No d Orbitals but Walsh Diagrams and Maybe Banana Bonds: Chemical Bonding in Phosphines, Phosphine Oxides, and Phosphonium Ylides

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I. Introduction

The subject of this review is the nature of the bonding in phosphines, phosphine oxides, and phosphonium ylides. This is because recent linked developments have occurred in the understanding of the bonding in these compounds. Now it might be thought on first sight that these familiar compounds are already well studied and that most aspects of their bonding should be understood by now. As we shall see this is not so. It is true that the themes will be familiar, for example the geometry of tricoordinate phosphorus(III) compounds and the nature of multiple bonding in tetracoordinate phosphorus(V) compounds. However the nature of the discussion bears little resemblance to the current textbook version, especially in the case of multiple bonding.

For each of the molecules treated, the discussion is split roughly in two, a qualitative and a quantitative part. A common theme running through all three qualitative discussions is the great usefulness of an analysis based on qualitative molecular orbital theory and the associated Walsh diagrams.[1-8] Another common theme, which could be viewed as a corollary of the first, is that an examination of structural correlations can be a powerful tool for an understanding of bonding.[2-7,9] In many cases the quantitative studies provide substantial support for the qualitative ideas.[10-13] But in the case of multiple bonding the results of some calculations[14] undermine the whole basis of the Walsh diagram approach. Therefore we shall find that some of the current major issues in bonding theory are thrown sharply into relief by the studies described. The review draws heavily on three recent comprehensive surveys[1-3] of the structure and bonding in organophosphorus compounds, in general, which cover the literature to the middle of 1993. Tables 1–4 are composed of selections

Declan G. Gilheany was born in Tyrone, N. Ireland. He studied chemistry at Queens University Belfast and obtained his Ph.D. degree in 1983 under the supervision of Dr. B. J. Walker, having also been appointed temporary lecturer in organic chemistry during 1980–81. From there he became a lecturer in synthetic organic chemistry at St. Patrick's College, Maynooth, Ireland. During the period 1988–90, he was a Fulbright Visiting Professor at Massachusetts Institute of Technology in the laboratory of Professor K. Barry Sharpless. He moved to his present position at University College Dublin in 1992. Dr. Gilheany's main research interests lie in the area of catalytic asymmetric synthesis, structure and mechanism in organophosphorus chemistry, especially the applications of P chiral compounds and the synthesis of heterocycles. However since his Ph.D. studies he has always taken a keen interest in the electronic structure of the molecules he uses in the laboratory and so has retained an interest in main group bonding theory.

of relevant structural and calculational data drawn from the more comprehensive tabulations in these surveys. The interested reader is referred to these previous surveys for detailed structural and computational data compilations, further discussions of the topics covered here, and discussions of other recent advances in the structure and bonding of organophosphorus compounds.

It should be noted that this reviewer's perspective is that of a synthetic chemist. Therefore the review is inevitably biased toward an atoms-in-molecules philosophy. By this is meant that the properties of a molecule may be inferred from the atoms that make it up because atoms and groups of atoms carry with them electronic attributes that are unchanging from one molecule to another. Some readers, especially non-theoreticians, may be surprised that this has to be mentioned at all but it must be acknowledged that the LCAO-MO approach used extensively in this review is neither rigorous nor the sole possible treatment of the electronic structure of molecules. We return to this general issue in section VI and for now it is sufficient to note that the three functional groups under discussion are related by just such considerations. Thus the description of bonding in phosphine oxides and phosphonium ylides which is most accessible and useful to synthetic chemists is based on the partition of the molecule into a phosphine part and the oxygen atom or methylene unit, respectively. For this reason we treat the bonding in phosphines first, developing the relevant Walsh diagram in detail, and then show how it may be used in the succeeding sections to illuminate the bonding in oxides and ylides.

A final introductory point is that none of the discussions of bonding in any of these molecules will make much use of the concept of virtual d-orbital involvement. This issue only arises of course because we are to adopt an atoms-in-molecules approach, and in particular one where we will utilize putative atomic orbitals to form bonds. In that context it has been definitely shown recently that the d-orbital concept is not useful in the description of main group bonding. Therefore that subject is treated first.

II. Noninvolvement of d Orbitals

For many years the description of the structure and bonding in phosphorus compounds was connected intimately with the concept of virtual d-orbital involvement in bonding in the main group of the periodic table. Although the concept has been discredited, its use still persists to a certain extent.[15,16] Therefore, although a number of critiques have been published before,[10,13,17,18] it is necessary at this point to review the subject once again.

Initially the involvement of d orbitals arose out of a particular qualitative difficulty concerning the existence of hypervalent molecules. In these there seemed to be more bonds from the central atom than would be permitted on the basis of the octet rule. Thus in the valence-bond picture of, for example, the SF_6 molecule, the six sulfur σ bonds have to be constructed from six equivalent d^2sp^3 hybrids.[19] However, the d functions used are virtual, not being occupied in the aufbau description of the ground-state sulfur atom. It is then said[20] that SF_6 is characterized by "outer d orbital participation in the bond" or that there is an "expansion of the valence shell of sulfur by promotion of an electron-(s) into a low-lying vacant d orbital(s)". Similar considerations applied to PF_5. The concept of d orbitals was then found convenient to describe two other π-type phenomena exemplified in phosphorus chemistry[21] by (i) the structure and stability of phosphine oxides and ylides (especially compared to their nitrogen analogues) and (ii) the shortening of formally single bonds such as the PO bonds in phosphates. These latter two phenomena involve d orbitals in π-type overlap with adjacent p orbitals.[20]

In this way the possession of "low-lying" d orbitals came to be seen as a fundamental difference between second and higher row elements of the periodic table explaining, for example, why silicon tetrafluoride hydrolyzes readily while carbon tetrafluoride does not, a problem touching on the existence of life itself.[22] Thus, since the work of Pauling,[23] there have been many papers dealing with participation of d-orbital basis functions in molecular orbitals for systems containing nontransition elements. Because of their more elaborate symmetry, d orbitals may form more kinds of bonds than can s and p orbitals and detailed and elaborate schemes were built up to use d orbitals to explain the various phenomena.[24–28] This early work is well summarized in a number of earlier reviews,[20,29–31] the most useful of which is that of Mitchell.[20]

At the outset distinction has to be made between *inner* and *outer* d orbitals.[32] This refers to the principal quantum number of the d orbital in relation to that of the other valence electrons. Inner d orbitals have a principal quantum number one less than that of the other valence electrons. Thus in the first transition metal series it is 3d, 4s, and 4p orbitals that are involved and the charge cloud for these d electrons lie mostly

within that of the s and p electrons. Since these d orbitals are occupied in the ground state atom, they are clearly required for description of the molecular wave function, and the question of their inclusion does not arise. This is the case for bonding in the transition metals[33] and will not be discussed further. Outer d orbitals, on the other hand, have the same principal quantum number as that of the other valence-shell electrons. The question of their involvement in bonding is much more problematic since they are not occupied in the ground state of the atom under consideration. Indeed the concept was never fully accepted by the chemical community, including Pauling,[19] and, from an initially small group of dissenters[34-44] among whom it is probably fair to single out Rundle,[37] the concept has now become redundant, at least among theoretical chemists. Its popularity probably peaked around about 1970 with the review by Mitchell[20] and the advent of the first *ab initio* calculations on these systems.

A. Alternative Models

The first reservation that has to be entered about virtual d orbital involvement in bonding is that there are alternative explanations of all the phenomena involved. One of the initial successes of the hybridization theory of bonding as proposed by Pauling[19,23] was the prediction of molecular stereochemistry in that bond directions are determined by the relative orientations of a set of hybrid orbitals on the central atom which are used to form bonds to the ligand atoms and to hold unshared electron pairs. However during the 1950s it was shown by Gillespie that successful prediction of molecular geometry does not require explicit reference to the bonding involved because the well known and useful VSEPR model[45-49] explains the geometry of most molecules. Also at about the same time a simple and fairly easily understood model was developed which explains the bonding in nonoctet (hypervalent) compounds and which does not require the use of d orbitals. This is the three-center, four-electron bond (or electron-rich bond) model proposed at various times by Pimentel,[34,35] Rundle,[36,37] Havinga and Wiebenga,[38,39] Pitzer,[40] and Musher[41] and developed in detail by Rundle[37] and Musher.[42-44] Bonding is envisaged as partly ionic, which removes the need to involve the d orbitals and explains why fluorine is a crucial ligand in hypervalence. This model has recently been formalized rather neatly by Cioslowski and Mixon[50] in the context of *ab initio* calculations. Better still the model explains well the bonding in other systems where the d-orbital concept does not apply, for example, noble gas derivatives[51,52] and the interhalogen compounds.[39] It is fair to say that it has now completely replaced the sp^3d^2 model for SF_6[17] and the sp^3d model for phosphoranes.[3] As we shall see in section IV.B there is also a simple alternative to the d-orbital concept as applied to $d\pi-p\pi$ systems.

