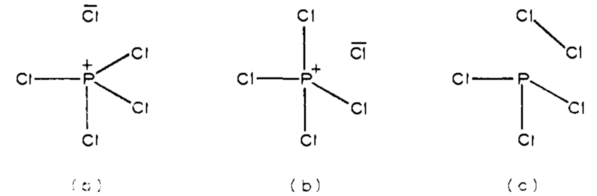

Figure 5. Some structures which maintain the octet and contribute to the valence-bond molecular wave function of PCl_5.

six bonding molecular orbitals involving combinations of fluorine z orbitals. These may be expressed by $\phi_l = a_l\chi(S)_l + b_l\chi(F)_l$, where l identifies the molecular orbital and $\chi(S)_l$ and $\chi(F)_l$ respectively represent the appropriate sulfur orbital and combined fluorine orbitals. If the mixing coefficients a_l and b_l are independent of l, another special case can be recognized. In these circumstances, the one-electron molecular orbitals can be rearranged (without changing the molecular wave function[30]) into the form $\psi_m = a\eta_m + bz_m$, where $m = 1, 2, \ldots, 6$ and η_m represents the six equivalent sp^3d^2 octahedral hydrid orbitals.[31] ψ_m defines a set of six localized two-center molecular orbitals, and the above condition specifies the requirement for the model utilizing hybridization in conjunction with two-electron bonds to be useful. It is not easy to define the precise condition that must hold for a_l to be independent of l, but in broad terms this requires that the sulfur valence-shell orbitals have similar energies in the molecular environment and similar interaction energies with the combinations of fluorine orbitals. It is not really necessary to specify the conditions more precisely, for this situation is essentially hypothetical, but we point to it as representing a different special case from that first mentioned. The bonding situation in SF_6 must be expected to be best represented by a description somewhere between the extreme models emphasizing no 3d-orbital participation on the one hand and perfect localized pairing on the other, and similarly for other related molecules. Currently there is much interest in which special model provides the most reasonable representation.

D. THE LIGAND FIELD CONTRACTION THEORY

Three principal theories have been given for dealing with the problem of 3d orbitals in bonds of second-row atoms. Pauling has suggested that since the 3d electron is so near to ionization it is removed in the presence of ligand atoms and attached to them as in structures a and b shown in Figure 5 for PCl_5, and correspondingly that the molecular wave function includes contributions from valence-bond structures of this type. Additionally, to prevent excessive positive charge at phosphorus, inclusion of structures of the type c has also been proposed.[31] Another viewpoint is the molecular orbital model[28] which has already been outlined for SF_6, and the third and most fully developed view is the ligand field contraction theory first suggested qualitatively by Craig, Maccoll, Nyholm, Orgel, and Sutton.[15] The starting point of this theory is that high valence states of second-row elements are especially found when the elements are bound to electronegative atoms or groups; the essential idea is that in such an electronegative environment the more diffuse orbitals are contracted more than the less diffuse, so that their electron densities are concentrated in the internuclear regions more or less to the same extent. Then the conditions for participation of d electrons in bond formation are met, and the usual theory of covalent binding can be applied. Moreover, it is implicitly assumed that the effect of the molecular environment also makes the 3s, 3p, and 3d orbitals rather closer in energy than is the case for the free atoms.

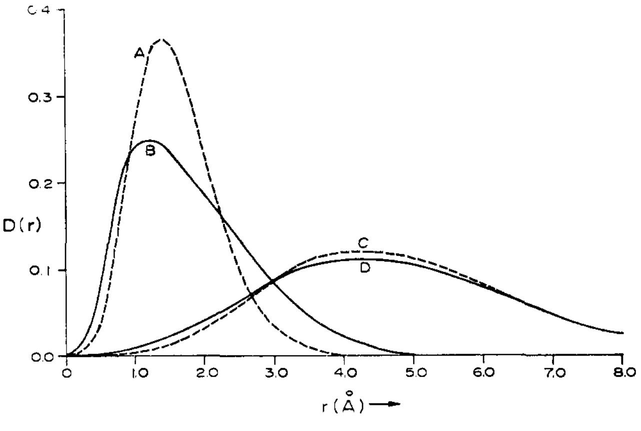

Figure 6. Comparison of distribution functions for 3d orbitals with one- and two-term radial functions: (A and B) for ^7F term of $S(sp^3d^2)$, (C and D) for "state" of average energy of $P(sp^3d)$. The broken lines correspond to single-term radial functions, and the continuous lines to two-term functions.

Model calculations for testing the contraction hypothesis have been developed by Craig and his collaborators. For molecular calculations, 3d atomic orbitals have been represented by single term radial functions as in eq 4. These simple functions are now known to be inaccurate in detail for low-energy terms of d^2 configurations.[16] Thus the simplest functions overestimate $R(r)$ at the maxima and cut off too rapidly at large r (Figure 6), but nevertheless they are useful for highlighting dominant features, and for d^1 configurations they provide better representations. The calculation of the influence of ligands on diffuse free atom orbitals is done by finding the total energy of an electron in a 3d orbital in the molecular field. The energy is then minimized with respect to the exponent α, the optimum value of which is different from the free atom, and in cases of practical interest is greater. Since the distance of maximum probability for the radial function in eq 4 is given by

$$r_{\max} = 3/\alpha \qquad (6)$$

where distance is measured in atomic units (1 au = 0.529 Å), the larger 3d exponents in the molecular environment correspond to contracted 3d orbitals. The field of the ligands surrounding the atom providing the 3d orbital was at first treated as a set of point sources located at the positions of the ligand atoms;[32] in a refinement, the ligands were represented by electrostatic potentials calculated from atomic wave functions.[33,34] In both these models the 3d orbitals are strongly contracted. For example, in SF_6 Craig and Zauli[33] find an orbital exponent of 1.22 (corresponding to $r_{\max} = 1.30$ Å) for

---

(30) J. A. Pople, *Quart. Rev.* (London), 11, 273 (1957).

(31) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(32) D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

(33) D. P. Craig and C. Zauli, *J. Chem. Phys.*, 37, 601 (1962).

(34) D. P. Craig and C. Zauli, *ibid.*, 37, 609 (1962).

the 3d orbitals of e_g symmetry. The corresponding calculation for an isolated sulfur atom gives an optimum 3d exponent of 0.61, corresponding to $r_{\max} = 2.65$ Å. These calculations also predict reduced promotion energies to the 3d levels.[35]

The work on 3d orbitals in SF_6 by Craig and Zauli[33] was based on an electrostatic model assuming that exchange interactions between ligands and central atom would not strongly affect the size of the 3d orbitals. More recent application of this method, however, has shown[35,36] that these exchange terms can, under certain conditions of ligand orbital and molecular structure, be of considerable importance when the 3d orbital physically overlaps ligand inner-shell electrons, and these exchange repulsions may even be sufficient to overcome the stabilizing effect of the electrostatic field. When exchange terms are included, bonding overlaps give additional exchange stabilization in many important examples, and these terms are sufficiently large in SF_6 to ensure increased 3d orbital availability in the molecular environment.[35] Similarly, model calculations for phosphoryl compounds, for example, F_3PO, indicate that the environment contracts the phosphorus 3d orbitals with π symmetry with respect to the P–O bond, and that these contracted 3d orbitals strongly overlap the oxygen $2p_\pi$ orbitals.[36] These conclusions are supported by semiempirical calculations of molecular properties[37] with the recently developed CNDO (complete neglect of differential overlap) method.[38]

As well as modifying 3d orbitals, the molecular environments may be expected to modify strongly other orbitals of high energy including 4s and 4p. For the neutral atoms Si to Cl, 4s is more stable than 3d,[39,40] although the bonding possibilities for 4s seem to be less than for 3d, both because of the spherical symmetry of 4s and because of the need for orthogonalizing to 3s.[35] Angular polarization of 3d orbitals may be anticipated in d_π-type bonding, and this can be accommodated by mixing in appropriate high-energy orbitals. However, this represents a refinement to the model of d-orbital bonding and (unlike radial polarization) is not a necessary condition for the concept to be acceptable.[36]

E. EXPERIMENTAL EVIDENCE FOR THE PARTICIPATION OF 3d ORBITALS IN BONDING

It has already been noted that the electron distribution in molecules like SF_6, ClF_3, and $POCl_3$ may be represented in more than one approximate way depending on the availability of 3d orbitals. The model calculations referred to in section II.D indicate that 3d-orbital participation may be expected in electronegative environments, although, at the present time, the value of this concept must be judged mainly in relation to the experimental evidence. One cannot, however, expect experiments to establish whether d orbitals are "really" used, anymore than experiments can show s and p orbitals definitely occur in the bonding of first-row elements, and this follows from the primitive nature of these bonding models which was emphasized in section II.A.

The basis for using the d-orbital model is that it enables many observed features to be brought into a coherent scheme, so providing a comprehensive descriptive framework. In the following analysis of observed properties in terms of 3d-orbital bonding, we aim to complement other recent studies of particular aspects of this problem.[41–45]

1. σ Bonds

Sulfur hexafluoride is in many respects representative of the bonding in this class of molecule. Chemically it is remarkably inert, being attacked readily only by powerful reagents, such as alkali metals[46] and strong Lewis acids.[47] In this respect, however, SF_6 is different from many of the other molecules, which tend to be reactive. The stability of SF_6 is kinetically controlled[48] and presumably is associated with the protective layer of fluorine atoms surrounding the central sulfur atom. The S–F bond length is[49,50] 1.56 Å and shorter than the value 1.64 Å calculated from the covalent single-bond radii including the Schomaker–Stevenson correction.[51]

The factors affecting inertness and lability in these molecules are not well understood. It is easy to accept that in a fully space-filled molecule like SF_6, access to the reactive center by an attacking group is obstructed, in contrast to SF_4 (incomplete trigonal-bipyramidal structure) where access is easy. In addition, there is the factor that bimolecular mechanisms of reaction are most easily available where the central atom has orbitals available to form one additional bond. In the case of SF_4, based on the s^2p^3d or sp^4d configuration of sulfur, promotion of one electron to sp^3d^2 allows new bonds to form to an attacking group. In SF_6 there is no further valence-shell promotion possible, and bimolecular mechanisms involving attack at sulfur seem ruled out; although by analogy with the occurrence of the PCl_6^- ion in crystalline PCl_5, one might be prepared to find a bimolecular transition state SF_6X^- leading finally to replacement of a fluorine by the atom X. The main point is that second-row atoms in their highest covalence states should be less readily attacked by nucleophilic reagents than those in lower states, and this is in accord with observation.

As participation by 3d orbitals in a bond hybrid increases, at the expense of 3s and 3p participation, we may expect bonds to become weaker. This is because of the higher energy (and less compact form) of 3d orbitals compared with 3s and 3p, even after taking account of the effects of the molecular field. On the other hand, with more 3d-orbital character the center of gravity of the electronic charge moves toward the ligands, which in a certain sense increases the ionic character of the

---

(35) K. A. R. Mitchell, *J. Chem. Soc.*, *A*, 2676, 2683 (1968).

(36) K. A. R. Mitchell, *Can. J. Chem.*, **46**, 3499 (1968).

(37) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

(38) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).

(39) P. Palmieri and C. Zauli, *J. Chem. Soc.*, *A*, 813 (1967).

(40) L. C. Cusachs and J. R. Linn, *J. Chem. Phys.*, **46**, 2919 (1967).

(41) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

(42) G. Cilento, *Chem. Rev.*, 60, 147 (1960).

(43) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, Chapter 17.

(44) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.

(45) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, Chapter 3.

(46) G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1198 (1964).

(47) J. R. Case and F. Nyman, *Nature*, **193**, 473 (1962).

(48) H. L. Roberts, *Quart. Rev.* (London), **15**, 30 (1961).

(49) V. C. Ewing and L. E. Sutton, *Trans. Faraday Soc.*, **59**, 1241 (1963).

(50) H. Braune and S. Knoke, *Z. Physik. Chem.* (Leipzig), **B21**, 297 (1933); L. O. Brockway and L. Pauling, *Proc. Natl. Acad. Sci. U. S.*, 19, 68 (1933).

(51) V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 63, 37 (1941).

bond, and favors the back-donation π-bonding mechanism to be discussed.

Some degree of π bonding through the back-donation mechanism is always to be expected in molecules with second-row atoms bonded to highly electronegative atoms, and this is likely in SF_6. Indeed, a part at least of the reduction (by 0.08 Å) in the observed S–F bond length from the covalent radius sum can be explained in this way. We should note that the expectation of reduced bond strength with increased 3d orbital participation is not an argument against 3d orbitals in the σ bonds of SF_6. It is the use of 3d orbitals that allows the formation of six electron-pair σ bonds, instead of a maximum of four using bonding combinations of 3s and 3p alone. Accordingly, one expects that the σ bonds in PCl_3 involve essentially 3s and 3p hybridization only, while in PCl_5 there is 3d participation. Consistently, the average bond energy in PCl_3 is greater[52] than that in PCl_5. The bonds in SF_6 are equivalent, but in PF_5 there is a trigonal-bipyramidal arrangement with two types of P–F bonds, designated axial and equatorial. Two structural determinations by electron diffraction have recently been made. The first[53] shows the length of the axial bonds to be 1.58 Å and the equatorial bonds to be shorter at 1.53 Å, and the second determination[54] indicates slightly greater differences (respectively 1.60 and 1.50 Å). Similar differences between axial and equatorial bond lengths are found in PCl_5[54,55] and $P(C_6H_5)_5$,[56] and for the PO_5 trigonal bipyramid in 2,2,2-triisopropoxy-4,5-(2′2′′-biphenyleno)-1,3,2-dioxaphospholene.[57] Investigations of force constants in PCl_5 and PF_5 confirm that the long (axial) bonds are weaker than the equatorial bonds.[58,59] This result is consistent with the model of 3d participation in the σ bonds, since for trigonal-bipyramidal molecules 3d participation in the σ hybrids is restricted to $3d_{z^2}$, and this orbital is oriented to contribute more to the axial bonds than to the equatorial bonds.