Secondly, during the 1950s, 1960s, and 1970s there were a multitude of experimental and theoretical investigations none of which confirmed unequivocally the validity of the concept of d-orbital involvement. This is well documented in the book by Kwart and King,[53] the problem being that no study could distinguish d-orbital involvement from an alternative explanation. Indeed it appeared that the d-orbital concept might fit into Popper's category of an unfalsifiable

theory.[54] Examples of phenomena which were investigated without definitive results are (i) bond length data in the series of ions XO_4^{n-} (X = Si, P, S, and Cl) which are all short relative to values reasonably expected for single bonds[28,33,55] and (ii) the planarity of trisilylamines.[56-59] Probably the last example where a determined effort was made to prove d-orbital involvement is the detailed study of a cyclic conjugated sulfone by Fraenkel and co-workers.[60] Even in 1986, after all the work that had gone before,[53] these workers felt able to claim that their study implicated p-d bonding "unequivocally and for the first time".[60] However, in the light of the results discussed below, it seems likely that in fact what they did, which was still very significant, was to show that cyclic conjugation occurred in their system.

B. Theoretical Studies

Since the experimental work had been so very contradictory it was hoped that calculations might lead to a more definitive answer. Indeed the early theoretical work was quite encouraging because it had concentrated on certain issues concerning the suitability of the valence atomic d orbitals for their task.[61-69] Two issues of concern were the size and energy of the d orbitals. Firstly the d orbitals are too large to overlap effectively with their potential s and p partners.[32,61] By consideration of the factors affecting the size,[62] namely unpaired electron spin assignments,[32,63,64] the number of promoted electrons,[32,64,65] and the formal charge on the central atom,[64] it was shown that this objection could be overcome. In particular the contraction of the d orbitals in a field of strongly electronegative ligands provided a neat explanation of why fluorine is able to induce the largest valence of a central atom. With regard to the energies of the d orbitals, which are too high in the isolated atom for effective hybridization with s and p orbitals,[20] it was also shown that a field of electronegative ligands could reduce the energies to reasonable values.[62,67,68]

In about 1970, with the advent of full *ab initio* calculations on these molecular systems, more detailed investigation of the bonding became possible. For example, early descriptions of the bonding in phosphine oxides (see section IV.A) involved either semipolar bonds without reference to d orbitals or ordinary covalent bonds constructed from appropriate hybrids that involve d orbitals. Since the former corresponds to zero population of d orbitals and the latter to a population of unity it was expected that an analysis of the d populations of the calculated wave functions would tell which was correct. And indeed the first calculations appeared to confirm the importance of d orbitals because, when d functions were left out, very inaccurate results were obtained and also their addition caused very large energy decreases. Certain calculations in particular had a very strong influence, at least on the community of practical phosphorus chemists,[70] for example the extended Huckel studies of ylides and phosphoranes by Hoffmann and co-workers[71-73] and the *ab initio* STO-3G studies by Van Wazer and co-workers on ylides and phosphine oxides.[74,75] This was despite the specific warning of Hoffmann[73] on the *deus ex machina* aspect of d orbitals.

However there were two problems which confused the theoretical analysis of these systems. These were
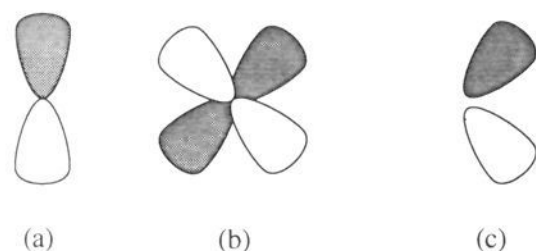
Figure 1. Polarization of a p orbital. (a) + λ(b) = (c). (Reprinted from ref 32. Copyright 1969 Nature.)

the incompleteness of most of the basis sets used and the requirement for polarization functions. Initially it was not well recognized that if the s and p basis sets used in the calculations were not saturated, that is addition of further s and p basis functions still gave energy lowering, then the added d functions would make up the difference and lead to an overestimation of the importance of d orbitals. Differences in basis set then lead to large differences in the importance of d orbitals from populations of 0.3 to greater than 1. Although the evidence for this was present from the start[2] (see section IV.E.2), it was only later that it was stated explicitly.[76] The difficulties were further compounded by the well-known dependence of population analysis on basis set.[76]

However even if the sp basis is saturated and the population analysis is foolproof, there is still a crucial role for d functions in the calculation of molecular properties, and most calculations, especially on third and subsequent row elements, will require their inclusion.[18,77-80] This is because they act as *polarization functions*.[18,32,78] Early in the development of quantum chemistry it was known[81] that a proper description of the σ bond in H_2 requires the use of a pσ basis function on the proton. The purpose of this function is to polarize the wave function (*vide infra*) and thus permit the charge distribution to change shape, becoming more localized along the bond axis. This requirement is now routine,[82] and for second and subsequent row elements, the *most convenient* way to include polarization is again to add the next higher angular momentum functions, in this case d functions. To illustrate the effect of these polarization functions, consider an electron in a 2p state of a fixed hydrogen atom[32] (Figure 1a). Application of a steady fixed electric field in the z direction would polarize the charge and pull it in the z direction. The final perturbed shape is shown in Figure 1c. It can be seen that the charge cloud, and hence the wave function, of the perturbed state can be approximated by a superposition, of some amount, λ, of d orbital character, Figure 1b, on the original p orbital.[32] Hybrids of this kind, involving a small amount of d character, will often be the easiest way of expressing perturbations or polarizations of p orbitals, for example in molecules containing a large dipole moment or in strained ring compounds.[78] The d orbitals mixed in by this process are not suggested to have any independent existence. In fact it can be shown[18,32] that the d contribution which expresses the polarization of a 2 p orbital is a 2d orbital and its function is merely to be of about the same size as the orbital it perturbs and to have the appropriate symmetry to provide the angular flexibility needed to direct the electron density efficiently into regions between bonded atoms.[18,78]

Needless to say, many theoretical workers were uneasy about ascribing a valence role to such polariza-

tion functions. During the 1970s there were a number of attempts to define circumstances in which one could say which role was taken by the d functions. For example Coulson[32] distinguished between *polarization* (d population < 0.1) and *participation* of d orbitals in bonding, where one or more complete d orbitals are used, and Ratner and Sabin[83,84] drew a similar distinction between the *qualitative* and *quantitative* necessity for d orbital inclusion in a basis set, while noting that the whole question is to some extent an artifact of the very convenient atom-centered LCAO method. Then, during the 1980s, it gradually became clear to the majority of theoretical workers that the maximum d population was about 0.3 in most cases and that it has no valence role. Examples of this conclusion are in calculations on, among many others, oxy- and thio-carbanions,[85,86] sulfur tetrafluoride,[17,87] and, especially significant, the *volte face* of Cruickshank[55] on the oxyanions of second row atoms. There was a minor renaissance[88-90] and some workers still find it useful to invoke some "mixing in" of a limited amount of d orbitals,[7,13,17] but it is now clear beyond doubt through the very recent work of Magnusson,[18] discussed below, that the d orbital concept is redundant. Good recent leading references to this literature are the paper by Magnusson,[18] those of Reed and Weinhold,[17] and Reed and Schleyer,[13] the latter of which, since they treat phosphine oxides, is discussed in detail in section IV.E.3a and the general review by Kutzelnigg[10] on bonding in main group compounds which is indispensable.

C. Calculations by Magnusson

Many workers studied the variation of the use of d functions in a calculation in order to determine their valence role and concluded that it was not large.[10,13,17,91,92] An interesting example which can be singled out is the work of Grein and Lawlor[93] who showed that the use of bond functions[94] replicated the beneficial effect of d functions in calculations on H_3NO as can be seen in Table 3. However the recent studies by Magnusson[18,95] are so comprehensive and give such unequivocal conclusions that they surely must be the final word on the subject. Therefore we reproduce below the main conclusions in some detail.

Magnusson[18] reported calculations for a very large number of compounds of second and third row elements, both normal valent and hypervalent, all at a comparable Hartree–Fock level. The basis set was of double-ζ quality and the experimental geometries were used. Single and multiple sets of five Gaussian d functions were added to the basis sets of all atoms except hydrogen (p function). The exponents of the d functions on the central atom were optimized in all cases as were those on selected peripheral atoms. The possibility of basis set superposition error was checked and avoided and also the results were compared to those obtained by adding Slater-type functions. The results are as follows:

(i) The most important observation is that the optimum d function exponent for any element changes very little from one compound to another, even those as different as H_2S and SF_6. Thus there is no support for the view that diffuse d orbitals on the central atom take part in bonding after being contracted by an electronegative ligand field; for example there is no

sign of any progressive contraction across the SF$_2$, SF$_4$, SF$_6$ sequence.[18]

(ii) There are large energy depressions for many other types of molecule than the allegedly hypervalent species, and there is no clear demarcation between them and the normal valency compounds. In fact when the energy depressions are measured *per bond* they show only limited variation. This suggests that the involvement of d functions is characteristic of the bond rather than the compound that contains it, and that the extra involvement of d functions in hypervalent molecules is simply because they have more bonds.[18]

(iii) There are also energy depressions on the addition of d functions to the basis sets of *peripheral* atoms. The energy increment per added function is much greater for the central atom but per bond there is no difference.[18]

(iv) There are also energy depressions in compounds of *second row* elements, and when the results are obtained at the same basis set level the contrast between second shell and third shell behavior is less spectacular than usually reported.[18]