Consistency with 3d-orbital participation does not, of course, exclude other models. The molecular orbital theory based on 3s and 3p orbitals only[28] is also compatible with a relative weakening of the axial bonds, and the same trends are found in the valence-shell electron-pair model of Gillespie.[60,61] The latter is at its best in rationalizing ground-state stereochemistry but does not attempt to indicate more precise electron distribution. To an extent, it can be taken with the spd hybridization model insofar as both depend on the approximation of perfect pairing.

An interesting observation for five-coordinate phosphorus compounds with different ligand groups is that the most electronegative groups are found in axial positions.[62–64] This may be rationalized within the molecular orbital scheme which neglects 3d contributions,[65] but this is also consistent with 3d-orbital participation since, as discussed previously, availability of the $3d_{z^2}$ orbital for bonding is increased when directed at more electronegative groups.

Other evidence related to electron distribution is limited. Investigation of the PF_4 radical by esr spectroscopy[66] points to small 3d character for the unpaired electron, but this is not necessarily inconsistent with 3d character in the bonding orbitals. The first ionization potential of SF_6 has been found[67] by photoelectron spectroscopy to be 15.4 eV. This value is consistent with those of other fluorides (HF, 15.8; F_2, 15.7; SiF_4, 15.4 eV)[68] and suggests that the ionized electron has come from a lone pair on fluorine. The ionization potential of the fluorine atom is of course higher (17.4 eV), the reorganization on molecule formation being nearly the same whatever the attached atom. Electron drift from sulfur to fluorine is also indicated by the fact that the SF_5 group is strongly electron-withdrawing;[69] additionally, it is known that SF_6 has a large cross section for electron capture giving the short-lived SF_6^- ion.[70]

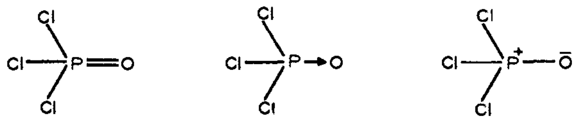

Figure 7. Bonding structures for phosphoryl chloride.

2. π Bonds

a. General Considerations

Alternative models have been proposed for bonds between oxygen and second-row elements in high valence states, as, for example, in phosphoryl compounds and the sulfoxides. Phosphoryl chloride, $POCl_3$, may be considered representative, and it has been formulated in the three ways indicated in Figure 7. Attempts have been made to distinguish these formulations by measurements relating to the polarity of the P–O bond. The coordinate bond and ionic bond formulations are obviously closely similar, but even the d_π–p_π double-bond formulation gives some polarity in the same direction. The latter follows both from the expected polarity of the σ bond and from the electron distribution of the d_π and p_π atomic orbitals.[15] The region of π-orbital overlap lies nearer to the oxygen than the phosphorus (see Figure 8), and the electron distribution in the bond is not so different from that described by $^+P–O^-$ as would at first appear. Measurements of bond refractions have been interpreted in terms of the P→O coordinate bond,[71] whereas ^{13}CH coupling constants in a series of compounds containing the group $>P(=O)CH_3$ have been interpreted to suggest

---

(52) S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev.* (London), **17**, 204 (1963).

(53) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).

(54) G. V. Romanov and V. P. Spiridonov, *Zh. Strukt. Khim.*, **8**, 159 (1967); *J. Struct. Chem.*, 8, 131 (1967).

(55) M. Rouault, *Ann. Phys.* (Paris), **14**, 78 (1940).

(56) P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964).

(57) R. D. Spratley, W. C. Hamilton, and J. Ladell, *J. Amer. Chem. Soc.*, **89**, 2272 (1967).

(58) F. A. Cotton, *J. Chem. Phys.*, **35**, 228 (1961).

(59) P. C. Van Der Voorn, K. F. Purcell, and R. S. Drago, *ibid.*, **43**, 3457 (1965).

(60) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

(61) R. J. Gillespie, *Angew. Chem. Intern. Ed. Engl.*, 6, 819 (1967).

(62) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).

(63) A. J. Downs and R. Schmutzler, *Spectrochim. Acta*, **23A**, 681 (1967).

(64) J. E. Griffiths, R. P. Carter, and R. R. Holmes, *J. Chem. Phys.*, **41** 863 (1964).

(65) P. C. Van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966).

(66) P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964).

(67) D. C. Frost, C. A. McDowell, J. S. Sandhu, and D. A. Vroom, *J. Chem. Phys.*, **46**, 2008 (1967).

(68) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, Appendix IV.

(69) W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3072 (1962).

(70) C. A. McDowell, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 506.

(71) R. G. Gillis, J. F. Horwood, and G. L. White, *J. Amer. Chem. Soc.*, **80**, 2999 (1958).

that the central phosphorus atom is nearly neutral, and that the double-bond formulation is better.[72] In general, such discussions depend on so many simplifying assumptions that single items of evidence are not in themselves convincing. One should consider which theoretical model provides the best basis for understanding the experimental evidence as a whole.

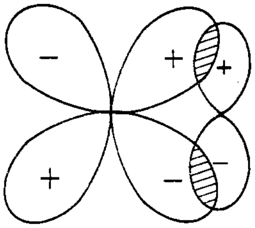

Figure 8. Overlap for a d_{π}–p_{π} bond.

In the first instance, ground-state bonding schemes are usually derived in relation to observed stereochemical arrangements; that is, the underlying σ-bond framework is treated in terms of hybridized atomic orbitals forming electron-pair bonds in the internuclear regions, and in addition π molecular orbitals may be superimposed on the basic σ framework. Quite often localization of the π molecular orbitals is not possible. In such cases, conjugation is predicted, and experimental investigations of the effects due to it often provide useful clues to d-orbital participation in the electronic structure.

Until refined wave functions can be developed for the systems of present interest, we are bound to discuss electronic structure with primitive descriptions developed essentially from stereochemical considerations. Their applicability in other contexts is not too clear; indeed, even applied to stereochemistry there may be difficulties. For example, in H_2O there are reasons to believe that bonding σ molecular orbitals are bent so that regions of maximum electron density are not precisely on the internuclear axes.[73]

b. Spectroscopic Evidence

Many methods for investigating electron distribution in molecules are spectroscopic in the strict sense that they depend ultimately upon the properties of two molecular states, a ground state and an excited state, although the excitation is not necessarily electronic. One can expect that the smaller the energy difference between ground and excited states the more immediately relevant to the electronic ground state the measurement should be, insofar as the disturbance caused by excitation is less. In practice the smallest transition energies are used in the radiofrequency spectroscopies including nuclear magnetic resonance. The spectral interpretations, however, give difficulty. For example, nmr chemical shifts and coupling constants are difficult to correlate with p_{π}–d_{π} interactions.[74] Nuclear quadrupole measurements in principle are sensitive to the electric field in the region of a nucleus with spin greater than $^1/_2$ and have been interpreted to support 3d-orbital participation in molecules of second-row elements by a number of authors.[75–77] But in order to make detailed estimates of the participation of d orbitals, quantitative assumptions always have to be made both about the ionic character of the bonds and the detailed form of the atomic orbitals used in bond formation, and this may reduce the reliability of the estimates. Information on the distribution of unpaired electrons has been obtained by the methods of electron spin resonance. In the species $C_6H_5Si(CH_3)_3^-$,[78] $(C_6H_5)_3P^-$,[79] and $(C_6H_5)_3PO^-$,[80] the unpaired electrons appear to be delocalized over the phenyl groups and the second-row atom. In each case suitably oriented 3d orbitals can be shown to be capable of interacting with the first antibonding orbitals of the phenyl groups to form delocalized molecular orbitals, but we should note that at present little is known about the properties of 3d orbitals when an electron is added and the original structure reorganizes.

At the other extreme where the transition energy is large, as in ultraviolet spectroscopy, it is possible that the relatively small energetic effects of 3d orbital participation in the ground state could be masked. For example, on the basis of variation in wavelengths of absorption maxima in the uv spectra of phosphoryl compounds, only very weak conjugation is indicated for vinyl groups[81] and phenyl groups[82] (although the conjugation seems to be stronger with pyrrole[83]), but other evidence not depending on electronic excitation in the same way gives a different result. Thus, 3d-orbital conjugation has been suggested by the sensitivity of reaction rates of vinyl groups to a neighboring phosphoryl group,[81] although in general the apportioning of observed effects to inductive influences and d_{π}–p_{π} coupling is hazardous.[84] Changes in intensities of uv transitions can, however, be helpful to the question of d-orbital participation in particular cases, and this is discussed further below.

c. Structural Evidence

Earlier, because of the frequent difficulty of unambiguously interpretating physical measurements in terms of 3d-orbital bonding, there was a feeling that stereochemical evidence gave the most reliable support to this theory, and this came especially from the close relationship between approximate models of ground-state electronic structure and stereochemistry. Certainly the stereochemistry of phosphoryl compounds, for example, POF_3, fits in with the model emphasizing d_{π}–p_{π} interactions between phosphorus and oxygen superimposed on a σ framework formed by sp^3 hybrids at phosphorus. Consistently with it, there is essentially tetrahedral stereochemistry at phosphorus, and the distortions from exactly tetrahedral angles ($\angle FPO = 116°$ and $\angle FPF = 102.5°$)[85] can be put down to electrostatic repulsions associated

---

(72) P. Haake, W. B. Miller, and D. A. Tyssee, *J. Amer. Chem. Soc.*, 86, 3577 (1964).

(73) R. F. W. Bader and G. A. Jones, *Can. J. Chem.*, 41, 586 (1963).

(74) E. A. V. Ebsworth and S. G. Frankiss, *J. Amer. Chem. Soc.*, 85, 3516 (1963).

(75) M. Dixon, H. D. B. Jenkins, J. A. S. Smith, and D. A. Tong, *Trans. Faraday Soc.*, 63, 2852 (1967).

(76) E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2459 (1961).

(77) M. A. Whitehead, *J. Chem. Phys.*, 36, 3006 (1962).

(78) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 59, 53 (1963).

(79) M. W. Hanna, *J. Chem. Phys.*, 37, 685 (1962).

(80) M. I. Kabachnik, V. V. Voevodskii, T. A. Mastryukova, S. P. Solodovnikov, and T. A. Melenteva, *Zh. Obshch. Khim.*, 34, 3234 (1964); *J. Gen. Chem. USSR*, 34, 3277 (1964).

(81) M. I. Kabachnik, *Tetrahedron*, 20, 655 (1964).

(82) H. H. Jaffé, *J. Chem. Phys.*, 22, 1430 (1954).

(83) C. E. Griffin, R. P. Peller, K. R. Martin, and J. A. Peters, *J. Org Chem.*, 30, 97 (1965).

(84) L. A. Leites, I. D. Pavlova, and Yu. P. Egorov, *Teor. i Eksperim. Khim., Akad. Nauk Ukr. SSR*, 1, 311 (1965); *Chem. Abstr.*, 63, 13024 (1965).

(85) Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, 20, 164 (1952).

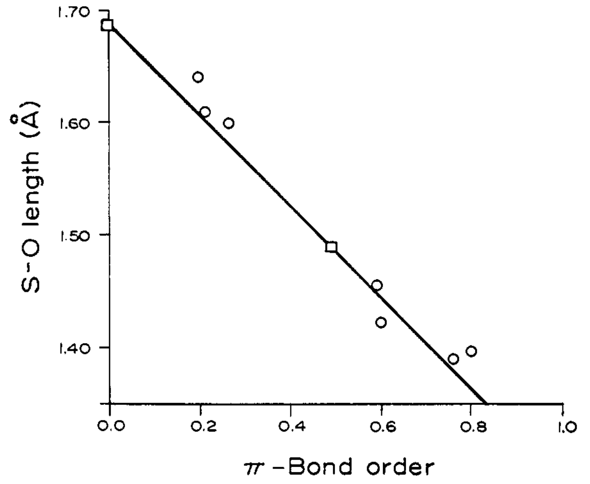

Figure 9. S–O bond lengths and π-bond orders.

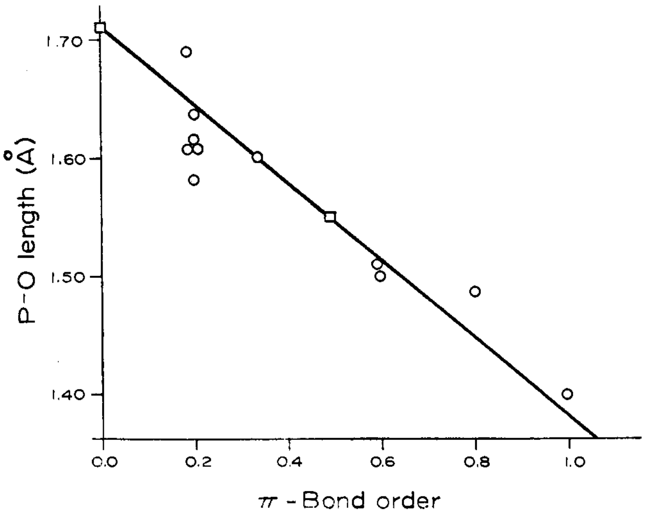

Figure 10. P–O bond lengths and π-bond orders.

with the phosphorus–oxygen multiple bond.[61] The experimental evidence indicates that the P–O bond in phosphoryl derivatives is very strong. The P–O stretching constant in POF_3 is 11.4 mdynes/Å,[86] the bond length is 1.45 Å,[85] and the bond energy term is 130 kcal $mole^{-1}$.[87] It is not easy to find pure single bonds for comparison because π bonding is always possible when phosphorus is bound to an atom containing unpaired electrons, and it is difficult to envisage a bond without some multiple character. Nevertheless, in some other molecules π bonding is certainly less. Thus single bonds in phosphates are usually in the range 1.55–1.65 Å, the largest known being 1.67 Å in sodium triphosphate.[88] The P–O bond energy term in POF_3 can be compared with the values of about 92 kcal $mole^{-1}$ found for molecules $(RO)_3P$, where R is an alkyl group.[52] If therefore, we treat the phosphoryl P–O bond crudely as a sum of σ and π components, without including more detailed interactions, we find a π contribution in POF_3 near 38 kcal $mole^{-1}$. It is noteworthy that this is considerably less than the π contributions of 80–90 kcal $mole^{-1}$ in carbonyl groups.[89] This difference can be assigned to a combination of factors including the different shapes of p_π and d_π atomic orbitals and the greater P–O bond length. These together ensure that much of the p_π–p_π overlap charge in the carbonyl group occurs in a region of stronger effective nuclear field than in d_π–p_π overlap in the phosphoryl group.

Cruickshank[90] has reviewed much structural information for molecules in which second-row atoms are bonded approximately tetrahedrally to strongly electronegative atoms, and has interpreted the evidence in terms of d_π–p_π bonding. This analysis is mainly of bond-length changes, and in particular of shortenings that can be correlated with π-bond effects. Plots of bond lengths and π-bond orders are reproduced in Figures 9 and 10. A problem in this field is to determine the relative contributions of π bonding and σ bonding. It is by no means easy to give precise standard values to bond lengths of single σ bonds between first- and second-row elements. Frequently, sums of covalent radii are used with the Schomaker–Stevenson correction for electronegativity differences.[31,51] The limited evidence suggests that these rules work quite well, but the basis of the theory of p_π–d_π bonding does not, of course, depend on their precise accuracy.

First-row elements (especially nitrogen and oxygen) tend to show large valence angles when bonded to second-row elements (especially silicon and phosphorus), and some comparisons of bonds between first-row atoms with bonds between first- and second-row atoms illustrating this effect are provided by (1) the nearly tetrahedral bond angle in ethers[91] as compared with the large SiOSi angle in disiloxanes (greater than 140°);[92–94] (2) the bent structure of methyl isothiocyanate and the linear heavy-atom framework in silyl isothiocyanate,[95] although in the trimethylsilyl derivative the SiNC angle is 154°;[96] (3) the pyramidal framework of trimethylamine in contrast to the planar framework of trisilylamine.[97]

The larger angles in bonds between first- and second-row elements have been related to a partial back donation of electronic charge from the lone-pair orbitals of the first-row atom into 3d orbitals of the second-row atom. The opening of the angle may be considered as a means of optimizing the π bonding, although alternatively the opening may be explained by repulsions between the increased electron density of the partial double bonds.[98] Angle increases to the full extent required to maximize π interactions are not always possible, for the σ bonds are changed during this process. In general, an increased angle at a first-row atom is interpreted to mean increased 2s character in the σ bond with concomitant increased bond energy and shortened bond length. This is an oversimplification, for the increase in bond energy (σ and π contri-

---

[86] H. Siebert, *Z. Anorg. Allgem. Chem.*, **275**, 210 (1954).

[87] F. Ebel and E. Bretscher, *Helv. Chim. Acta*, **12**, 450 (1929).

[88] D. R. Davies and D. E. C. Corbridge, *Acta Cryst.*, **11**, 315 (1958).

[89] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co. Ltd., London, 1958.

[90] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

[91] "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

[92] A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, *Acta Chem. Scand.*, **17**, 2455 (1963).

[93] R. F. Curl and K. S. Pitzer, *J. Amer. Chem. Soc.*, **80**, 2371 (1958).

[94] H. Kriegsmann, *Z. Electrochem.*, **61**, 1088 (1957).

[95] D. R. Jenkins, R. Kewley, and T. M. Sugden, *Proc. Chem. Soc.*, 220 (1960).

[96] K. Kimura, K. Katada, and S. H. Bauer, *J. Amer. Chem. Soc.*, **88**, 416 (1966).

[97] K. Hedberg, *ibid.*, **77**, 6491 (1955).

[98] R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **42**, 2496 (1964).

butions combined) through the angle opening has to be balanced against both increased promotion energy at the first-row element and any geometrical constraints. Nevertheless, these considerations do suggest that refinement of the correlations between measured bond lengths and calculated π-bond orders should perhaps take some account of changing hybridization within the σ bond. Other effects have been recognized to influence properties of bonds between first- and second-row elements, including the proximity of polarizing cations[99,100] and the nature of substituents at the second-row atom.[101]

d. The Back-Donation π-Bonding Model

A consequence of the back-donation π-bonding mechanism is that lone-pair electrons formally in the valence shell of nitrogen or oxygen should be less localized when these atoms are bonded to second-row elements, and it is satisfying that there is chemical evidence in support. Examples are provided by (1) the low basicity of trisilylamine;[97] (2) the observation that disiloxane (unlike dimethyl ether) does not form adducts with BF_3 and BCl_3;[102] and (3) the lower basicity of siloxanes compared with ethers demonstrated by comparing abilities as proton acceptors in hydrogen-bond formation.[103]

So far, we have treated the alternative formulations of bonds between first- and second-row atoms as though they are independent. Experimentally it is known that the bonds are usually polar, and the polarity may be related to their chemistry, an example being the highly electrophilic nature of phosphorus in phosphoryl compounds.[104] However, even if the ionic formulation is first emphasized, some reorganization in the $^+P–O^-$ fragment is inevitable. At oxygen, the extra electron increases electron repulsions in this region, and so causes an expansion of the valence-shell orbitals of O^- compared with neutral oxygen. This mechanism favors a tendency to back donate from oxygen. At phosphorus, there is a tendency to receive charge, since there can be no doubt that the electron affinities of the $3d_\pi$ orbitals in P^+ allow a gain in stability. Therefore, starting with the $^+P–O^-$ formulation, conditions at both phosphorus and oxygen are favorable for some degree of back donation. This mechanism depends on the ionic nature of the σ bonds, and indeed indicates the possibility of 3d-orbital participation in bonds which, in terms of the simplest possible valence considerations, do not require double bonding. The d_π bonding model, therefore, represents a refinement that allows discussion of more detailed interactions. This is important in the theory of the phosphazenes[105,106] and also seems necessary in some nominal triple bonds as, for example, the N–S bond in the gaseous compound NSF_3. This bond is only 1.42 Å in length,[107] and it seems unreasonable to describe it by a double dative bond. Furthermore, recent structural determinations of molecules containing the unit $>P{=}C<$ show the P–C bond length to be close to 1.71 Å (single-bond length 1.84 Å) and the three bonds at carbon to be coplanar.[108–111] This is consistent with d_π–p_π interactions, whereas the model emphasizing ionic contributions would predict the angles at carbon to be nearer the tetrahedral angle. In triphenylphosphoranylideneketene

$$(C_6H_5)_3P{=}C{=}C{=}O$$

the P–C bond length is 1.65 Å and the PCC bond angle is 146°.[112] The value of this angle again suggests that the ionic formulation is not sufficient, but that interactions involving phosphorus 3d orbitals are stereochemically important.[112]

Double-bonding interactions utilizing 3d orbitals are also expected with the second-row elements sulfur and chlorine, and the structural evidence for $3d_\pi$ bonding in molecules and ions like SO_3, SO_2F_2, and ClO_4^- closely follows that outlined earlier for silicon and phosphorus compounds. In molecules containing the fragment XOX, where X is in turn the elements Si, P, S, Cl, a reduction may be anticipated both in the ionic character of the X–O σ bonds and also in the degree of 3d-orbital involvement. As the atomic number of X increases, there is a tendency for the XOX angle to close, and both electrostatic and π-bonding factors are expected to contribute to this structural change.[90,98] It is difficult to determine which is dominant, and because of their interdependence more precise evaluation of their relative importance is of uncertain value.

A structural determination[113] of Cl_2O shows the bond angle (111°) and bond length (1.70 Å) to be close to those with essentially single bonding, and thereby confirms that p_π–d_π interactions between oxygen and chlorine are much less than, for example, between oxygen and silicon. In terms of the electronegativity difference S–N bonds may also be expected to have comparatively weak d_π–p_π interactions, although additional substituents at the second-row element can modify them. Electron-attracting substituents at the second-row atom favor electron release from lone pairs on neighboring first-row atoms, and conditions for this mechanism are most favorable if each first-row atom has two orbitals for interaction with the $3d_\pi$ orbitals. These interactions should be easier with two-coordinate oxygen than with three-coordinate nitrogen; on the other hand, two-coordinate nitrogen does have two available orbitals to contribute to the π-bonding interactions. We should, therefore, qualify the earlier statement that interactions in S–N bonds are likely to be comparatively weak, since the considerations just mentioned allow an accentuation of π interactions in, for example, $(FSN)_4$ compared with $(SNH)_4$, and this (in part at least) accounts for the differences in average S–N bond length measured for these compounds, being respectively 1.60 and 1.67 Å.[114,115]

e. The S–C Bond

The possibility of 3d-orbital contributions to S–C bonds in

---

(99) A. N. Lazarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 235 (1964); *Chem. Abstr.*, 60, 12677 (1964).

(100) A. N. Lazarev and T. F. Tenisheva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 403 (1964); *Chem. Abstr.*, 61, 1390 (1964).

(101) G. Engelhardt and H. Kriegsmann, *Z. Anorg. Allgem. Chem.*, 336, 286 (1965).

(102) M. Onyszchuk, *Can. J. Chem.*, 39, 808 (1961).

(103) R. West, L. S. Whatley, and K. J. Lake, *J. Amer. Chem. Soc.*, 83, 761 (1961).

(104) R. F. Hudson, *Advan. Inorg. Chem. Radiochem.*, **5**, 347 (1963).

(105) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(106) N. L. Paddock, *Quart. Rev.* (London), 18, 168 (1964).

(107) W. H. Kirchhoff and E. B. Wilson, *J. Amer. Chem. Soc.*, **84**, 334 (1962).

(108) T. C. W. Mak and J. Trotter, *Acta Cryst.*, 18, 81 (1965).

(109) F. S. Stephens, *J. Chem. Soc.*, 5640 (1965).

(110) F. S. Stephens, *ibid.*, 5658 (1965).

(111) P. J. Wheatley, *ibid.*, 5785 (1965).

(112) J. J. Daly and P. J. Wheatley, *ibid.*, *A*, 1703 (1966).

(113) J. D. Dunitz and K. Hedberg, *J. Amer. Chem. Soc.*, **72**, 3108 (1950).

(114) G. A. Wiegers and A. Vos, *Acta Cryst.*, 16, 152 (1963).

(115) R. L. Sass and J. Donohue, *ibid.*, **11**, 497 (1958).

organic sulfides is controversial.[116–119] This proposal has often been seen in relation to the formulation of the electronic structure of thiophene by Longuet-Higgins,[120] although recent esr studies of dibenzothiophene radical anions and related heterocycles indicate 3d-orbital involvement may be small.[121] The electronegativity difference in S–C bonds is zero on the Pauling scale[31] and would seem unfavorable for appreciable 3d participation. Nevertheless, interactions which probably involve 3d orbitals, have been indicated by substituent interference experiments for –SH and related groups[122,123] in monosubstituted and *para*-disubstituted benzenes. The method has been thoroughly analyzed[124] and depends on the effect of substituents on the intensity of the transition near 2600 Å in the uv absorption spectrum. The special feature of this approach is that the probability of the transition is related to the electronic distribution of only the ring atoms for both ground and excited states; a limitation is that the method cannot distinguish between interactions of the substituent 3d and 4p orbitals with the π orbitals of the ring, although the former seem likely to be more important.

III. 3d Orbitals in Delocalized π Bonds

Many of the cyclic molecules based on alternating patterns of first- and second-row atoms (for example, phosphazenes, metaphosphates, and siloxanes) are thought to involve, to some degree, electron delocalization over the –A–B–A–B– framework. It is supposed that the second-row atoms participate especially through their 3d orbitals. In the following, this suggestion is analyzed both theoretically and in relation to the experimental evidence.

A. THEORY OF CYCLIC DELOCALIZATION

The possibilities of electron delocalization have been analyzed quite generally in terms of the symmetries of the interacting atomic orbitals,[125,126] by methods extending the well-known Hückel treatment of benzenoid molecules.[127] For planar molecules, it is possible to separate the atomic orbitals into sets which are noninteracting in the one-electron approximation. Orbitals antisymmetric to reflection in the molecular plane may be treated separately from those that are symmetric, respectively contributing to π and σ molecular orbitals. It is assumed that the σ molecular orbitals may, to a close approximation, be localized, and that delocalization effects are thus particularly associated with the π electrons.

The benzenoid hydrocarbons suggest that electron delocalization enhances stability.[128] This extra thermochemical stability is possessed in principle by any system where electrons are delocalized within an enlarged region of low potential, as for example in the problem of an electron in a potential box.[129,130] It is anticipated that there will be similar enhanced stabilities for molecules with second-row atoms in ring frameworks, if they are able to maintain cyclic delocalization. In benzenoid systems, there is also an extra chemical inertness, but this is difficult to discuss theoretically, since it is determined rather more by kinetics than by the over-all thermodynamics of reaction schemes.

The simple Hückel-type molecular orbital method is used, in part because it provides first approximation estimates of energy eigenvalues and wave functions for the complex molecules of interest here rather more readily than the valence-bond theory. But the decisive advantage is that molecular orbital methods exhibit the symmetry-determined aspects of the solutions to the cyclic delocalization problem in a clearer way than do valence-bond methods, and this is of the greatest importance. In molecules made of the heavier elements, quantitative calculations become less and less reliable, and reliance must be increasingly placed on the less detailed, but more fundamental, symmetry arguments.

The discussion[125,126] to be given applies to planar monocyclic $(AB)_n$ molecules with ring bond lengths and ring angles fixed to conform to the molecular symmetry group D_{nh}. Molecular orbitals are formed by combining the available atomic orbitals according to the requirement that they transform like representations of this symmetry group. It is convenient to number A sites $p = 1, 2, \ldots, n$, and the B sites $p = {}^3/_2, {}^5/_2, \ldots, n + {}^1/_2$, so that the symmetry-determined groupings of atomic orbitals at A and B sites are

$$\begin{aligned} \phi_l^{A} &= n^{-1/2}\sum_{p=1}^{n} e^{2\pi i l p/n} A_p \\ \phi_l^{B} &= n^{-1/2}\sum_{p=1}^{n} e^{2\pi i l (p+1/2)/n} B_{p+1/2} \end{aligned} \qquad (7)$$

The orbitals are usefully classified by l, the ring quantum number, with allowed values given by

n odd $\quad l = 0, \pm 1, \ldots, \pm(n-1)/2$

n even $\quad l = 0, \pm 1, \ldots, n/2$

Molecular orbitals are formed by combining ϕ_l^A and ϕ_l^B to give minimum energy; for p_π–p_π interactions the energies are given by the roots of the two-row secular equations

$$\begin{vmatrix} \alpha_A - E & 2\beta\cos l\pi/n \\ 2\beta\cos l\pi/n & \alpha_B - E \end{vmatrix} = 0 \qquad (8)$$

where α_A and α_B are the respective Coulomb integrals, and β is the resonance integral.[11,20]

Different atoms are ordinarily accommodated in the same scheme through differences in their Coulomb integrals as in $\alpha_B = \alpha_A + \rho\beta$, where ρ is a parameter that measures the electronegativity difference of the orbitals of A and B. For $\rho = 0$ solutions of the secular equation (eq 8) give the results for monocyclic rings of like atoms, and Hückel's rule applies. This rule expresses the larger delocalization energies per electron for neutral molecules with 6, 10, 14, ..., π electrons than for molecules with 4, 8, 12, ..., π electrons. As ρ increases,

---

(116) V. Baliah and M. Uma, *Tetrahedron*, 19, 455 (1963).