(v) There is a strong response in the optimum exponent and d function energy increment to change of bond length. The optimum d function exponent on the peripheral atom also changes.[18]

(vi) Finally there is no difference in the role of d functions between normal and hypervalent compounds. They facilitate the transfer of electronic charge into the internuclear bonding region at the expense of the outer parts of the valence wave function. So the occupations of the d functions are strongly dependent on the degree of charge transfer from the central atom and the number of electron pairs formally arranged around the central atom. In short their purpose is to enable the efficient description of rapidly varying internuclear molecular potentials.[18]

There still remained the possibility, raised by Messmer[14] that hypervalent bonding might be facilitated by d-orbital involvement in correlated wave functions. In a more recent study, Magnusson[95] has addressed this possibility in a similar manner to the above study using calculations incorporating high levels of electron correlation. He did indeed find that d functions were essential and in fact the energy attributable to d function supplementation of the basis set is much greater in configuration interaction calculations than at the HF level.[95] Also the role of d functions in correlated calculations was different from that in HF calculations but once again it was not a valence role. This was indicated by the same sorts of observations as enumerated in i–v above. In particular d functions added to the basis set provide a fairly constant 52 kJ mol^{-1} of the MP4 correlation extra energy per valence shell electron pair, irrespective of the coordination number of the central atom.[95] Interestingly the optimum d function exponent in the correlated calculation is quite different from that in the HF case, reflecting the different role of d functions in the two cases. In the correlated case the d-function role is atom centered and provides angular correlation in contrast to the bond-centered polarization functions.

We also leave the final word on this with Magnusson;[18] "accordingly, any resemblance between d functions in molecular wave functions and the valence d orbitals of excited second row atoms is an artefact of the electronic structure model; they should not be called d orbitals".

III. Phosphines

Subjects which have been of concern in bonding theory applied to phosphines are: (i) the trivalency of phosphorus, (ii) the bond angles in phosphines and amines, (iii) the much larger barrier to inversion in phosphines than in amines, (iv) the lower basicity and greater nucleophilicity of phosphines than amines, and (v) how the previous topics relate to each other. Most of these issues are characteristic of differences between the second and subsequent rows of the periodic table, and they can all be simply encapsulated by stating that we require an explanation of the following series of bond angles (Table 2) whose differences have been described as spectacular:[96]

H$_3$P	93.4°	H$_3$N	106.7°
F$_3$P	97.8°	F$_3$N	102.4°

Thus we wish to know why main group 5 hydrides are pyramidal, why the angle at phosphorus is smaller, and why the response to fluorine substitution is different in the second and third rows. This has been discussed extensively but not satisfactorily in the past, especially in the case of the smaller bond angle in F$_3$N and the larger one in F$_3$P. This is not surprising since these observations together comprise an especially strenuous test of any theory, qualitative or quantitative.

At the outset we must note that these bond angle differences which we have set as the test of the various theories are due, at least in the second row, to very small differences in energy.[97] Thus the molecular energy for H$_2$O (for which the problem is similar) was found[98] to be relatively insensitive to even large changes in molecular geometry with only a 2.6 kJ mol^{-1} difference in energy between bond angles of 90° and 120°. A similar result was found for the bond lengths.[98] That is not to say however that these energy differences are unimportant considering, for example, the extensive use to which optically active phosphines have been put. Below are enumerated the factors which may be relevant to any discussion of this topic:

i. The size of the central atom and its ligands. There is more room around the phosphorus atom. For example, in ammonia at the NH bond distance of 101 pm, the distance between the hydrogens at a bond angle of 106.7° is 160 pm, whereas the corresponding distance in phosphine at its bond angle of 93.4° is 206 pm. Note that these numbers are well within twice the van der Waals radius for hydrogen (240 pm). It should be noted that steric arguments can be misleading here; for example, as Huheey *et al.*[15] point out, the increase in van der Waals radius is paralleled by increase in covalent radius and the two tend to cancel out.

ii. The electronegativity of the central atom and the ligands. In the change from H to F, bonds to N change polarity, whereas bonds to P merely increase in polarity toward the ligand.

iii. The extent of sp mixing in the valence orbitals of the central atom which in turn depends on factors iv and v.

iv. The s/p energy separations which are smaller for phosphorus than for nitrogen. By using promotional

energies,[99] sp[3] hybridization is predicted to be more likely in phosphorus than in nitrogen. For example, the NH bond strength is 391 kJ mol^{-1} and PH is 321 kJ mol^{-1} while the 2s–2p promotional energy is 965–1197 kJ mol^{-1} for nitrogen[1] and 3s–3p is 560–840 kJ mol^{-1} for phosphorus.[1]

v. The sizes of s and p orbitals which are comparable for the second row, whereas for higher rows the s orbitals are significantly smaller than the p orbitals.[10] Thus the nitrogen 2s and 2p orbitals both have their radial maxima at about 50 pm from the nucleus while the phosphorus 3s is at about 80 pm and phosphorus 3p is at about 100 pm. The difference arises because the 2p orbitals are not subject to an orthogonality constraint from core orbitals, whereas 2s and all other p orbitals are subject to such constraint.[100] The similarity in size for the second row orbitals will lead to a greater importance of 2s/2p correlation effects. If there is no sp mixing in the third and subsequent rows, a phenomenon which has been termed orbital nonhybridization,[101] then it must be because this factor outweighs factor iv.

vi. The radial maxima for phosphorus 3s and 3p orbitals which occur at larger distance from the nucleus than in nitrogen.

vii. The overlap capability to the same atom. For N and P this is different. This is probably less important. For example the calculated NH overlap integral[1,102] at the typical bond length (101 pm) is 0.55 while the same calculation for PH overlap integral gives 0.5, both values are based on overlap of s orbitals. A similar calculation for NC and PC overlap based on s and p orbitals gives 0.55 and 0.29, and for NF and PF overlap the values are 0.2 and 0.16.

A. Qualitative Analyses

There are three qualitative approaches which have been used extensively to explain the bonding in phosphines; the directed valence, valence-shell electron-pair repulsion (VSEPR) theory, and the qualitative molecular orbital (Walsh diagram) analyses. The former two have been the usual basis of previous discussions.[21,103–108] As we shall see, some of these analyses are more elegant than others and are capable of providing greater insight. In particular we will show that a simple previously undescribed extension to the Walsh diagram approach enables all of the data to be explained with one hypothesis.

1. Directed Valence Analysis

This is the simplest, most accessible, and so most common analysis of the bonding in phosphines.[21,103–108] The following sequence of hypotheses is the best explanation which threads through the mass of factors, choosing those which fit together to explain all the observations:

A. Bonding in H_3P involves p[3] orbitals (at 90°) and that in H_3N involves sp[3] orbitals (at 107°). This is because either (i) there is sp mixing in nitrogen but there can be no sp mixing in phosphorus[101] or (ii) bonding is normally by p orbitals[19] but H_3N cannot have a bond angle of 90° for steric reasons, being forced out to 107°. The explanation may be a combination of these. The possible steric reasons are as follows: (i) The hydrogens are forced to be within their van der

Waals radii at the smaller angles; this is possible but is considered less important.[15] (ii) There is ionic character in the NH bonds putting positive charge on the hydrogens which repel each other[19,109] (this is also a size effect since the smaller the atom, the more electronegative). It has been estimated[109] that this contributes only about 5° of the bond angle expansion in ammonia. (iii) There is repulsion between the NH bond pairs. This is considered to be the most important.[15,96] That the bond angle in H_3N is less than tetrahedral is considered to be due to extra repulsion from the lone pair.

B. Fluorine substitution in H_3N moves the bond pairs more toward the ligand (it being more electronegative) leaving room for the bond angles to relax toward 90°.

C. Fluorine substitution in H_3P makes the phosphorus atom more positive thus allowing a certain amount of hybridization by either (i) decreasing the sp promotion energy, (ii) reducing all energy levels, (iii) contracting all orbitals so that the overlap mismatch is not so bad, or (iv) a combination of these factors. The increase of bond angle in methyl-substituted phosphines cannot be explained in this way so recourse has to be made to steric arguments.

So, in summary, for phosphorus the size of the central atom means that electronic factors control the situation while for nitrogen its small size means that steric factors dominate. Note that in either case it is a size effect—the lesser radial extent of the s orbital for phosphorus is what makes sp mixing difficult.

Although the directed valence approach can explain all of the bond angle observations, it is unsatisfactory for a number of reasons. First it is not elegant. It is necessary to graft on extra hypotheses without experimental support to explain each effect as it arises. The existence of the phenomenon then becomes the proof of the explanation. Second it is actually deficient in a number of important ways:

i. The analysis above makes no comment on the possibility of a planar geometry for the molecule. This can be done, at the same time generating an explanation for the inversion barriers but it is through further hypotheses.

ii. The derivation of simple bond angle/sp ratio formulae is shown by calculation to be incorrect (see section III.B.2).

iii. The analysis assigns the phosphine nonbonding (lone pair) of electrons to the phosphorus valence s orbital which implies a spherical distribution of this electron density. The lower basicity of phosphine than ammonia is then often taken as evidence for this nondirectionality of the phosphorus lone pair because it is less available for bonding to an incoming hydrogen than is the nitrogen lone pair. An alternative casting of this basicity argument is that protonation to give phosphonium ion involves rehybridization from p[3] to sp[3] in the case of phosphorus but not in the case of nitrogen. This requires energy; therefore phosphines are weaker bases. The greater basicity of the methylphosphines fits the pattern[106] since, as the bond angle increases, there is more s character in the bonding and so less rehybridization is required and as the methyl phosphines have wider bond angles they are stronger bases. However there is not a strong relation between bond angle and basicity in the methylphosphines[1] and

there is a very great deal of evidence (dipole moments, nucleophilicity, etc.) that the main reactivity of phosphines is just such directional activity of nonbonded electrons. So it is necessary to be especially resistant in this context to the temptation to identify nucleophilic or basic properties with the nonbonding ("lone pair") electrons.

iv. This last problem is caused by what is possibly the worst drawback. The analysis takes an unphysical approach to the problem. This is because one cannot just take three p or four sp³ orbitals and interact them one at a time with three ligand orbitals. It is imperative that symmetry-adapted linear combinations (SALCs) of the ligand orbitals be formed before interaction with the central atom orbitals[4,97,110,111] (*vide infra*).

This reviewer recommends, to the extent that it is still used in freshman chemistry courses, that the directed valence analysis be abandoned completely in the teaching of chemistry. It is inelegant, wrong in some respects and leads to unnecessary confusions such as the inherent prediction of nondirectional, nonbonding electron density. Ironically the use of this analysis and relying only on promotion energies for the prediction of sp mixing has sadly misled a few authors into the statement that promotion is energetically more favorable in nitrogen than phosphorus, contrary to the facts. Since there is a much better method (VSEPR) for explaining molecular geometry to freshman, there is no excuse to use this method.

2. VSEPR Analysis

During the late 1970s some doubts had arisen regarding the VSEPR method. There are of course the handful of well-known exceptions[48] but more seriously some authors[112,113] had cast doubt on the theoretical basis of the method, studies having shown, for example in the H_2O/H_2S system,[112] that the lone pair/lone pair repulsions are not stronger than bond pair repulsions. But now the method has been put on a sound theoretical basis through its identification by Bader[114,115] with the Laplacian of the charge density. Furthermore, now that Gillespie[48] has identified the size of bond-pair domains (rather than repulsion effects) as being the critical factor and with the use of bent bonds for multiple bonding (*vide infra*), many individual analyses are simpler and the method has had a new lease on life, a notable success being the simple explanation of the structure of H_2CSF_4.[14,48] The application of VSEPR to phosphines is straightforward[47,48,106] using the following sequence of hypotheses:

A. Phosphorus has five electrons in the valence shell, and three one-electron ligands leads to a classification of an eight-electron AY_3 system. The four electron pairs are expected to adopt a tetrahedral arrangement. Since one of the electron pairs is nonbonding and therefore larger in the vicinity of A, a pyramidal arrangement around A is expected with the bond angle less than the regular tetrahedral.

B. The difference between the angles at phosphorus and those at nitrogen is explained by a further axiom of VSEPR which is that as the size of the atom core increases the nucleus retains more control over its nonbonding pair. This further increases the size of the nonbonded pair. Thus the larger phosphorus is expected to have narrower angles to ligands than nitrogen.

C. As ligand electronegativity increases (fluorine substitution) it draws the bonding pair toward it. Therefore the space occupied in the valence shell of A by the domain of the bonding pair decreases and the angle between the AY bonds correspondingly decreases.[48] This explains the decrease in bond angle on fluorine substitution in ammonia.

D. Unfortunately the increase in bond angle on fluorine substitution in phosphine still remains a problem. It may be that we should never expect very simple qualitative analyses to answer all the subtle details of molecular geometry. Gillespie[46] was well aware of this difficulty and attributed it to the unique character of hydrogen as a ligand. He argued[46] that the angle in phosphine is especially small because the density of the bonding electron pair is to a certain extent spread out around the hydrogen nucleus. A counter-argument here would be that ammonia has a higher bond angle than trifluoroamine. A rejoinder would be that the greater electronegativity of nitrogen draws the hydrogen electron density more into the bonding region increasing the effective size of the hydrogens. There may be some hope for a more satisfactory formal explanation along these lines here in the fact that the shape of electron domains changes in a subtly different way from H_3N to F_3N than from H_3P to F_3P. Thus in the H_3N/F_3N change bond pair polarization switches direction from central atom to ligand. In H_3P/F_3P bond pair polarization merely increases toward ligand. However, as we shall see (section III.B.3) the ligand which we should regard as being unique is the fluorine ligand because it can produce π-type bond-strengthening effects.

3. Walsh Correlation Diagram Analysis

The most satisfactory approach to this problem is based on qualitative molecular orbital theory.[4,110,111,116-118] This is well documented in the excellent book by Albright, Burdett, and Whangbo,[4] and its application to phosphines has been reviewed.[1] However the discussion which follows differs from these in two respects. First the possibility that the P 3s orbital is not involved in bonding is explicitly taken into consideration in the orbital energy diagrams. Second a simple extension of the analysis enables all of the experimental data to be rationalized in a satisfactory way. Since this extension does not appear to have been described before, it is developed here for the first time.

After the plethora of hypotheses used in the foregoing analyses it is a relief to be able to rely on just one. Walsh's rule[119] for predicting molecular shape may be stated simply as follows:[4] "A molecule adopts the structure that best stabilises the HOMO. If the HOMO is unperturbed by the structural change under consideration, the occupied molecular orbital lying closest to it governs the geometrical preference".

The two Walsh diagrams for AY_3 species are shown in Figure 2, parts A and B, with and without sp mixing, respectively, and assuming that the Y atoms provide s orbitals for bonding. In the case of Figure 2B the s orbital on the central atom, $1a_1$, is simply left out of the analysis as if it is not in the valence shell. In other words it is assumed in Figure 2B that orbital overlap effects outweigh energy effects for atom A (see introduction to section III). The largest effect of this is that
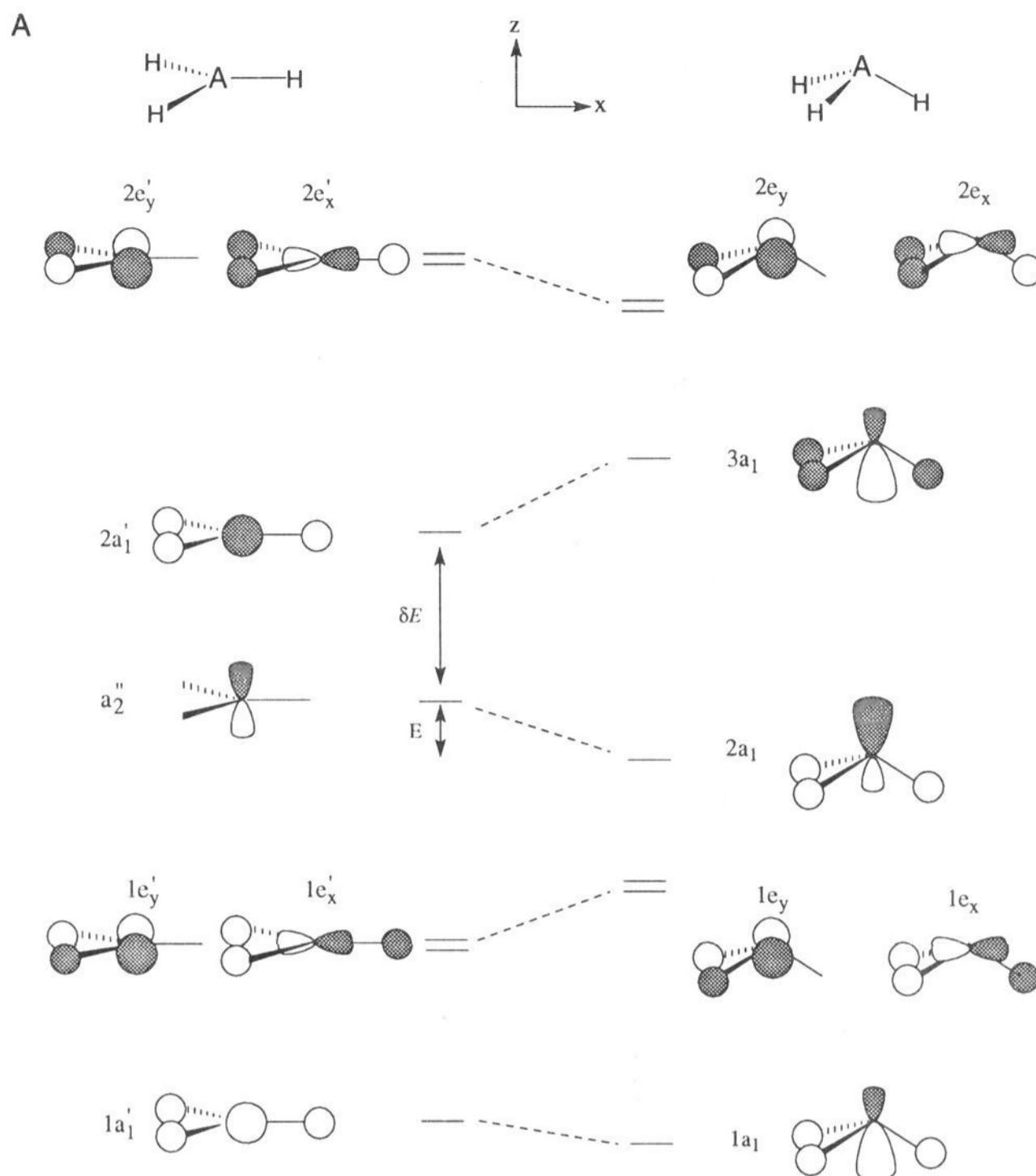
Figure 2A. Correlation between the molecular orbitals of planar and pyramidal H_3A, including the s orbital on A. (Reprinted from ref 4. Copyright 1985 Wiley.)