(117) R. Breslow and E. Mohacsi, *J. Amer. Chem. Soc.*, 84, 684 (1962).

(118) A. Mangini, *J. Chim. Phys.*, 56, 240 (1959).

(119) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, 20, 417 (1964).

(120) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, 45, 173 (1949).

(121) R. Gerdil and E. A. C. Lucken, *J. Amer. Chem. Soc.*, 87, 213 (1965).

(122) L. Goodman and R. W. Taft, *ibid.*, 87, 4385 (1965).

(123) L. Goodman and L. J. Frolen, *J. Chem. Phys.*, 30, 1361 (1959); W. K. Musker and G. B. Savitsky, *J. Phys. Chem.*, 71, 431 (1967).

(124) L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Amer. Chem. Soc.*, 87, 1012 (1965).

(125) D. P. Craig, *J. Chem. Soc.*, 997 (1959).

(126) D. P. Craig in "Theoretical Organic Chemistry (Kekulé Symposium)," Butterworth & Co., Ltd., London, 1959, p 20.

(127) E. Hückel, *Z. Physik*, 70, 204 (1931).

(128) D. P. Craig in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 1.

(129) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p 70.

(130) L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p 95.

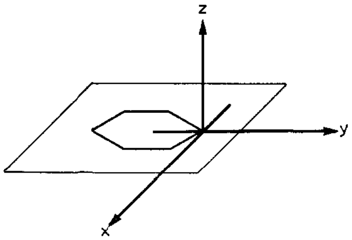

Figure 11. Local axes in planar rings. In nonplanar rings, the local axes may be defined with respect to the local planes.

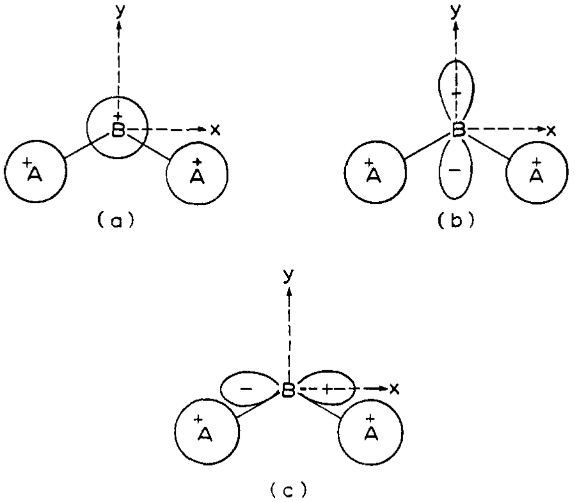

Figure 12. "Birds-eye-view" of interacting orbitals: (a) p_z–p_z system, (b) p_z–d_{yz} system, (c) p_z–d_{xz} system. (a) and (b) are homomorphic; (c) is heteromorphic.

differences between the $4m + 2$ and $4m$ series become less marked, and quite generally effects due to delocalization fall off as the electronegativity difference between the A and B atoms in the ring increases. Consistent with this statement, aromaticity is less strongly developed in *sym*-triazine or borazine than in benzene.[131,132]

Now the simple molecular orbital method is applied to $(AB)_n$ molecules, where the A atoms provide p_π orbitals and the B atoms provide d_π orbitals. A convenient (xyz) coordinate system at each ring atom is fixed with the z axis perpendicular to the molecular plane and the y axis directed radially to bisect the ring angle, as shown in Figure 11. The d orbitals antisymmetric to reflection in the molecular plane are d_{xz} and d_{yz}. Simple molecular orbital theory shows that the secular equation (eq 8) given earlier for cyclic p_π–p_π interactions applies equally for cyclic p_π–d_{yz} interactions, with appropriate choice of Coulomb and resonance integrals. Consideration of p_π–d_{xz} bonding, on the other hand, introduces new features resulting from the symmetry properties of d_{xz} orbitals which ensure that the overlap integrals, and therefore the resonance integrals, alternate in sign around the ring (see Figure 12). In p_π–p_π and p_π–d_{yz} systems the signs of these integrals are the same. Systems with constant sign of interaction around

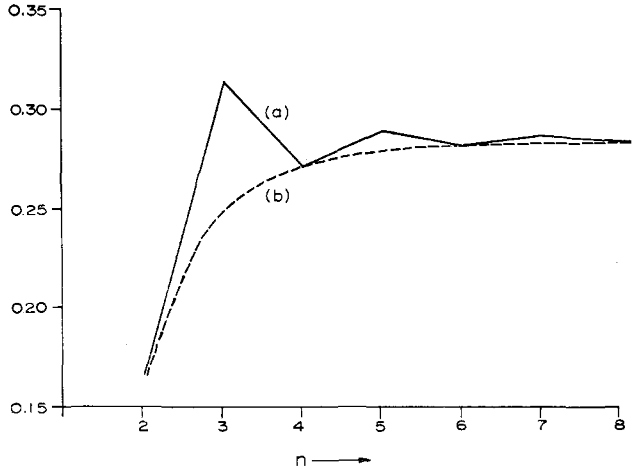

Figure 13. Delocalization energies per electron (in units of β) for $(AB)_n$, assuming $\alpha_B = \alpha_A + \beta$: (a) homomorphic system, (b) heteromorphic system.

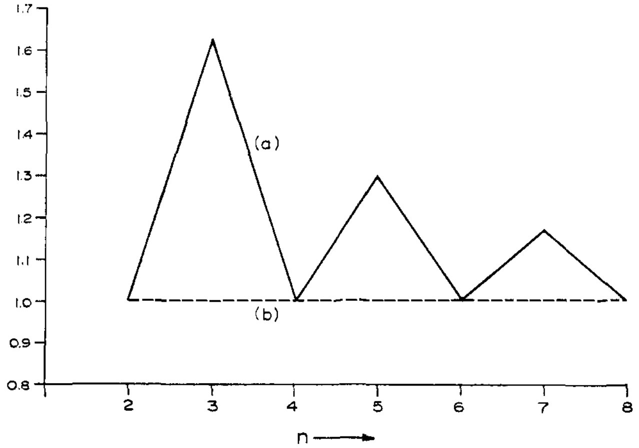

Figure 14. Energy of highest occupied orbital (in units of β and on a scale with the energy zero fixed by α_A) for $(AB)_n$ assuming $\alpha_B = \alpha_A + \beta$: (a) homomorphic system, (b) heteromorphic system.

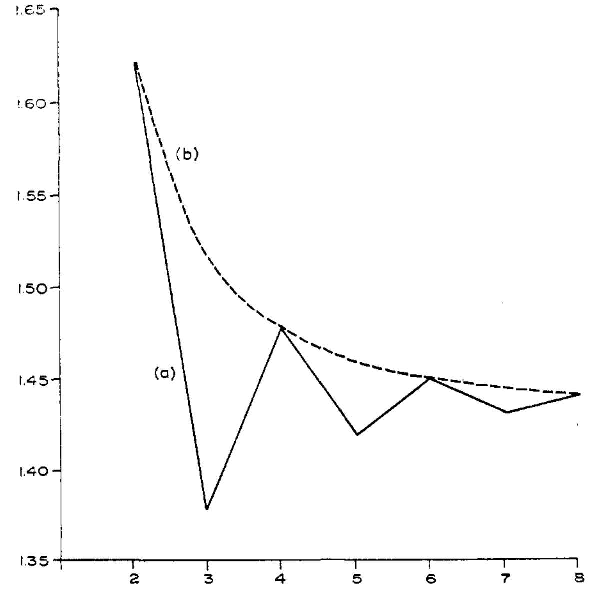

Figure 15. Electron density at B in $(AB)_n$, assuming $\alpha_B = \alpha_A + \beta$: (a) homomorphic system, (b) heteromorphic system.

---

(131) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967.

(132) H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1966, p 377.

the ring have been termed homomorphic, and those with alternating signs of interaction termed heteromorphic.[126] The secular equation for heteromorphic systems is

$$\begin{vmatrix} \alpha_{\mathrm{A}} - E & 2\beta \sin l\pi/n \\ 2\beta \sin l\pi/n & \alpha_{\mathrm{B}} - E \end{vmatrix} = 0 \qquad (9)$$

α_{A} and α_{B} are the Coulomb parameters for the two types of orbitals, and β is the resonance parameter. Solution of this secular equation for different numbers ($2n$) of ring atoms shows that the delocalization energy per π electron now increases steadily to a limit with increasing ring size. Consequently, there is no Hückel-type alternation of properties with ring size, and, in particular, delocalization energy per electron for $n = 4$ is greater than that for $n = 3$.[125,133]

The contrast between homomorphic and heteromorphic systems may be highlighted by solving the secular equations (eq 8 and 9) and comparing calculated properties for different ring sizes. Delocalization energy per electron, the energy of the highest occupied molecular orbital, and the electronic charge on B are compared graphically in Figures 13, 14, and 15. For each property the homomorphic system shows an alternation, indicative of the operation of Hückel's rule, but by contrast the heteromorphic system shows no alternation. These trends are fundamental and independent of particular choices of parameters; moreover, they should allow comparison with experimentally measured quantities. So far, however, the model is highly idealized. For instance, in planar molecules both types of d_π orbital may be expected to take part in bonding with p_π orbitals on neighboring atoms, and the more general secular equation in the Hückel approximation is [134]

$$\begin{vmatrix} \alpha - E & 2i\beta_{xz} \sin l\pi/n & 2\beta_{yz} \cos l\pi/n \\ -2i\beta_{xz} \sin l\pi/n & \alpha_{xz} - E & 0 \\ 2\beta_{yz} \cos l\pi/n & 0 & \alpha_{yz} - E \end{vmatrix} = 0 \qquad (10)$$

where the Coulomb integrals α, α_{xz}, and α_{yz} respectively belong to the p_π, d_{xz}, and d_{yz} orbitals. The resonance integrals β_{xz} and β_{yz} are functions of both the molecular geometry and the binding energies of the interacting atomic orbitals. This notation includes explicitly that d_{xz} and d_{yz} orbitals are symmetrically inequivalent in the molecular field, and therefore that different properties are to be associated with each.

If the d_{xz} and d_{yz} orbitals have equal Coulomb parameters, an alternative formulation of the π bonds is possible, first given by Dewar, Lucken, and Whitehead.[135] They showed that by reorienting the $3d_\pi$ orbitals, by taking the linear combinations in eq 11, the π molecular orbitals may be localized, so

$$d_\pi{}^a = 2^{-1/2}(d_{xz} - d_{yz})$$
$$d_\pi{}^b = 2^{-1/2}(-d_{xz} - d_{yz}) \qquad (11)$$

that ring conjugation is broken at each center which provides d_π orbitals (Figure 16). Delocalization now extends over three centers and the bonding is analogous to that in allylic bonds. Total π energies may still be substantial but the value per π electron is now independent of ring size for a series of planar $(AB)_n$ systems with constant angle at B. This prediction, which contrasts with those from the cyclic delocalization models, may in principle be tested experimentally. Theoretically, these delocalization models have been compared within the Hückel molecular orbital approach, and conditions described for each to be of value.[136] The clear result is that the more different the electronegativities of the two d_π orbitals the greater the breakdown of the three-center delocalization model. In certain cases the latter may work well, but for optimum performance it requires a ring angle of 90° at the B atoms and the d_{xz} and d_{yz} orbitals to have equal energies.

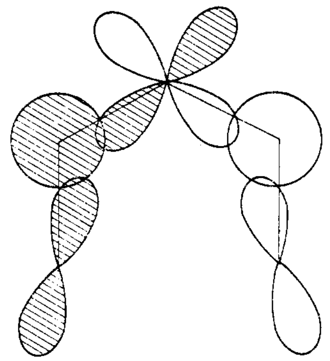

Figure 16. Projection of atomic orbitals to be combined in molecular orbitals for three-center or "island" delocalization.

B. BONDING IN THE CYCLIC PHOSPHAZENES

The cyclic phosphazenes (also known as phosphonitriles or phosphonitrilic compounds) of general formula $(NPX_2)_n$ have in recent years been extensively investigated and several reviews are available.[106,137–140] A dominant feature of these molecules is the great variety of possibilities available through variation of exocyclic groups X and ring size. The fluorides provide the most extensive series with individual cyclic compounds characterized from $n = 3$ to $n = 17$,[141] and there is evidence also for even larger rings.[142] This behavior is unusual. In general, very large rings are unfavorable in relation to chain molecules because the entropy of ring closure becomes progressively more negative with increasing ring size.[143] The explanation of the existence of the large ring phosphazenes may, in part, be found in the theory of electron delocalization to be discussed below, but other contributing factors include the ability of the nitrogen bond angle to adopt values from a wide range to suit particular molecular conformations.

The ring structures of the phosphazenes are rather stable. Reactions below 200° involve substitution of side groups, and

---

(133) D. P. Craig and N. L. Paddock, *Nature*, 181, 1052 (1958).

(134) D. P. Craig, Special Publication No. 12, The Chemical Society, London, 1958, p 343.

(135) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

(136) D. P. Craig and K. A. R. Mitchell, *ibid.*, 4682 (1965).

(137) N. L. Paddock and H. T. Searle, *Advan. Inorg. Chem. Radiochem.*, 1, 347 (1959).

(138) C. D. Schmulbach, *Progr. Inorg. Chem.*, 4, 275 (1962).

(139) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 62, 247 (1962).

(140) T. Yvernault and G. Casteignau, *Bull. Soc. Chim. France*, 1469 (1966).

(141) A. C. Chapman, N. L. Paddock, D. H. Paine, H. T. Searle, and D. R. Smith, *J. Chem. Soc.*, 3608 (1960).

(142) N. L. Paddock, personal communication.

(143) G. Gee, Special Publication No. 15, The Chemical Society, London, 1961, p 67.

Table II

Geometries of Cyclic Phosphazenes $(NPX_2)_n$[a]

Molecule	—Bond angles, deg— NPN	XPX	PNP	Bond lengths, Å P–N	P–X	Ref
$(NPF_2)_3$	120	100	120	1.56	1.52	149
$(NPF_2)_4$	123	100	147	1.51	1.51	150
$(NPCl_2)_3$	120	102	120	1.59	1.99	151, 152
K-$(NPCl_2)_4$	121	103	132	1.58	1.99	153
T-$(NPCl_2)_4$	122	103	135	1.56	1.99	154
$(NPCl_2)_5$	118	102	149	1.52	1.96	155
$(NPBr_2)_3$	119	103	121	1.58	2.18	156
$(NPMe_2)_4$	120	104	132	1.60	1.80	157
$[NP(NMe_2)_2]_4$	120	104	133	1.58	1.68	158
$[NP(NMe_2)_2]_6$	120	103	147	1.57	1.67	159
$[NP(OMe)_2]_4$	122	105	132	1.57	1.60	160
$[NP(OMe)_2]_8$	117	101	137	1.56	1.58	161

[a] All bond lengths and bond angles represent mean values. When X consists of more than one atom, the quoted P–X bond length is that to the atom bonded to phosphorus. Me represents the methyl group.

orientation patterns are beginning to be recognized.[144–146] At higher temperatures polymerization[106] or thermal rearrangement[147] may occur; the -P-N-P-N- pattern is maintained although in detail may be different from that of the original phosphazene. The halophosphazenes are less reactive than other comparable phosphorus halides. For example, $(NPCl_2)_3$ has a much higher stability to hydrolysis than PCl_5,[137] and also the rate of exchange of radioactive chlorine with $(NPCl_2)_3$ is several orders of magnitude less than the reaction with phosphoryl chloride.[148]

1. Structural Data

Structural data from X-ray crystallographic determinations of the cyclic phosphazenes are collected in Table II.[149–161] Features of particular interest include the following.

(1) All molecules with $n = 3$ have planar (or very nearly planar) ring frameworks.

(2) Molecules with n greater than 3 have nonplanar ring frameworks, but for the exceptions of $(NPF_2)_4$, which has D_{4h} symmetry, and $(NPCl_2)_5$, which approaches ring planarity by means of reentrant angles but does not approach D_{5h} molecular symmetry.

(3) All P–N ring bond lengths are considerably less than the single bond value of 1.78 Å, and most are less than 1.60 Å.

(4) All molecules of formula $(NPX_2)_n$ have equal ring bond lengths (within experimental error), although in $N_3P_3(C_6H_5)_2Cl_4$, in which the two phenyl groups are bonded to the same phosphorus atom, the ring bond lengths are significantly unequal,[162] the shortest being 1.56 and the longest 1.62 Å.

(5) Averaged ring angles at phosphorus are always between 117 and 123° and are usually close to 120°.

(6) Ring angles at nitrogen are close to 120° for trimeric molecules, but are larger for other ring sizes. For $(NPX_2)_4$, the nitrogen angle is 147° when $X = F$ and 132° when $X = CH_3$; moreover, the largest ring angle is found with the shortest P–N ring bond (1.51 Å), and the smallest ring angle with the longest P–N ring bond (1.60 Å).

2. Model of Bonding

Bonding in the phosphazenes is initially discussed in relation to the observed stereochemistries. It is assumed that at phosphorus the σ structure is based on sp^3 hybridization with distortion from tetrahedral symmetry, and that the nitrogen structure is based on sp^2 hybridization with two approximately trigonal hybrids (tr_1 and tr_2) for the ring σ bonds, the third hybrid (referred to by tr_3 in the later discussion) being radially directed. In a first approximation tr_3 is doubly occupied and the π system involves interaction of $2p_\pi$ orbitals at nitrogen with $3d_\pi$ orbitals at phosphorus. This formulation is oversimplified since it would require the ring angle at nitrogen to be no more than 120°. In line with the discussion in II.E this angle may open if the lone-pair charge formally at nitrogen is partially fed into phosphorus acceptor orbitals, which are most likely 3d orbitals. For planar phosphazenes, the 3d orbitals symmetric to reflection in the molecular plane, specifically $3d_{z^2}$, $3d_{x^2-y^2}$, and $3d_{xy}$, may contribute to a second delocalized system at right angles to the first. The component molecular orbitals antisymmetric and symmetric to reflection in the molecular plane are respectively termed π and π'.[105] In a nonplanar molecule this dual π system may still operate although the $2p_\pi$ orbital at nitrogen would also be overlapped by $3d_{x^2-y^2}$ and $3d_{xy}$, and the tr_3 orbital by $3d_{xz}$ and $3d_{yz}$. This model is sufficient for describing the stereochemistry of the phosphazenes, but other evidence indicates that it may be refined further.

3. Ligand Field Splitting of 3d Orbitals

The phosphorus site symmetry in the cyclic phosphazenes is at most C_{2v}, and this is sufficiently low to completely remove the free-atom 3d-orbital degeneracy.[105] This ligand field splitting may have important consequences for the nature of the 3d-orbital ring bonding.[136] Phosphorus 3d orbitals in molecular environments appropriate to planar halophosphazenes have been investigated theoretically using a model including exchange.[35] In the π system it is found that the $3d_{yz}$ orbital is weakly bound and diffuse, especially because of the strong exchange repulsions, through overlap with inner orbitals on exocyclic atoms that would be experienced by $3d_{yz}$ on

---

(144) M. Becke-Goehring, K. John, and E. Fluck, *Z. Anorg. Allgem. Chem.*, 302, 103 (1959).

(145) A. C. Chapman, D. H. Paine, H. T. Searle, D. R. Smith, and R. F. M. White, *J. Chem. Soc.*, 1768 (1961).

(146) S. K. Ray and R. A. Shaw, *ibid.*, 872 (1961).

(147) B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *ibid.*, 4459 (1964).

(148) D. B. Sowerby, *ibid.*, 1396 (1965).

(149) M. W. Dougill, *ibid.*, 3211 (1963).

(150) H. McD. McGeachin and F. R. Tromans, *ibid.*, 4777 (1961).

(151) F. Pompa and A. Ripamonti, *Ric. Sci.*, 29, 1516 (1959).

(152) A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960).

(153) R. Hazekamp, T. Migchelsen, and A. Vos, *Acta Cryst.*, 15, 539 (1962).

(154) A. J. Wagner, A. Vos, J. L. de Boer, and T. Wichertjes, *ibid.*, *Suppl.*, 16, A39 (1963).

(155) A. W. Schlueter and R. A. Jacobson, *J. Amer. Chem. Soc.*, **88**, 2051 (1966).

(156) E. Giglio and R. Puliti, *Acta Cryst.*, 22, 304 (1967).

(157) M. W. Dougill, *J. Chem. Soc.*, 5471 (1961).

(158) G. J. Bullen, *ibid.*, 3193 (1962).

(159) A. J. Wagner and A. Vos, *Rec. Trav. Chim.*, **84**, 603 (1965).

(160) G. B. Ansell and G. J. Bullen, *Chem. Commun.*, 430 (1966).

(161) N. L. Paddock, J. Trotter, and S. H. Whitlow, *J. Chem. Soc.*, *A*, 2227 (1968).

(162) N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **19**, 693 (1965).

contraction. These destabilizing influences are much less for the $3d_{xz}$ orbital which is directed between the surrounding groups. This latter orbital has a more favorable bonding exchange, but the most important influence is the electrostatic field which contracts $3d_{xz}$ from its free atom form. This evidence suggests, therefore, that the $3d_{xz}$ orbital is more readily available for bonding interactions than the $3d_{yz}$ orbital, and as a consequence the π system is heteromorphic and cyclically delocalized.[136] In the π' system, the molecular environment calculations indicate a substantial contraction of the $3d_{x^2-y^2}$ orbital, but the $3d_{xy}$ and $3d_{z^2}$ radial functions are left more or less unchanged from the free atom form. As for $3d_{yz}$, stabilization of $3d_{xy}$ and $3d_{z^2}$ is prevented by rather large repulsive exchange terms through overlap with nonbonding electrons. It should be noted, however, that these investigations of 3d orbitals in phosphazenes only considered 3d-orbital contributions to ring bonding, and it is possible that $3d_{z^2}$ could be stabilized by exocyclic interactions. In that event it could be useful to take the appropriate linear combination of $3d_{x^2-y^2}$ and $3d_{z^2}$ to form the $3d_{y^2}$ orbital,[90] and to treat the π' system as involving mainly overlap of tr_3 at nitrogen with $3d_{y^2}$ at phosphorus. Under conditions of strictly tetrahedral symmetry at the d center $3d_{y^2}$ is degenerate with $3d_{xz}$ so indicating an equality of the π and π' systems; in actual molecules the site symmetry is lower and the π and π' systems are unequal. Experimental observations are the only means available for deciding which of the two systems is the more important, as at present theoretical calculations are not sufficiently precise to be helpful in this regard. Whether $3d_{y^2}$ or $3d_{x^2-y^2}$ should be used for the π' system is largely undetermined; broadly $3d_{x^2-y^2}$ becomes more useful as ring π bonding predominates over exocyclic π bonding. But whichever orbital is chosen, the essential features are unchanged; particularly the π' system is delocalized and homomorphic, the latter contrasting with the π system.

4. *Comparison with Benzene*

Inevitably there is a tendency to discuss aspects of phosphazene chemistry in relation to that of benzene. This may not be entirely helpful, partly because in the phosphazenes the heteromorphic system seems to be energetically most important, and partly because in any event the energetic effects due to p_π–d_π double bonding are rather less than p_π–p_π interactions in bonds between first-row atoms. Differences between phosphazene and benzenoid aromatics are shown by spectra and magnetic susceptibilities. The uv spectra of the halophosphazenes do not show the characteristic benzenoid bands, and indeed the phosphazene spectra seem to be well correlated with transitions involving exocyclic halogens.[106] Similarities between the two types of spectra are not necessarily expected, for symmetry restrictions on ring $\pi \rightarrow \pi^*$ transitions are different. Thus for the p_π–d_{xz} molecular orbitals in the phosphazenes transitions from the top occupied orbitals to the bottom unoccupied orbitals are forbidden.[106] Diamagnetic susceptibilities perpendicular to ring planes are essentially different for p_π–d_{xz} delocalization compared to p_π–p_π delocalization. The latter π system is well known to provide enhanced diamagnetic susceptibilities; the former π system, on the other hand, is expected on theoretical grounds to show paramagnetic ring currents.[163] The measured anisotropy[163] of $(NPCl_2)_3$ is in the same sense as benzene but has a smaller value (-10.5×10^{-6} compared with -60×10^{-6} cgs unit). In practice interpretation of the susceptibility measurements is difficult, both because of the uncertain contributions of the σ electrons and because the π and π' systems in the phosphazenes are likely to contribute in opposite directions. So far, it has not been possible to obtain information on the ring molecular orbitals in the phosphazenes by esr spectroscopy.

5. *Thermochemistry*

In line with the structural data, thermochemical measurements are also consistent with a strengthening of the P–N bonds in excess of the single-bond value. This evidence has been reviewed by Craig and Paddock[105] who conclude that the ring bonds in $(NPCl_2)_3$ are about 6–10 kcal mole^{-1} stronger than a single P–N bond. Measurement of the heat of combustion of $(NPCl_2)_4$ suggests that the ring bonds in the tetramer are slightly stronger than those of the trimer. However, such thermochemical methods tend to be insensitive to small energy differences, and consequently a different approach was made.[164] This involved measuring heats of polymerization of the chlorophosphazenes as a function of ring size and showed the polymerization of these compounds to be exothermic, but decreasingly so for increasing molecular weight. With the assumption that each of the molecules polymerizes to the same high polymer, the heat of formation of each $NPCl_2$ unit in $(NPCl_2)_n$ is found to increase with increasing ring size up to $n = 7$ (the highest investigated). This observation is consistent with that expected theoretically for $2p_\pi$–$3d_{xz}$ bonding, and since other factors are involved, including π' bonding, it is concluded that the $2p_\pi$–$3d_{xz}$ bonding interactions are the dominant influence and therefore that they are energetically lower than the π' system.

6. *Ionization Potentials*

If the π system has lower energy than the π' system, ionization may be expected to involve the highest occupied level of the π' system. In agreement with expectation for homomorphic systems (Figure 14), a Hückel alternation is found for the early members of a number of phosphazene homologous series, including the fluorides, chlorides, and methyls.[165,166] For example, for the fluorides the values of the first ionization potential are 11.6 eV for $n = 3$, 10.9 eV for $n = 4$, and 11.1 eV for $n = 5$, after which the values are essentially constant. Always the trimer has the highest value. This fits the theory, but the differences are somewhat too large. Paddock[142] has noted that reorganization of the 3d electron structure in the positive ions should especially favor 3d-orbital bonding in the first member of the series, since each phosphorus atom "feels" a larger positive charge in the trimeric ring compared with the others. This may well contribute to the larger ionization potentials of the trimers.

Consistently with the theory discussed for 3d-orbital participation, the fluorides have higher ionization potentials than the chlorides, and the methyls are smaller still.[166] This trend is the same as that for the exocyclic groups alone, but it is likely

---

(163) D. P. Craig, M. L. Heffernan, R. Mason, and N. L. Paddock, *J. Chem. Soc.*, 1376 (1961).

(164) J. K. Jacques, M. F. Mole, and N. L. Paddock, *ibid.*, 2112 (1965).

(165) C. E. Brion, D. J. Oldfield, and N. L. Paddock, *Chem. Commun.*, 226 (1966).

(166) C. E. Brion and N. L. Paddock, unpublished work.

that the molecular values would be larger if ionization only involved the exocyclic groups.