$2a_1'$ has to be set at or slightly below the energy of a_2'' in the planar form. Within each figure is shown the correlation of the orbitals as a function of the geometry change from planar trigonal to pyramidal. The detailed discussion of how these orbital sets are constructed and correlated is given in Albright *et al.*[4] Note that the orbitals are derived by simple qualitative symmetry considerations and thus any calculation that may be done on the system must yield results of these symmetries although, of course, the energy ordering may be different.[116] The analysis of the molecular geometry is then as follows:

A. From either part A or B of Figure 2 it can be seen immediately that for eight-electron systems such as amines and phosphines the pyramidal geometry will be preferred. This is a second-order Jahn–Teller effect[4] and will be particularly large in Figure 2B because the amount of stabilization energy E is inversely proportional to the energy gap δE between HOMO and LUMO in the planar form[4] which we have set near zero in Figure 2B.

B. The difference in bond angle between amines and phosphines and the higher barrier to inversion of phosphines can be easily explained in a number of ways depending which of the Walsh diagrams are correct. The simplest is that change from N to P involves change from part A to B in Figure 2. However explanation purely in terms of Figure 2A is also possible without difficulty. The energy gap δE is influenced by the nature of the central atom (its size, electronegativity, etc.) and by the nature of the ligands. Figure 3 shows the effect on δE of changing from nitrogen to phosphorus. This is caused by the lower electronegativity of phosphorus and/or the increased bond lengths to phosphorus.[1,4] In any event the smaller δE for phosphorus leads to a greater stabilization energy E in the pyramidal case so we expect phosphines to be more pyramidal than amines i.e. smaller bond angles. Also the energy barrier to the inversion process is higher since the transition state for that process is assumed to be the planar configuration (but see section III.B.7.).

C. It is in the explanation of the effect of substituent electronegativity that this analysis comes into its own. A very electronegative substituent causes all orbitals to decrease in energy, especially those that have coefficients on the substituent. Consider Figure 2A again; on replacement of hydrogen by fluorine, for example, all of the occupied MO levels will move down, but that of the a_2'' orbital will be less affected since it is not located on A. Thus the energy gap δE will be smaller for F_3A than H_3A and it is expected to have a smaller valence angle and larger inversion barrier. Thus

B
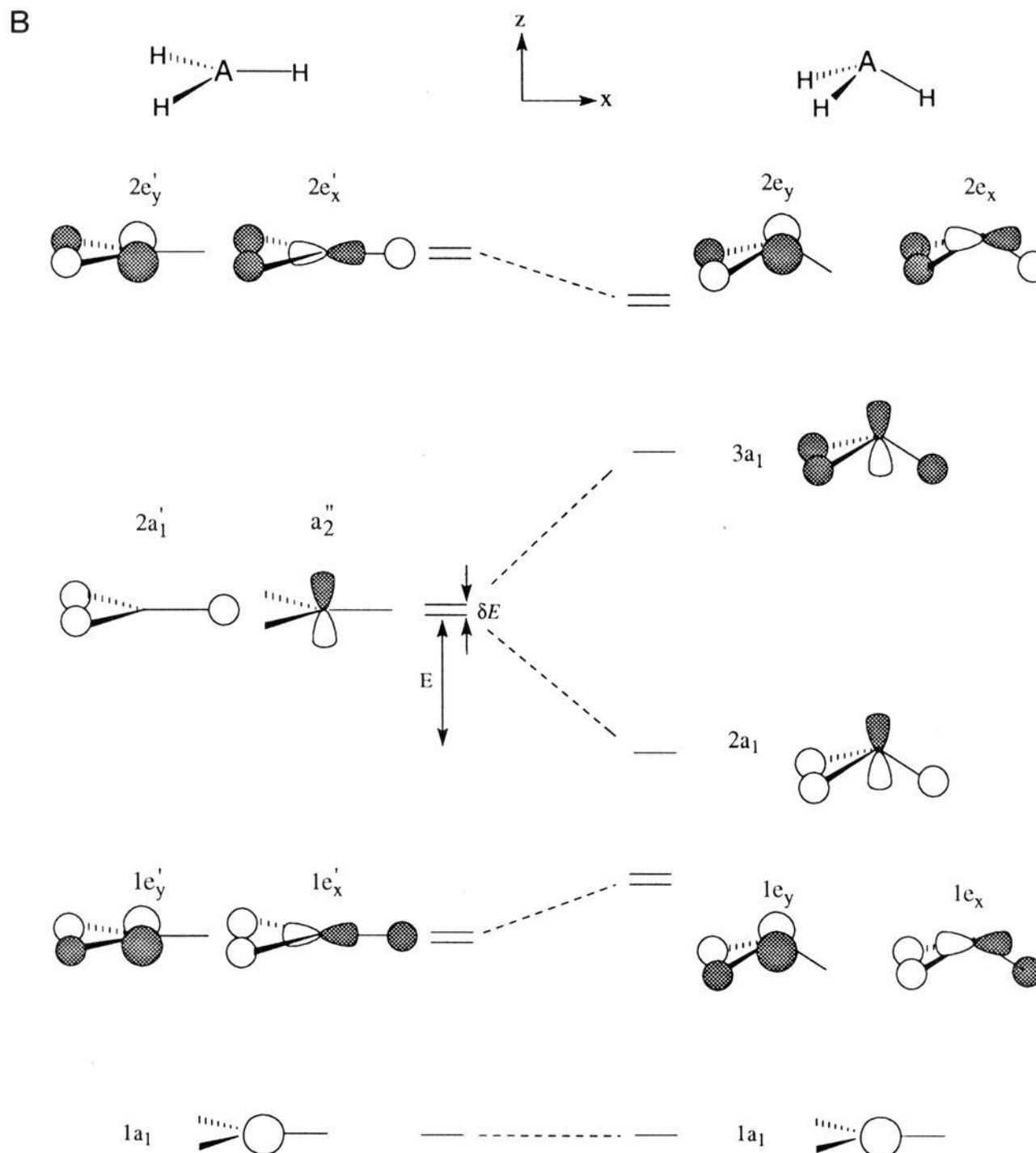
Figure 2B. Correlation between the molecular orbitals of planar and pyramidal H_3A, excluding the s orbital on A.
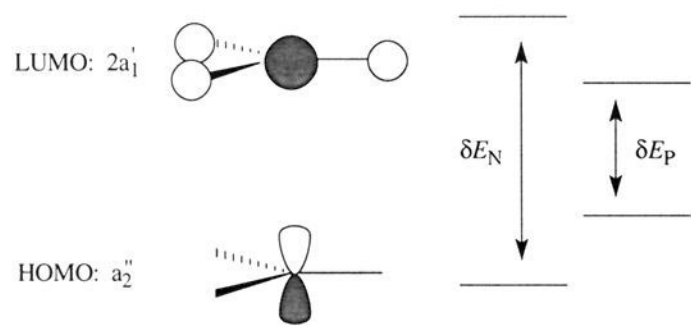
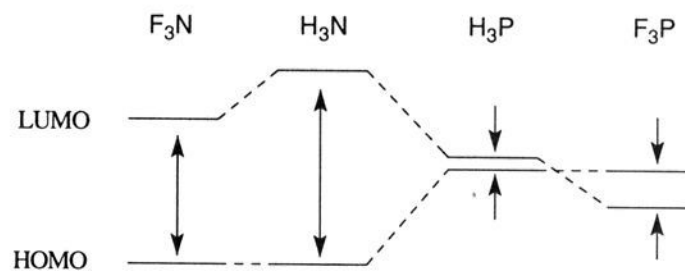**Figure 3.** Effect on HOMO–LUMO energy separation (δE) in planar H_3A of a change in A from nitrogen to phosphorus. (Reprinted from ref 1. Copyright 1990 Wiley.)

Figure 4. Effect on HOMO–LUMO energy separation in planar Y_3A of changes in both A (nitrogen to phosphorus) and Y (hydrogen to fluorine).

is explained the smaller valence angle in F_3N than in H_3N and its larger inversion barrier. Now consider the situation where Figure 2B is operative for phosphorus. Fluorine substitution will again lower the $2a_1'$ orbital but here this will have the effect of *increasing* δE leading to less stabilization on pyramidalization and hence the wider bond angles for F_3P. Actually the explanation of the substitution effects does not require that Figure 2B be operative, merely that the HOMO–LUMO energy gap be small or zero for phosphine in the planar form. The overall argument is summarized by Figure 4 which shows that the effect of fluorine substitution decreases δE in the case of nitrogen and increases it in the case of phosphorus. This rather satisfying explanation is reminiscent of that for the different effects of substitu-

tion on the normal Diels–Alder reaction compared to the Diels–Alder reaction with inverse electron demand.[120]

D. An analysis of the effect of π-bonding capability of the ligands is also possible and is detailed in the book by Albright *et al.*[4] In particular they show how π-acceptor properties of ligands (e.g. the p orbital of a BH_2 group or π^* of a CO group) should lead to planarity at A and decreased inversion barrier and vice versa for π-donor ligands such as a halogen atom or NH_2 group.