7. The Influence of Exocyclic Groups

The influence of the exocyclic group on ring bonding has already been suggested by structural evidence. For example, in the tetrameric phosphazenes the methyl and fluorine derivatives provide the extremes in ring bond length and nitrogen ring angle, and this seems to hold more generally. Craig and Paddock[105] noted the steady increase of the P–N ring stretching frequency in $(NPX_2)_3$ molecules with increasing electronegativity of the exocyclic group X; the frequency increases from 1180 cm^{-1} for methyl to 1287 cm^{-1} for fluorine. All experimental evidence points to stronger ring bonding with fluorine than with methyl, and it should be emphasized that this contrasts with the prediction of the ionic model which neglects 3d orbitals. The latter model would also predict increased negative charge at nitrogen, and this seems inconsistent with the weakness of the halophosphazenes as bases, although the basicities can be increased with exocyclic amino groups.[106, 167]

8. Distribution of Electron Density

Estimates have been made of the partitioning of electron density between ring nitrogen and phosphorus atoms as a function of ring size. The experimental evidence is of two types. The first refers to general electron density variation and the second to the nitrogen lone pairs. In the first category both the reduction in the phenol O–H stretching frequency caused by hydrogen bonding to the phosphazenes[168] and ^{31}P nmr chemical shifts[169] are consistent with an electron drift from nitrogen to phosphorus as n increases. In the second category estimates have been made of the basicities of $(NPCl_2)_n$ by measuring solubilities of HCl in chlorophosphazene solutions.[165] The evidence from these measurements indicates a tendency for the basicities to alternate; rings with $n = 4$, 6, and 8 are more basic than those with $n = 5$ and 7. Consistently the average nitrogen ring angle is 17° larger in $(NPCl_2)_5$ than in $(NPCl_2)_4$. In principle, steric factors could be relevant to the explanation of the opening of nitrogen ring angles, but although such influences are important in particular respects, for example, in limiting the possibilities for molecular conformation of nonplanar rings,[170] it does not seem possible to explain in this way the large angle in the tetrameric fluoride (147°) as compared with that in the tetrameric dimethylamide (133°) in which the exocyclic groups are much larger. An alternation has also been observed for reactivities; thus nucleophilic attack at phosphorus is faster[148] for $(NPCl_2)_4$ and $(NPCl_2)_6$ than for $(NPCl_2)_5$, and this fits in with the evidence from basicities.

9. The Dual π System

The experimental basis of the dual π system has now been discussed. This model has been applied to other features of the cyclic phosphazenes, including flexibility and molecular conformation,[105] but its special value derives from providing a means for discussing the detailed variation of properties with ring size. Indeed, the correlations between theory and experiment in this field give support to the wider concept of 3d-orbital participation in bonds of second-row elements.

10. Exocyclic π Bonding

Evidence for exocyclic π bonding is found in the detailed structural arrangements of the exocyclic groups in $[NP(OMe)_2]_8$[161] and $[NP(NMe_2)_2]_4$.[158] In the second molecule the exocyclic P–N bond lengths may be compared directly with the ring P–N bond lengths, and since the exocyclic bonds are on average 0.10 Å longer than the ring bonds, it is very probable that the former are weaker. This difference seems too large to be due solely to differences in σ bonding, and therefore the most likely explanation is that the exocyclic π interactions are weaker than the ring π interactions.[105]

Exocyclic π bonding through participation of $3d_{xz}$, $3d_{x^2-y^2}$, and $3d_{z^2}$ orbitals may be expected with all groups that are able to release electrons to phosphorus by π interaction, and this may involve either lone-pair donation or hyperconjugation. Conditions for electron donation cannot always be straightforwardly interpreted according to simple electronegativity trends, as may be seen by comparison of exocyclic bond lengths in $(NPCl_2)_3$ (P–Cl = 1.99 Å) and in $(NPF_2)_3$ (P–F = 1.51 Å). The difference (0.48 Å) is significantly greater than that between the bond lengths of HCl and HF, the latter being only 0.35 Å.[91] Since hydrogen and phosphorus have the same electronegativity values on the Pauling scale,[31] simple bond-length considerations based on covalent radii and electronegativity difference corrections predict these two bond-length differences to be closely similar. The appreciable divergence probably reflects the influence of π bonding, and the comparison just given suggests a greater π bonding in P–F than in P–Cl. On the simplest electronegativity grounds, fluorine would be considered a poorer donor than chlorine, and in the σ bond this consideration undoubtedly applies. For the π bond, more subtle influences may operate as, for example, has been noted from analysis of wave functions of HCN[13] and BN compounds.[171, 172] In C–N and B–N bonds, the σ electrons seem to be distributed with a net drift to nitrogen, the most electronegative atom, whereas the π electrons are distributed in the reverse sense. In the cases of P–F and P–Cl exocyclic bonds in phosphazenes, the apparently greater π bonding in the P–F bond may be rationalized as follows: since fluorine is more electronegative than chlorine, the P–F σ bond should be more ionic than the σ bond in P–Cl, and because of the larger negative charge, the π atomic orbitals of fluorine are expected to be expanded more with better π-donation possibilities.

11. Delocalization Energy

A feature that has been referred to above, but not properly discussed, is the fact that the bond-energy terms, E(P–N), for the chlorophosphazenes are only about 6–10 kcal $mole^{-1}$ greater than that for a single P–N bond. At first sight this is hard to reconcile with the structural evidence which points so emphatically to bonding interactions additional to the σ

---

(167) D. Feakins, W. A. Last, and R. A. Shaw, *Chem. Ind.* (London), 510 (1962).

(168) N. L. Paddock and D. R. Smith, quoted in ref 105.

(169) L. G. Lund, N. L. Paddock, J. E. Proctor, and H. T. Searle, *J. Chem. Soc.*, 2542 (1960).

(170) K. A. R. Mitchell, Thesis, University of London, 1963.

(171) O. Chalvet, R. Daudel, and J. J. Kaufman, *J. Amer. Chem. Soc.*, 87, 399 (1965).

(172) R. Hoffmann, *J. Chem. Phys.*, 40, 2474 (1964).

bonds. It is of course a well-known result from the study of bond-energy terms in molecules of first-row elements that π bonds are generally weaker than corresponding σ bonds, essentially because the overlap of π atomic orbitals occurs in regions of lower effective nuclear field than the overlap of σ atomic orbitals. However, it seems that the difference between σ and π energies of bonds formed by first- and second-row atoms cannot wholly be explained in this way, because it would point to small π effects over-all, in contradiction to the structural evidence.

The explanation for the apparently small π contributions is twofold. The main point is that the whole procedure of partitioning between σ and π components is on unsure ground. It depends on applying a value of the σ-bond energy measured in one valence state to calculations of energies in a different valence state. Also, the distinction between σ and π bonds is often now invalid from the strict symmetry point of view. The following example will illustrate. It depends on a comparison of P–O bonds in trivalent molecules of the type $P(OR)_3$ with those in pentavalent phosphoryl compounds R_3PO. According to conventional valence theory, the outer shell of phosphorus in the first molecule contains four electron pairs, but in the second molecule there are five electron pairs. Consequently, electron repulsions must be increased in the phosphoryl compound, leading to a reduction in the effective nuclear field in the overlap region of R_3PO compared to $P(OR)_3$. This indicates that E(P–O) deduced for $P(OR)_3$ is likely to exaggerate the σ contribution in the P–O bond of R_3PO, thereby apparently diminishing the size of the π contribution. Increased electron repulsion, therefore, is one reason why E(P–N) is comparatively small in the phosphazenes.

The second reason for small π energies is the neglect of the energy to compress a σ bond from the single-bond length to that appropriate for a bond with π character.[173] In the phosphazenes, this reduction in P–N bond length is about 0.20 Å. The compression energy is not in any sense "lost," since the observed molecular bond lengths are those that minimize total energy without regard to allocation between σ and π contributions, but the distribution between the two will be affected. The concept of compression energy is well known for delocalized systems of first-row atoms; for benzene it has been estimated to be as high as 30 kcal mole^{-1}.[174,175] Comparative values are not known for phosphazenes, but the bond-length reduction is often greater than that for benzene (0.15 Å).

These considerations of π-bond energies highlight the problems in deducing the additional contribution assignable to delocalization energies in phosphazenes and related molecules, and it must be concluded that this concept is less useful than for benzenoid aromatics. The position should be clearer with more extensive thermochemical data.

C. OTHER $(AB)_n$ SYSTEMS OF FIRST- AND SECOND-ROW ELEMENTS

Molecular systems with alternating atoms from the first and second rows are known for nearly all combinations of the first-row elements B, C, N, and O with the second-row elements Al, Si, P, and S. Structural evidence for 3d-orbital bonding in systems formed from either O or N with the second-row atoms Si, P, and S has been discussed by Cruickshank,[90] and structural data for $(AB)_n$ systems of this sort have been collected by Allcock.[131] In the cyclic molecules (for example, metaphosphates, trimeric sulfur trioxide, silazanes), a dual π system of molecular orbitals may again be associated with the ring bonds. However, in the wider use of this theory there are some differences from the phosphazenes. The first concerns the influence of exocyclic π bonding. For the phosphazenes, this is much less important in the interpretation of structure and chemical behavior than ring π bonding. On the basis of structural evidence this is also true of the thiazyl molecules, but in, for example, metaphosphates, metaphosphimates, and polymeric sulfur trioxide, exocyclic π bonding is the more important. A more nearly equal partitioning of the π bonding between exocyclic and ring bonds occurs in the sulfanuric halides.

The simple molecular orbital treatment of ring π bonding is readily extended to include exocyclic π bonding.[176] The main result is that as exocyclic π bonding increases over ring π bonding, then the symmetry-determined aspects of ring π bonding, as expressed in heteromorphic or homomorphic behavior, tend to become less prominent. This may also happen for another reason. Increased exocyclic π bonding results in the ring angle at the second-row element being less, and this contributes toward increased puckering of the ring. Strictly, distortions from planarity blur the distinction between heteromorphic and homomorphic character, although for small distortion this classification is likely to remain useful and may even be useful with large distortions, provided the ligand field splitting of the 3d orbitals is sufficiently small that these orbitals can be combined linearly to effect equalization of ring overlaps.[176]

The value of the dual π model in systems other than the phosphazenes has still to be tested in detail, and this is because the experimental data (other than structural) are much less extensive than for the phosphazenes, and few relevant properties are known as a function of ring size. Consequently, structural evidence must be heavily relied upon with tests against other evidence wherever possible.

1. *Metaphosphates and Linear Phosphates*

Structural determinations by X-ray crystallography have been made for a considerable number of cyclic and linear phosphates, and averaged values for metaphosphate anions are quoted in Table III.[177–183] The data are consistent with dominant π bonding in the exocyclic bonds, but comparison with the expected P–O single-bond length (1.72 Å) does suggest that π bonding is present in the ring bonds also. In essential respects, analogous trends in bond lengths and angles are shown by the linear phosphates, structures having been deter-

---

(173) J. C. McCoubrey, personal communication to N. L. Paddock quoted in ref 106.

(174) C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.*, 48, 293 (1952).

(175) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, 63, 41 (1941).

(176) K. A. R. Mitchell, unpublished work.

(177) E. D. Eanes and H. M. Ondik, *Acta Cryst.*, **15**, 1280 (1962).

(178) H. M. Ondik, *ibid.*, 18, 226 (1965).

(179) D. W. J. Cruickshank, *ibid.*, 17, 675 (1964).

(180) H. M. Ondik, S. Block, and C. H. MacGillavry, *ibid.*, 14, 555 (1961).

(181) H. M. Ondik, *ibid.*, 17, 1139 (1964).

(182) O. H. Jarchow, *ibid.*, 17, 1253 (1964).

(183) K. H. Jost, *ibid.*, 19, 555 (1965).

Table III

Geometries of Metaphosphate Anions

	Bond angles, deg			*Bond lengths, Å*		
Molecule	*POP (ring)*	*OPO (ring)*	*OPO (exo-cyclic)*	*P–O (ring)*	*P–O (exo-cyclic)*	*Ref*
$LiK_2P_3O_9\cdot H_2O$	130	101	121	1.61	1.48	177
$Na_3P_3O_9$	127	101	120	1.62	1.48	178
$Na_3P_3O_9\cdot H_2O$	124	102	121	1.62	1.48	178
$(NH_4)_4P_4O_{12}$	131	104	122	1.61	1.49	179
$Na_4P_4O_{12}\cdot 4H_2O$ (monoclinic)	132	100	121	1.61	1.49	180
$Na_4P_4O_{12}\cdot 4H_2O$ (triclinic)	134	101	121	1.60	1.47	181
$Na_2H_2P_4O_{12}$	132	106	119	1.60	1.47	182
$Na_6P_6O_{18}\cdot 6H_2O$	130	99	120	1.61	1.49	183

mined for $(NaPO_3)_x$,[184] $(KPO_3)_x$,[185] $(RbPO_3)_x$,[186] $[Na_2H(PO_3)_3]_x$,[187] $(AgPO_3)_x$,[188] and $[Pb(PO_3)_2]_x$.[189] Small variations in ring bond lengths are found in the measured structures of the metaphosphates. Interpretation of these variations is not easy because many factors can operate, including changes in σ-bond hybridization, nonbonded repulsions, and the polarizing effects of neighboring cations. In general, if a bond of short length (say shorter than average for the particular molecule) genuinely reflects large π contributions, the adjacent ring angles should be greater than average. Such a relationship has been noted[106] in the structure of monoclinic $Na_4P_4O_{12}\cdot 4H_2O$ and may be recognized to varying extents in other metaphosphates.

A weak bond alternation is found in the long-chain phosphates. An example is $[Pb(PO_3)_2]_x$ for which successive backbone P–O lengths are 1.53, 1.57, 1.54, 1.62, 1.51, 1.62, 1.53, 1.56 Å, and similar "greater-and-shorter" variations are shown in other polyphosphates.[189] It would be useful to have a more highly refined determination on one or more of these structures because strictly these variations are not significant, although, taken together, the present evidence does suggest the alternations may be real. If so, this structural feature could be connected with a phenomenon first described by Longuet-Higgins and Salem.[11,190] These authors discussed features of aromatic hydrocarbons with $4m + 2$ π electrons as a function of ring size and showed that there is a tendency toward alternating bond lengths in large rings. This is easily visualized as the result of the diminishing π energy per electron with increasing *m*; eventually the π energy is insufficient to overcome the σ-bond compression energy, and localized π bonds become more stable. This theory has been applied to $(AB)_n$ systems[191,192] and the main results are the following.