Of the various analyses this one is the most elegant in the sense that one hypothesis explains all data. However we are still saying that this is how the orbitals must be based on experimental observations. So the hypothesis still remains to be tested by calculation, particularly the reversal of HOMO and LUMO in the

planar form of F_3P. There have been many calculations of the energy barrier to inversion in phosphines and estimates of frontier orbital energies for some of these molecules.[1] For example, Marynick[121] has estimated the HOMO and LUMO energies in NH_3 and PH_3 and found them to be as expected on this model. However there has been no study of all of these molecules at the same calculational level giving the HOMO–LUMO energy gap in the planar form. The whole area is further complicated by the possibility of T-shaped transition states for inversion (see section III.B.7). The MO's of these T-shaped structures can be derived by qualitative molecular orbital methods[4] similar to those used to generate Figure 2A, and an explanation of the higher inversion barriers based on them is also possible.

It may be coincidental that the analysis presented above (A–D) works well. First there should be a relation between the bond angle found in the pyramidal case and the size of the inversion barrier; the smaller the bond angle, the higher the barrier (see section III.B.7). But in the case of phosphine it is found that increasing fluoro substitution increases the barrier[122,123] contrary to this expectation. Much more seriously, in using Figures 2A/2B to analyze the bonding in the fluorides, we have in fact transgressed our own rule regarding symmetry adapted linear combinations (section III.A.1). Not only is the main bonding orbital contributed by fluorine now a p orbital but also we cannot ignore the filled orbitals on the fluorine. Thus to be strictly correct we require a correlation diagram between 16 valence orbitals which, although complex, has been done.[111,124,125] More particularly, we need to consider the possibility of interaction between filled nonbonding fluorine orbitals with the AF antibonding combinations. This is referred to as *negative hyperconjugation*, and it turns out that an explanation of the bond-angle variations can be based on it (see section III.B.3).

B. Quantitative Analyses

Apart from some honorable exceptions[126-129] it is only in the last decade that useful[130] calculations on these systems have become available. While the earlier studies could reproduce, after great effort, energies and experimental parameters, for example inversion barrier,[126] computational limitations restricted detailed studies of geometry and orbital occupancy. Indeed, even now, the introduction of more than a few heavy atoms restricts the amount of reliable information that can be obtained. It must be emphasized that considerations of basis set adequacy and geometry optimization are very important in calculations on systems including third row elements. A number of studies have shown that conclusions can be very basis set dependent.[1,132-137] It has become clear that the best split valence and the double-ζ basis sets which are acceptable for carbon and other second row elements are unsuitable generally for the detailed investigation of compounds of higher row elements.[1] At least double-ζ quality basis sets with polarization terms and full geometry optimization along with some form of electron correlation would seem in general to be desirable.[1,133,138,139]

Table 1 gives the results (geometry and total energy) of a selection of the best recent calculations on phosphines. As can be seen from Table 1, it does indeed

Table 1. Results of Calculations on Phosphines Y_3P

molecule	calculation[a]	energy[b]	r(P–Y), pm	∠YPY, deg	ϵ_{HOMO},[c] eV	ref(s)
H_3P	3-21G	−340.7045	142.3	96.1		140,141
	3-21G#	−340.7542	140.2	95.0	−10.39	134,143
	3-21G*	−340.8140	140.2	95.2		140,141
	4-31G#	−342.0763	140.8	94.0		134
	4-31G*	−342.0903	140.9	92.8		144
	>DZ+P	−342.3764	141.4	94.0		129
	6-31G*[d]	−342.3948			−8.13	123
	6-31G*	−342.4480	140.3	95.4		141
	DZ+P+CI	−342.5551	141.6	92.5		145
	6-31G*+MP2[e]	−342.5515				141
	DZ+P+CI[f]	−342.6437	141.3	93.7		133
	EXPT[g]	−343.9150[h]	141.2	93.4		146
	SCM-Xα-DV				−6.08	147
F_3P	3-21G#	−635.8855	155.0	97.1	−12.30	134, 143
	4-31G#	−638.4124	157.4	97.0		134
	6-31G*	−639.1292	156.4	97.3		142
	>DZ+P[i]	−639.2697				137
	6-31G*+MP2[e]	−639.7495				142
	>DZ+P+C	−639.8578	156.3	97.1		148
	EXPT[g]		157.0	97.8		149
	SCM-Xα-DV				−7.90	147
Me_3P	3-21G#	−457.2378	187.7	101.5	−8.59	134,143
	4-31G#	−459.0200	188.3	101.1		134
	EXPT[g]		184.7	98.6		150
	SCM-Xα-DV				−4.90	147

[a] All self-consistent field, contracted Gaussian-type basis sets and geometry optimized by the gradient method, unless noted otherwise, symbols 3-21G, 4-31G DZ and Xα-DV have their usual meanings:[97] *, a set of six d-type polarization functions added to basis set; #, set of five d-type polarization functions added; P, other combinations of polarization functions added; CI, with electron correlation by configuration interaction; C, with correlation by Møller–Plesset perturbation theory. [b] Total electronic energy in hartrees; 1 hartree = 27.2 eV = 2625 kJ mol⁻¹. [c] HOMO energy. [d] Geometry optimized by PRDDO method at 4-31G* for P and 3-21G for C; HF calculation using the 6-31G basis set on C,H not attached to P. [e] Using geometry found at the 6-31G* level. [f] Slater-type basis set. [g] From Table 2. [h] Estimated in ref 126. [i] Four sets of d-type functions.

require very large basis sets with polarization and correlation corrections to get acceptable results. A common observation with lower level calculations is that the bond distance is too short by about 1 pm and bond angle is too large by 2°. These features are coupled since a shorter bond distance increases the repulsion between the PH bonds leading to increased bond angle (see section IV.D.2). Such discrepancies are usually remedied by correlation correction but the number of published calculations which include such corrections is small.[1]

Only a few of the *ab initio* calculations on phosphine have any detailed discussion of the bonding and these are discussed below (section III.B.2-5). Also it is disappointing that orbital energies are not given in the later calculations so comparisons to the qualitative analyses above are difficult. However there is one useful empirical calculation which does give orbital energies and it is discussed in section III.B.6. As well as the various studies of basis sets already mentioned, there have been a number of other test calculations as well as calculational studies on the conformation of phosphines, the degree of conjugation in aromatic, vinyl, and acyl phosphines, the aromaticity of phospholes, and the anomeric effect involving second row substituents. Overviews of all of these have been included in a previous review.[1]

1. A Note on Localization Procedures

The LCAO-MO description of chemical bonding[97] leads to a set of molecular orbitals formed by the overlap of atomic orbitals centered at different atoms which are classified as bonding, nonbonding, or antibonding and which are completely delocalized about all the constituent atoms. Unfortunately this description is deficient from the point of view of a practical chemist because it does not immediately lead to a description of the chemical bonds.

To overcome this the use of a localization procedure is a common practice in MO calculations, the initial *canonical* MO's being transformed into *localized* molecular orbitals (LMO's). These are a set of MO's that would appeal to a practical chemist for which the charge probability density of each bonding MO is localized in the region of one of the bonds, the overall wave function being unaffected.[97] Then the bonding MO's may be identified with the chemical bonds. However there are an infinite number of such transformations possible,[97] many of them corresponding to localized MO's, so that a procedure or criterion for generating them consistently is also required. Three such procedures are (i) that which generates the energy localized MO's,[151,152] defined as that set of orbitals which minimizes interorbital repulsion and exchange energy; (ii) that which generates the exclusive MO's,[153,154] usually called the Boys LMO's, defined as that set which maximizes the sum of the squares of the distances between the orbital centroids; (iii) the natural localized molecular orbitals,[155,156] derived from a natural bond orbital analysis,[157] which correspond more closely to the picture of localized bonds and lone pairs as basic units of molecular structure, are much easier to calculate and give results usually in good agreement with the other LMO methods.[155]

Normally the different localization methods give similar results but not in the case of phosphine oxide as we shall see in section IV.E.3. An interesting point about these localization methods is that they sometimes lead to "banana bonds" for multiple bonds. For example the energy-localized MO's for N_2 are three equivalent curved bond orbitals spaced 120° apart from one another, the "banana bonds", in contrast to the familiar σ bond and two π bonds.[97] A similar result may be obtained for the alkene and carbonyl groups using the Boys method.[158] Thus localization procedures tend to obscure σ/π separability which has also been a useful concept in chemistry. This aspect is often avoided by a preliminary examination of the canonical orbitals, especially the HOMO, to see if it has π properties and is already strongly localized; if it has, it is then excluded from the localization procedure. For example, the HOMO of ethylene is excluded in the localization procedure to preserve the familiar σ/π description of the carbon–carbon double bond.[97]

2. Calculations by Magnusson

One of the most detailed studies of the bonding in phosphines is contained within the series of papers by Magnusson[11,12,143,159] on the series of molecules H_nAY_{3-n} (A = 2nd/3rd row main group element, Y = H, CH_3, CF_3, NH_2, OH, F). The analysis was based on the results of calculations at the single configuration restricted Hartree–Fock level using the 3-21G basis set supple-mented by polarization functions in the case of the second row elements (3-21G# basis set). The calculations were carried out at optimum geometries but the results of bond angle variation studies were obtained at fixed a AH bond length which may compromise any conclusions about effects of geometry variation because it is well known[126,133,160,161] that the equilibrium bond length decreases when going from the C_{3v} to the D_{3h} conformation.