(1) For heteromorphic systems, bond alternation is especially likely for small ring size and for the small electronegativity difference (ρ) between the orbitals provided by A and B.

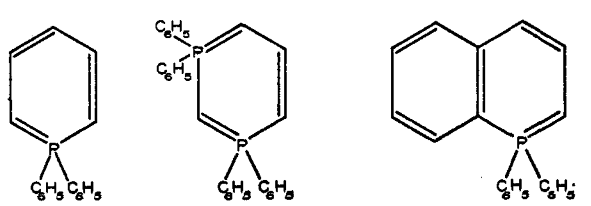

Figure 17. Some known cyclic methylene phosphoranes.

(2) For homomorphic systems the result found by Longuet-Higgins and Salem remains provided ρ is below a certain critical value. If ρ is larger, bond alternation is not expected. Thus as ρ increases, less mixing of the π atomic orbitals occurs, and for sufficiently large ρ the structure with equal bond lengths is maintained by the σ electrons.

The effective electronegativity difference between phosphorus and oxygen orbitals in phosphate π bonds cannot, for reasons previously discussed, be estimated from atomic data, but the effect of the molecular environment and σ-charge migration is to reduce the free-atom difference. Therefore, the bond alternation observed in the long-chain phosphates may indicate predominantly homomorphic interactions, and this is also consistent[106] with the greater stability of the trimetaphosphate ion compared to other metaphosphates and to the polyphosphate chain.[193] Strictly, more evidence is needed before one can be confident about this explanation. Thus, properties of the metaphosphates are much less strongly dependent on ring size than is the case for the phosphazenes, and examples of this insensitivity are shown by oxygen ring angles (Table III) and ^{31}P nmr chemical shifts. To illustrate the latter, the ^{31}P chemical shifts of the three well-established metaphosphates ($n = 3$, 4, and 6) are respectively 21.2, 23.4, and 22.4 ppm relative to 85% H_3PO_4.[194,195] By contrast the phosphazenes show much greater variations; typically for $[NP(OC_6H_5)_2]_n$ values are −17.9 ppm for $n = 3$ and 0.6 ppm for $n = 4$.[196]

2. Cyclic SN and PC Rings

On present evidence, the phosphazenes show the dual π system more clearly than other molecules. The related molecular series of general formulas $(NSX)_n$ and $(R_2PCR')_n$ are of interest for comparison because in these the π′ components seem likely to be diminished. Cyclic thiazyl derivatives $(NSX)_{3,4}$ are known,[197] but generally are less stable than the phosphazenes. In the thiazyls, the sulfur lone pair seems to prevent stabilization of the $3d_{x^2-y^2}$ orbital.[105] This results in $2p_\pi$–$3d_{xz}$ being the only important supplementary interactions, and in (NSF_4) these interactions are localized in alternate double and single bonds[114] rather as for cyclooctatetraene. Ring molecules based on a cyclic alternating pattern of phosphorus and carbon are still unknown, although they do now seem within reach following the preparation by Märkl[198,199] of some cyclic methylene phosphoranes including those illustrated in Figure 17. On the current theory, the π′-bonding mechanism is restricted for PC molecules because

---

(184) K. H. Jost, *Acta Cryst.*, 14, 844 (1961).
(185) K. H. Jost, *ibid.*, 16, 623 (1963).
(186) D. W. J. Cruickshank, *ibid.*, 17, 681 (1964).
(187) K. H. Jost, *ibid.*, 15, 951 (1962).
(188) K. H. Jost, *ibid.*, 14, 779 (1961).
(189) K. H. Jost, *ibid.*, 17, 1539 (1964).
(190) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), A251, 172 (1959).
(191) D. W. Davies, *Nature*, 194, 82 (1962).
(192) C. W. Haigh and L. Salem, *ibid.*, 196, 1307 (1962).
(193) E. Thilo, *Advan. Inorg. Chem. Radiochem.*, 4, 1 (1962).
(194) E. Fluck, *Z. Naturforsch.*, 20b, 505 (1965).
(195) E. J. Griffith and R. L. Buxton, *Inorg. Chem.*, 4, 549 (1965).
(196) M. L. Nielsen and J. V. Pustinger, *J. Phys. Chem.*, 68, 152 (1964).
(197) O. Glemser, *Angew. Chem. Intern. Ed. Engl.*, 2, 530 (1963).
(198) G. Märkl, *ibid.*, 2, 153 (1963).
(199) G. Märkl, *ibid.*, 3, 147 (1964).

carbon has no lone pairs suitable for bonding interactions with empty 3d orbitals at phosphorus. Also, the exocyclic bond at carbon may hinder angle opening and the attainment of planarity, and thereby reduce the effectiveness of p_π–d_π interactions. This should especially destabilize the larger rings.

3. The Phosphinoborines

The phosphinoborines, $(R_2PBR_2')_n$, based on a framework of alternating phosphorus and boron, are of interest because of a surprising inertness to heat and chemical action,[200,201] particularly since P–B bonds are normally thought to be comparatively weak. The magnitude of E(P–B) is indicated[202] by estimated enthalpy changes for the addition reactions

$$(C_6H_5)_nPH_{3-n} + BH_3 \longrightarrow H_{3-n}(C_6H_5)_nP\text{–}BH_3$$

for which ΔH ranges from -31 kcal mole^{-1} for $n = 1$ to -38 kcal mole^{-1} for $n = 3$. At a first approximation the P–B bond in these adducts may be considered to be based on a dative σ bond, and correspondingly it is expected that the P–B bonds in the phosphinoborines also involved dative contributions to the σ bonds. The presence of such bonds between phosphorus and boron inevitably restricts the possible exocyclic groups. The attachment of strongly electron-attracting groups to either phosphorus or boron is likely to destabilize the system: at phosphorus because of the reduced ability of phosphorus to donate, and at boron because of the increased need for donation from phosphorus. These simple considerations seem consistent with the general features of these molecules, although there is a suggestion by Burg and Wagner[201] that in addition to the coordinate σ bond between phosphorus and boron, charge is back-donated from the B–H bonds into vacant 3d orbitals at phosphorus. In principle, this is not unreasonable insofar as the P–B dative σ bond involves an electron drift to boron, the slightly less electronegative atom, but at present there seems to be no compelling evidence that this mechanism makes an important contribution to stability.

Table IV

Molecular Geometries of Phosphinoborines

Molecule	*Bond angles, deg* BPB	CPC	PBP	*Bond lengths, Å* P–B	P–C	Ref
$[(CH_3)_2PBH_2]_3$	118	100	112	1.94	1.84	203
$[(CH_3)_2PBH_2]_4$	125	103	104	2.08	1.84	204

In terms of the principles discussed earlier, the molecular field in known phosphinoborines does not seem promising for 3d-orbital participation, and since the estimated P–B single-bond distance is 1.98 Å the structural evidence given in Table IV[203,204] indicates that these molecules are based on frameworks without substantial double bonding. Also, the high stabilities of B–H bonds in phosphinoborines[201] seem inconsistent with a mechanism that involves some degree of B–H bond weakening. The B–H stretching frequency in $[(CH_3)_2PBH_2]_3$ indicates no weakening in the bond compared with that in the borohydride ion.[205] All this evidence weakens the case for substantial use by 3d orbitals.

Clues to 3d-orbital participation in phosphinoborines could perhaps be recognized through study of properties as a function of ring size. Trimeric phosphinoborines are found to be generally more stable than the tetramers,[200] but this may be for steric reasons. The structural data reported in Table IV for $[(CH_3)_2PBH_2]_4$ suggest that the methyls bonded to phosphorus and the hydrogens bonded to boron interact sterically, causing a difference in bond lengths and bond angles between this structure and that of the corresponding trimer. In $[(CH_3)_2PB(CH_3)_2]_4$, which has not so far been prepared, the steric hindrance is likely to be greater. Simple considerations of nonbonded distances in $[(CH_3)_2PBH_2]_4$, for a series of molecular conformations, indicate that the reported shape, with D_{2d} symmetry and the phosphorus atoms lying at the corners of a square,[204] is best for minimizing steric interactions between the exocyclic groups.[176] This factor is less critical in the trimers and may explain the relative stabilities of trimers and tetramers. Overcrowding of the exocyclic groups inevitably hinders chemical attack, and on this viewpoint the high stability of the phosphinoborines is mainly kinetically controlled.

4. Four-Membered Rings

An interesting feature of cyclic systems based on alternating first- and second-row atoms is the rather frequent occurrence of four-membered rings. Some particular four-membered ring molecules based on frameworks of Al and O,[206,207] and also on Al and N,[208] have a surprisingly high thermal stability, bearing in mind that four-membered rings are normally considered strained. Double bonding by means of 3d orbitals does not, however, seem important for aluminum bonding; indeed a dominant feature of the structural chemistry of this atom is its attainment of valence saturation by means of single bonding.[209,210] The comparative stability of the four-membered ring molecules must be ascribed partly to their ability to minimize nonbonded repulsions and partly to an extra resonance stabilization that arises through lack of perfect pairing of the ring bonds. It seems probable that the assumption of perfect pairing of the ring σ-bonding orbitals fails for molecules with small ring angles, and that σ delocalization becomes more important. Nevertheless, wherever comparative evidence is available, it does seem that four-membered rings are chemically more reactive than corresponding six- or eight-membered rings.[211]

Participation by 3d orbitals is possible in other four-membered ring molecules. The length of the ring Si–N bond in $[(CH_3)_3SiNSi(CH_3)_2]_2$ is 1.72 Å,[212] which is not significantly

---

(200) A. B. Burg, ref 143, p 17.

(201) A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **75**, 3872 (1953).

(202) M. A. Frisch, H. G. Heal, H. Mackle, and I. O. Madden, *J. Chem. Soc.*, 899 (1965).

(203) W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

(204) P. Goldstein and R. A. Jacobson, *J. Amer. Chem. Soc.*, **84**, 2457 (1962).

(205) N. L. Paddock, *Roy. Inst. Chem.* (London), *Lectures, Monographs, Rept.*, No. 2 (1962).

(206) H. Schmidbaur and M. Schmidt, *Angew. Chem. Intern. Ed. Engl.*, **1**, 549 (1962).

(207) H. Schmidbaur and M. Schmidt, *J. Amer. Chem. Soc.*, **84**, 1069 (1962).

(208) H. Schmidbaur and M. Schmidt, *Angew. Chem. Intern. Ed. Engl.*, **1**, 327 (1962).

(209) D. C. Bradley in "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, New York, N. Y., 1962, p 410.

(210) A. W. Laubengayer, ref 143, p 78.

(211) W. Fink, *Angew. Chem. Intern. Ed. Engl.*, **5**, 760 (1966).

(212) P. J. Wheatley, *J. Chem. Soc.*, 1721 (1962).

different from the average ring bond lengths in the two molecular forms of $[(CH_3)_2SiNH]_4$[213] and is shorter than the expected single bond length (1.80 Å). Likewise, an increased strength of the ring P–N bonds in $(Cl_3PNCH_3)_2$ is indicated by measured bond lengths[214] and estimated bond energies.[215]

The four-membered phosphorus–nitrogen ring molecules of formula $(R_3PNR')_2$ are dimers of the phosphinimines $R_3P{=}NR'$. Formally, the main structural difference between these two molecular types is that the monomer involves a double P–N bond, whereas the dimer has two P–N σ bonds, and since either form may be found, depending on the nature of R and R′, the balance between them is a very fine one. The conditions of acceptable 3d orbital radial functions for bonding are more stringent for d_σ bonding than for d_π bonding[15] and consequently a rather more electronegative environment at phosphorus is needed for the formation of a dimer. Consistently, dimerization is favored by electron-withdrawing groups at phosphorus; thus Cl_3PNCH_3 is dimeric, whereas $(C_6H_5)_3PNC_2H_5$ is monomeric.[216] Another correlation is with the basicity of the parent amine H_2NR'. Thus, the greater the basicity, the greater the tendency for dimerization.[217] Again this suggests that supplementary d_π bonding may be significant in the dimers. An interesting contrast is shown in sulfur–nitrogen chemistry, since the molecule F_3SN shows no tendency to dimerize. This is not well understood.

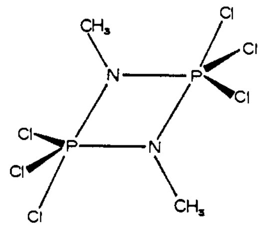

Figure 18. The molecular structure of $(Cl_3PNCH_3)_2$.

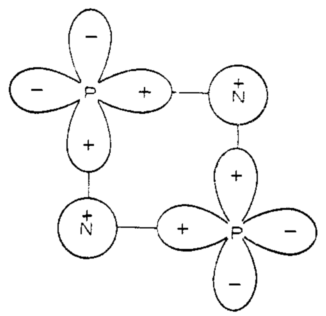

Figure 19. "Birds-eye-view" of orbital overlap for supplementary ring π bonding in $(Cl_3PNCH_3)_2$.

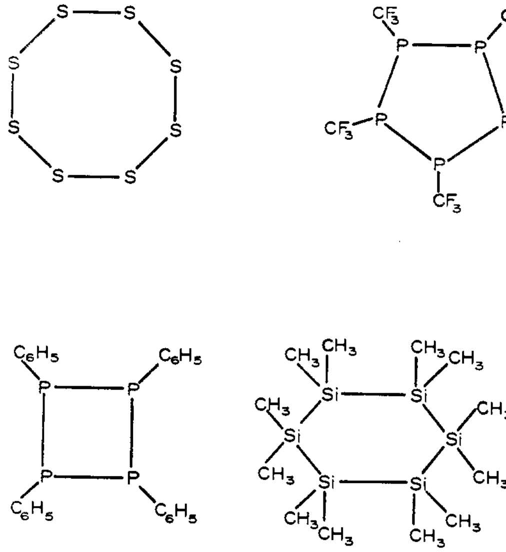

Figure 20. Some cyclic molecules with homoatomic frameworks based on second-row atoms.