The actual analysis of the bonding was done by examination of the contribution each atomic orbital makes to Mulliken overlap populations in conjunction with its contribution to gross atomic populations.[162] Populations were analyzed both within each MO and over the whole molecule. The idea is that the contribution of a particular orbital to gross population will run counter to its contribution to overlap densities. An atomic orbital involved heavily in bonding must share charge with the orbitals of its partner atom; its contribution to the overlap density may be high but the gross population term will be very much reduced from the value expected for orbitals that are substantially nonbonding (about 2.0). Now it is well known that Mulliken populations are sensitive to the basis set used[97] which danger was averted by standardizing the basis sets and checking that they were adequate. This, together with the advantages, difficulties, and justifications of the approach was discussed fully by Magnusson.[11,12,134,143,159] It can be seen from Table 1 that the 3-21G and 3-21G# basis sets are at the lower end of a scale of adequateness but Magnusson has shown that some of his qualitative conclusions are not affected by changing to a larger basis.[11]

The key finding is that there is not a simple relationship between molecular geometry and the ratio of central atom s orbital involvement in molecular bonding to that of central atom p orbital involvement, as reflected in electron density distributions. It was found that there is not a smooth increase in the s-orbital contribution to bonding as the bond angle rises. As expected the tendency to maximize nonbonding s density results in no s-orbital contribution to bonding over much of the lower part of the bond angle range. In fact it was found that in the main group 5 hydrides the contribution of s electrons to overlap density is antibonding at a bond angle of 90°. As the bond angle increases, this contribution crosses to bonding (the crossover point is different for the hydrides of other groups) but only approaches significance near to 120°. This comes about because the coefficients of the atomic orbitals in each MO vary with bond angle (again not linearly). Specifically, the proportion of s density contributing to the lowest energy valence MO rises. Note that Magnusson refers to the ratio of s to p orbital involvement in bonding as a hybridization ratio.[11,12,134,143,159] This is a little different from the idea of hybridization familiar to organic chemists for example, which refers to a localized description of the bonding (*vide infra*).

a. Comparison of Phosphine and Ammonia. For phosphine and ammonia the calculations yield the expected four valence MO's with the symmetries shown in Figure 2A although the exact form of the orbitals is rather different.[1,11,12] The contributions of the valence atomic orbitals to gross atomic and overlap (in paren-

theses) populations in H_3N and H_3P at their respective minimum-energy-optimized geometries[163] are as follows:

H_3N	2s: 1.67 (0.10) $2p_{xy}$: 2.32 (0.49) $2p_z$: 1.90 (0.05)
H_3P	3s: 1.77 (0.00) $3p_{xy}$: 1.76 (0.45) $3p_z$: 1.55 (0.19)
	3d: 0.127 (0.054)

In H_3N, at its optimized geometry, the 2s orbital provides a proportion of the NH overlap density. In H_3P, at its optimized geometry, the 3s provides none. This arises because its contribution to bonding in the lowest valence MO ($1a_1$ in Figure 2A) is exactly cancelled by an antibonding contribution in the HOMO ($2a_1$ in Figure 2A). In ammonia on the other hand the bonding contribution is much larger than the antibonding. Since the 3s orbital in phosphine provides no contribution to the PH bonding we must regard it as the main component of nonbonding electron density. But the main contribution to the s density comes from the lower $1a_1$ MO and the HOMO is mainly the $3p_z$ orbital. It was found that there is a relation between bond angle and orbital occupancy—s orbital occupations fall as the bond angle is raised, but the relation is not linear. The fall is more rapid near the end of the range (120° for H_3A). Thus even in H_3N where the bond angle is constrained to be 106.7° the s electrons only account for about 15% of the nitrogen contribution to bonding.

So the s electrons remain nonbonding and the bond angle can be mainly understood as the balance between the p_z and the p_{xy} orbitals, the latter orbitals providing most of the bonding. It remains to explain why the angle is large in ammonia if the more stable case is where s electrons are nonbonding. Magnusson states, without calculational justification, that this is due to steric factors because bond angle cannot be reduced any further since the hydrogens, which are already very close (see section III.A.1), will be forced too close together. This explanation was also advanced by Petke and Whitten[127] in their early ab initio comparative study of phosphine and ammonia, and Goddard[100] has advanced a similar argument but identifies the repulsion between the bond pairs as the important interaction. Hall[113] has argued similarly and has tried to quantify such an interaction.

Note that there is a small d-orbital population in H_3P. Other workers have found similar low d-orbital populations.[126,127,164] As we have seen in section II there is no valence role for d orbitals, rather their function is calculational, providing necessary orbital polarizations. For example, Magnusson[143] found that in PH_2-CH_3 the d population occurs in the uppermost e orbital where it appears to improve the directional properties of phosphorus 3p orbitals overlapping with carbon 2p orbitals, 3s orbitals being unavailable in MO's of e symmetry. The effects of varying amounts of polarization functions can be clearly seen in Table 1 (e.g., cf. 3-21G* and 3-21G# results).

In summary, the advantage gained by isolating s electrons in a nonbonding role often appears to offset any potential value of sp mixing in bonding. Where there is relatively low symmetry, s orbitals can contribute in an antibonding manner to the HOMO thus cancelling out any bonding in the lowest energy valence MO. Reducing the bond angle in AH_3 reduces the symmetry and thus increases the nonbonding s density, thus lowering the energy, until the process is halted by

steric constraints. Thus s orbital contributions to bonding are most in evidence in the second row because it is here that steric constraints are largest—the atoms being smaller. Hybridization in lower symmetry molecules is thus expected to be negligible in many cases, and the ground-state configurations of many molecules, especially third row hydrides, will have central atom s populations close to s^2, with bonding provided mainly by p orbitals. It is only in higher symmetry molecules (for example D_{3h} in the cases considered here) that s orbital bonding can be expected to be significant where s density is debarred from contributing to the HOMO by symmetry considerations.

b. Bonding in Substituted Phosphines. Magnusson[143] also studied substituted main group hydrides. He found the same patterns of s, p, and d orbital contributions to bonding as for the hydrides described above. The s orbitals are chiefly employed in the lower MO and p orbitals in the upper but as in H_3P the HOMO is exceptional, containing substantial antibonding s character. In particular monosubstituted phosphines inevitably are less symmetrical, and it was found that segregation of the s and p electron density to nonbonding and bonding orbitals respectively is achieved to a high degree in them even though the bond angles are near 100° in most cases.

In trisubstituted cases e.g. trimethyl, once again, as symmetry is lowered (bond angle decrease), the s orbital overlap density drops to negative values and the s orbital populations rises to nearer the s^2 nonbonding values. Once again the variation with bond angle is not linear and the s orbital only begins to make a significant contribution to bonding at the top of the range of bond angle.[143] A further consideration here is that there may be additional valence-shell MO's to which the s density may contribute in an antibonding manner and a certain amount of segregation is still possible, in contrast to phosphine itself which has only the four valence-shell MO's of Figure 2A. A striking example of this effect was found[143] in the planar geometry of F_3P where there is indeed an extra high lying a_1' orbital[111,124] and maximum nonbonding s density is achieved.

Working with H_3AY series (Y = CH_3, NH_2, OH, F), Magnusson showed that the s-orbital contribution to the AY overlap density is much reduced from its value in the parent hydride irrespective of the electronegativity of the substituent.[12] The effect did not extend to the AH bonds which retain the characteristics they possess in the unsubstituted hydrides. This effect is also present in the H_2PY series but to a much lesser degree, because the s orbital contribution is already very low in H_3P. This is relevant to the Walsh–Bent hypothesis which is that atomic p character tends to concentrate in orbitals directed toward electronegative substituents.[165] The idea is that the energy is minimized by placing charge in those parts of the molecule where the potential is lowest, tightly bound s character near the central atom in its bond to the less electronegative atom(s) and less tightly bound p character near the electronegative substituent in its bond to the central atom. There are then consequences for bond angle in the sp ratios that result. Magnusson has shown,[12] again for H_2AY molecules, that, although there is a sharp drop in s orbital participation in the AY bond, this response is unrelated to electronegativity of substituent

and all of it is due to the mechanism of segregation which can occur when the symmetry is lowered by substitution. However this conclusion is challenged by Reed and Schleyer[142] (see section III.E.3) using a different population analysis.