The structural arrangement at each phosphorus in $(Cl_3PNCH_3)_2$ fits closely to the trigonal-bipyramid arrangement (see Figure 18) with one axial and one equatorial nitrogen, and one axial and two equatorial chlorines.[214,218] The P–N bond length variation around the planar four-membered ring is perhaps to be connected with the difference between axial and equatorial bond lengths in trigonal-bipyramidal structures. This difference for P–N bonds (0.15 Å) is similar to that for the P–Cl bonds (0.13 Å). The three σ bonds at each nitrogen are coplanar and again suggest that the nitrogen lone pairs, accommodated in $2p_z$ orbitals, are involved in supplementary π bonding. Interest centers on the form of this π bonding, and it could be that this molecule provides an example of the three-center island type bonding first proposed by Dewar, Lucken, and Whitehead.[135] Orbital overlap in this scheme is indicated diagrammatically in Figure 19. The orbitals $3d_\pi{}^a$ and $3d_\pi{}^b$ (eq 11) correspond to two of the 3d orbitals normally considered available for supplementary π bonding in trigonal-bipyramid structures, and although these orbitals are not strictly equivalent in the molecular environment, it is probable that differences between them are quite small. For $3d_\pi{}^a$ and $3d_\pi{}^b$ orbitals of very different energy, this π system would progressively be concentrated in alternate bonds, but at the moment there is no way of measuring the influence of this π effect, which must be superimposed on the bond-length variation of the σ bonds. Structurally, other molecules of formula $(R_3PNR')_2$ resemble that described for $(Cl_3PNCH_3)_2$.[219,220]

D. RINGS WITH HOMOATOMIC FRAMEWORKS

In the second row, catenation is found for silicon, phosphorus, and sulfur, and some representative molecular examples are illustrated in Figure 20. The molecules covered by the formula $(RP)_n$ have attracted considerable interest because of the possibilities of high thermal stability and 3d-orbital participation in bonding.[200] The latter has been suggested mainly on account of the strong uv absorption and feeble basicity of the cyclic phosphines;[221–223] these properties contrast with those

---

(213) G. S. Smith and L. E. Alexander, *Acta Cryst.*, 16, 1015 (1963).

(214) H. Hess and D. Forst, *Z. Anorg. Allgem. Chem.*, 342, 240 (1966).

(215) P. A. Fowell and C. T. Mortimer, *Chem. Ind.* (London), 444 (1960).

(216) S. Trippett, *J. Chem. Soc.*, 4731 (1962).

(217) I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, 30, 3044 (1960); *J. Gen. Chem. USSR*, 30, 3018 (1960).

(218) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc.*, *A*, 1203 (1966).

(219) J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967).

(220) A. J. Downs, *ibid.*, 628 (1967).

(221) W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Amer. Chem. Soc.*, 85, 2462 (1963).

(222) W. Mahler and A. B. Burg, *ibid.*, 79, 251 (1957).

(223) W. Mahler and A. B. Burg, *ibid.*, 80, 6161 (1958).

of ordinary tertiary phosphines. Structurally, on the other hand, there is no clear evidence for supplementary π bonding. The P–P bond length is usually close to 2.22 Å and is not markedly affected by substituents or the phosphorus valence state.[205,224,225] A general difficulty, however, is to determine standard single-bond lengths. S–S bond lengths have, for example, been analyzed as a function of dihedral angle, but the bond-length changes are small, and it is difficult to bring out the relative importance of lone-pair repulsions and π bonding.[226]

At present, discussion of 3d-orbital bonding in the ground states of these systems is not well based, essentially because there is not sufficient experimental evidence, and with the molecules available it is not easy to see how this can be overcome. Progress may be possible if some new systems, that more directly involve $3d_\pi$ cyclic bonding, can be synthesized. Craig[126] has pointed to the molecule $(PF_2)_6$ (Figure 21) as being well suited for this purpose, and attempts at the synthesis of this and related molecules could be useful.

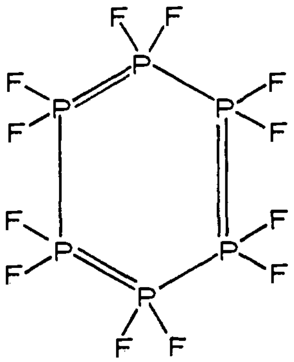

Figure 21. Hypothetical $(PF_2)_6$.

A suggestion of $3d_\pi$ delocalized bonding has come with the recent report of the radical anion of $[Si(CH_3)_2]_6$, and an investigation by esr spectroscopy has shown that the unpaired electron is delocalized over all six Si atoms.[227] The uv spectra of molecules with Si–Si bonds indicate that 3d interactions may be significant,[228] at least in excited states. A concerted attack on the electronic structure of systems of this general sort could lead to refinement of the underlying aspects of bonding models, and thereby provide useful leads to new polymer systems.

IV. d Orbitals of Third- and Later Row Atoms

It is commonly assumed that the covalent bonding models developed for first-row molecules are, to a reasonable approximation, applicable to molecules formed by atoms of high atomic number. For second-row atoms, we have seen that in particular circumstances free-atom atomic orbitals may be modified in molecular environments, and this is likely to become increasingly important with atoms of higher polarizability. The degree of d-orbital participation in valence states of atoms of the third and successive rows has not so far been thoroughly tested. Recent considerations of bonding in this area of the periodic table have been particularly directed at the interhalogens[229] and compounds of the rare gases,[230–232] and there has been a tendency to minimize d-orbital participation in these compounds, mainly on account of the large promotion energies indicated for the free atoms.[233] So far, little is known either about the radial functions of d orbitals in excited configurations of these atoms or about the sensitivity of d-orbital properties to molecular environment. By analogy with SF_6 and related molecules of second-row atoms, there is the possibility that electronegative environments may encourage valence-shell d-orbital availability for the higher members of groups VB to VIIIB. If this is so, central-atom d-orbital involvement may be significant in such molecular species as BrF_5, $XeOF_4$, TeF_6, and ICl_4^-, but rather less significant in, for example, Br_3^- and I_5^-.

The bonding models which can accommodate minimal d-orbital participation are those mentioned in section II, namely the molecular orbital model and the valence-bond resonance model. The molecular orbital scheme, which in its simplest form uses only p orbitals, readily accounts for particular structural features of the interhalogens and polyhalides including the tendency of bond angles to be close to either 90 or 180°.[229,234] Consistently with the three-center molecular orbital model,[235] measured I–I bond lengths in I_3^- are rather longer (2.9 Å is representative) than in the I_2 molecule (2.67 Å), and similarly bond lengths in other polyiodides and polybromides are longer than expected for essentially single bonds.[229] By contrast, in molecules in which the central atom is in an electronegative environment, for example, BrF_5, IF_7, and ICl_2^-, measured bond lengths are close to or even shorter than single-bond values,[229] and this does not seem consistent with multicenter bonding involving a deficiency of bonding electrons. The molecular orbital model predicts the bonds to be highly ionic. The weak covalent bonding is therefore supplemented by ionic contributions, and in a sense this may bring the bond order up to about unity. However, this argument may not be good, essentially because the simplest molecular orbital theory is well known to overemphasize ionic character.[230] Indeed, this has encouraged some authors to favor the valence-bond resonance model, and although this may be useful in particular cases,[230] in general there are difficulties in accounting for observed stereochemistries.[15] These problems are less severe with the conventional electron-pair bonding model provided the d orbitals have suitable properties, in particular, energies and radial sizes commensurate with those of s and p orbitals belonging to the same principal quantum number. Once the d-orbital bonding model has been investigated specifically for compounds of the rare

---

(224) D. E. C. Corbridge, *Topics Phosphorus Chem.*, 3, 57 (1966).

(225) A. H. Cowley, *Chem. Rev.*, 65, 617 (1965).

(226) A. Hordvik, *Acta Chem. Scand.*, 20, 1885 (1966).

(227) G. R. Husk and R. West, *J. Amer. Chem. Soc.*, 87, 3993 (1965).

(228) H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.* (Amsterdam), 2, 369 (1964).

(229) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, 3, 133 (1961).

(230) C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).

(231) J. Jortner and S. A. Rice in "Modern Quantum Chemistry," Part 1, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, p 15.

(232) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, 65, 199 (1965).

(233) J. Hinze and K. S. Pitzer in "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 340.

(234) E. E. Havinga and E. H. Wiebenga, *Rec. Trav. Chim.*, 78, 724 (1959).

(235) G. C. Pimentel, *J. Chem. Phys.*, 19, 446 (1951).

gases and related molecules, it should be easier to decide the relative merits of the various bonding models.

The measured bond lengths in the xenon fluorides are consistent with essentially single Xe–F bonds.[236,237] The simplest "p-orbital-only" molecular orbital model is not sufficient for XeF_6 as it predicts O_h symmetry, and current evidence indicates a distorted structure.[238,239] This may be accounted for by including other valence-shell orbitals in the molecular orbital model or, in another first approximation, by the model emphasizing sp^3d^3 hybridization and electron-pair bonds. It does seem, however, that the distortion of XeF_6 from O_h symmetry is smaller than would normally be predicted by the latter model, and this has encouraged Bartell to suggest that the distortion may be explained by a pseudo-Jahn–Teller effect,[240] involving mixing of low-lying excited states with the ground state. Clearly further investigations of the electronic structure of XeF_6 are needed.

The above considerations are directed especially at d-orbital participation in σ-bond formation. There is some experimental evidence consistent with d_π interactions in molecules of atoms in the higher rows of the periodic table, although these interactions are, in general, less significant to the over-all electronic structure than is found for $2p_\pi$–$3d_\pi$ interactions. The main reason for this reduced significance with heavier atoms depends on the longer bonds and, therefore, reduced overlap in regions of high effective nuclear field. The introduction of radial nodes in the overlapping orbitals has also been suggested to reduce bonding energies,[241] although this is not likely to be very significant since the nodes do not normally occur in the overlap regions. For atoms of higher rows, electronegativity differences in bonds tend to be rather small, except when an atom of higher row is bonded to one of the first row as, for example, is illustrated by the As–O bond. Electronegativity difference is now increased compared with that in a P–O bond, but the increase is not very large and cannot counterbalance the effect of the longer bond. Electron release from O to As is reduced, and the weakness of the π system is shown by the ability of the arsines $(CF_3)_2AsOR$ (R = methyl and t-butyl groups) to form adducts with BF_3.[242] Other evidence in favor of weaker $2p_\pi$–$4d_\pi$ interactions compared with $2p_\pi$–$3d_\pi$ interactions is provided by substituent interference experiments,[123] and by the esr spectra of some anions of silicon and germanium, in particular, those covered by the formulas $Me_3XC_6H_5^-$[78] and p-$Me_3XC_6H_4C_6H_5^-$,[243] where X = Si and Ge, and Me = CH_3. In each case, germanium withdraws electrons less effectively than does silicon, and structural evidence consistent with this result is provided by the bent framework formed by the heavy atoms in H_3GeNCO,[244] which contrasts with the linearity of the silicon compound H_3SiNCS. Both trisilylphosphine, $P(SiH_3)_3$,[245] and trigermylphosphine, $P(GeH_3)_3$,[246] are pyramidal, and their structures contrast with that of $N(SiH_3)_3$ which has a planar framework. Again, this suggests reduced p_π–d_π interactions for atoms in higher rows of the periodic table.

V. Concluding Remarks

In this review, an attempt has been made to show the value of the d-orbital bonding model for rationalizing features of the chemistry of the typical elements. Over the last few years, properties of 3d orbitals of phosphorus, sulfur, and chlorine in free atoms and in molecular environments have become better understood, but d orbitals of the higher row atoms, including the rare gases, have not yet been investigated thoroughly.

Discussion of ground-state bonding represents only the first step of a much wider program which covers the electronic structure of excited and ionic states, for both familiar and more transient molecules such as SiH_2,[247] PH_2,[248] and PO.[249] Contributions of d orbitals to electronic structure may, in general, be different in different excited states, and usually will differ also from the ground-state contribution. Attempts are being made to elucidate the role of d orbitals in excited states,[43,250,251] but much remains to be done. Good descriptions of electronic excited states will be necessary for the eventual treatment of transition states and reactivity. This important topic is beyond the scope of the present review, but so far, discussions of d orbitals in transition states are necessarily very qualitative.[45]

For the molecules considered in this review, progress in the development of electronic structure models depends, for the forseeable future, on combined theoretical and experimental approaches, and it is hoped that the interplay of the two may lead to improved theoretical descriptions and to sounder interpretation of experimental data.

Acknowledgments. The author is sincerely grateful to Professor D. P. Craig for originally suggesting that this review be written, and for his continued help and encouragement. Thanks are also due to Professor N. L. Paddock for kindly reading the manuscript, and to Professor D. W. J. Cruickshank and the Chemical Society for permission to reproduce Figures 9 and 10. Financial support by the Ministry of Technology (U. K.) is gratefully acknowledged.

---

(236) L. C. Allen and W. D. Horrocks, *J. Amer. Chem. Soc.*, 84, 4344 (1962).

(237) R. J. Gillespie in ref 233, p 333.

(238) L. S. Bartell, R. M. Gavin, H. B. Thompson, and C. L. Chernick, *J. Chem. Phys.*, 43, 2547 (1965).

(239) K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, *ibid.*, 44, 1726 (1966).

(240) L. S. Bartell, *ibid.*, 46, 4530 (1967).

(241) D. S. Urch, *J. Inorg. Nucl. Chem.*, 25, 771 (1963).

(242) A. B. Burg and J. Singh, *J. Amer. Chem. Soc.*, 87, 1213 (1965).

(243) M. D. Curtis and A. L. Allred, *ibid.*, 87, 2554 (1965).

(244) J. E. Griffiths and A. L. Beach, *Chem. Commun.*, 437 (1965).

(245) B. Beagley, A. G. Robiette, and G. M. Sheldrick, *ibid.*, 601 (1967).

(246) S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward, *ibid.*, 515 (1965).

(247) P. C. Jordan, *J. Chem. Phys.*, 44, 3400 (1966).

(248) P. C. Jordan, *ibid.*, 41, 1442 (1964).

(249) D. B. Boyd and W. N. Lipscomb, *ibid.*, 46, 910 (1967).

(250) J. Degani, A. Mangini, A. Trombetti, and C. Zauli, *Spectrochim. Acta*, 23A, 1351 (1967).

(251) E. L. Wehry, *J. Amer. Chem. Soc.*, 89, 41 (1967).