3. Calculations by Reed and Schleyer (Negative Hyperconjugation)

Reed and Schleyer[142] studied all normal valence polyfluorinated compounds of the second and third row elements in the context of the anomeric effect with central atoms other than carbon. The paper was one of a series concerned with the effects of *negative hyperconjugation*.[166] Hyperconjugation is the interaction of filled σ orbitals and empty π^* orbitals; for example the σ_{CH} bonds of the CH_2 group of cyclopentadiene with the π^* orbitals of the diene. Negative hyperconjugation is then the converse i.e. electron donation from π to σ^* orbitals as in π_C to σ^*_{CF} donation in $FCH_2CH_2^-$ anion.[167]

The calculations were done at the 6-31G* level with electron correlation by second-order Møller–Plesset perturbation theory and with transformation to the natural localized molecular orbitals (NLMO's). These calculations are at a significantly better level than those of Magnusson described in the previous section, but they confirm his result that there is not a strict relationship between bond angle and hybridization. The decomposition into NLMO's also enabled the estimation of the extent of negative hyperconjugation from nonbonding fluorine p orbitals into antibonding AF orbitals. This was found to be highly significant, explaining as it did a number of issues relevant to the anomeric effect. For our purposes however, more interesting is that the variation of bond angles in phosphine and ammonia and their fluorine analogues could also be explained. It was found that negative hyperconjugation favors wider FAF angles counteracting the tendency of electronegative fluorine to induce more p character in the central atom hybridization, the latter being in accord with the Walsh–Bent rule. Thus in the absence of negative hyperconjugation the bond angles in NF_3 and PF_3 tended toward 90° as the central atom is induced to utilize its p orbitals exclusively. On allowing the π effects to operate the bond angles open out, those in nitrogen's case to a greater extent than for phosphorus which is easily explained as an electronegativity effect.[142]

4. Calculations by Kutzelnigg

Kutzelnigg[10] also used fairly high level calculations (triple-ζ plus polarization) but with Boys transformation to localized molecular orbitals. He also found that there was not a strict relationship between bond angle and hybridization. The s:p ratio for the hybrids forming the NH bonds in H_3N was 1:2.90 while that for the PH bonds in H_3P was 1:3.83. The s:p ratios for the lone pairs was 1:2.37 for ammonia and 1:0.95 for phosphine. It can be seen that the values for the second and third row are not as dramatically different as would be expected from their different valence angles. In particular, in phosphine, there can be no suggestion of pure p bonds, nor can the lone pairs be regarded as pure 3s AO's. The reason there is confusion about the s:p ratios calculated on the basis of the valence angle

is that such a calculation assumes that the hybrids are orthogonal which they are not.[10,142,168]

Kutzelnigg[10] went on to explain why there is a higher s:p ratio (less hybridization) in phosphine than ammonia and the origin of the difference in their valence angles. His explanation lies in why there is hybridization in the first place for which he gives three reasons: (i) hybrid AO's overlap more efficiently, (ii) hybridization reduces the repulsion between the AH bond and the lone pairs, and (iii) hybridization favors larger bond angles. For the third row compounds all three of these reasons are less important.[10] This is because the 3s AO's are smaller and less diffuse than the 3p AO's, which reduces the Pauli repulsions both between the PH bonds and between the bonds and the lone pair and makes for less strengthening of the bonding on hybridization.
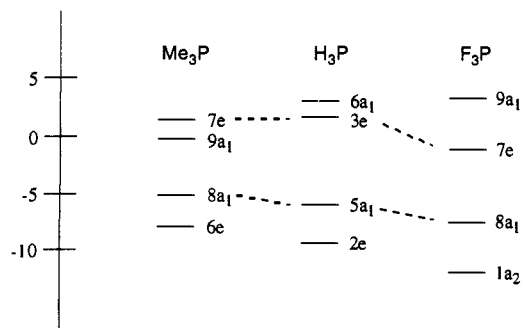
5. Other ab Initio Calculations

Lehn and Munch[126] found that in phosphine the HOMO is 88% localized on phosphorus with 15% P 3s and 73% P 3p character according to gross population analysis. This is in qualitative agreement with the results of Magnusson.[143]

Røeggen and Wisløff Nilssen[169] studied the difference between phosphine and ammonia using the extended geminal model[169] by partitioning the system into fragments corresponding to the core and valence parts of the molecule. They then examined how the intra- and interfragment energies varied with bond angle. They found that the difference in bond angle between phosphine and ammonia was due to a difference in the interaction of the valence and core fragments—this rises in energy with decreasing bond angle to a much larger degree in ammonia than in phosphine. The difficult part was analyzing which part(s) of the valence fragment was responsible for the difference and the authors did not commit themselves as to whether the bond pairs, lone pairs, hydrogens, or a combination were responsible.

Dixon et al.[170] have reported, in the course of studies on simple ylides, the only detailed valence bond calculation on phosphines. In their paper they give contour plots for the generalized valence bond orbitals, which are composed of two one-electron orbitals, in phosphine and methylphosphine and for comparison those of ammonia and methylamine. Mainly the results are similar except that the orbitals are more diffuse on phosphorus as expected by electronegativity. The difference is in the lone pair on phosphorus. In methylphosphine the outer, more diffuse, of the one electron orbitals of the lone pair shows a striking difference in comparison to its nitrogen counterpart. It is significantly broadened and no longer has its maximum density along the same vector as the maximum of the inner orbital of the lone pair. Rather the maximum lies almost directly behind the PC bond with some density over it. A similar difference was noted between the lone pairs of phosphine and ammonia. The presence of the methyl group is a significant perturbation on the lone pair on phosphorus in methylphosphine in that the lone pair is more remote from the methyl group.

6. Empirical Calculations

It is unfortunate that none of the later larger *ab initio* calculations give listings of orbital energies. However

Me₃P H₃P F₃P

5 —

— 7e ----- — 6a₁   — 9a₁
                   — 3e
0 — — 9a₁

-5 — — 8a₁ ---- — 5a₁ ---- — 8a₁
    — 6e   — 2e

-10 —   — 1a₂

Figure 5. Valence orbital energies (eV) of some phosphines calculated by the SCM-Xα-DV method. (Adapted from ref 147. Copyright 1983 American Chemical Society.)

in a careful study using the, only slightly, empirical SCM-Xα-DV method Trogler, Ellis and co-workers[147] investigated the nature of the frontier orbitals in phosphine, trimethylphosphine, and trifluorophosphine. The method used the experimental gas-phase geometries and, despite some assignment difficulties,[1,147,171] mostly reproduced accurately the experimental ionization potentials.[1,147] Detailed atomic compositions for the three compounds were also given.

It can be seen from Table 1 that there is a significant systematic difference between the HOMO energies derived from the Xα calculations and the *ab initio* results at both the 3-21G# and 6-31G* levels. However the trends on substitution are the same in that it was found that all orbital energies are raised by methyl substitution and all are lowered by fluorine substitution. It should be noted that the same result was found experimentally for the core levels by Sodhi and Cavell.[172] The orderings of frontier orbital energies in the three compounds are depicted schematically in Figure 5, and it can be seen that the LUMO is of e symmetry in H₃P and F₃P but is of a₁ symmetry in (CH₃)₃P. As expected, the HOMO is of a₁ symmetry.

The HOMO of Y₃P was found[147] to consist primarily of a lone pair sp hybrid on phosphorus. The ionization energy and orbital energy ordering (CH₃)₃P < H₃P < F₃P parallels the phosphorus s character of the HOMO: (CH₃)₃P 11% and 60% p; H₃P 14% s and 67% p; F₃P 29% s and 32% p. All of these trends follow the expected electron-withdrawing ability of the substituents CH₃ < H < F.

From an analysis of contour maps[147] of the HOMO in each case the back lobe of the sp hybrid interacts with the substituent attached to phosphorus in a σ-bonding fashion. However it is the LUMO contour maps which are the most interesting. In H₃P the 3e orbital possesses π symmetry with respect to the principal axis of symmetry and a similar type of orbital is found in F₃P and (CH₃)₃P, although in the latter it is not the LUMO. Although the symmetry is the same in these acceptor orbitals, there are some significant differences between them. In particular, the energy of 7e in F₃P is lower than that in H₃P of (CH₃)₃P and this might be expected to enhance the acceptor properties of F₃P. This point will be returned to in section IV.B. Note that the LUMO in H₃P is found to be the orbital of e symmetry here,[147] whereas it was taken to be that of a₁ symmetry in Figure 2A.

In a combined MNDO and PES study, Cowley *et al.*[173] tried to explain the enhanced basicity of less symmetrical phosphines. For example HPF₂ is much more basic than a consideration of the basicities of H₃P and F₃P would lead one to expect. They found that this was reflected in the trends of the ionization energies in that HPF₂ has a significantly lower first ionization energy than expected by extrapolation of those of H₃P and F₃P. This can be ascribed, in the now familiar way (see section III.B.2), to the lower symmetry, which allows lower energy orbitals to interact with the HOMO because they now have the same symmetry.

7. Studies on the Inversion Barriers in Phosphines

Since the previous major reviews of inversion barriers in main group 5 compounds[174,175] there have been a number of both qualitative and quantitative studies,[117,118,122,123,126,129,133,143,160,176,177] which have provided some more insight into the observed trends. In particular the much larger barrier to inversion in phosphines than in amines has been explained. The arguments based on the Walsh diagram approach (used in section III.A.3) for the difference in bond angle between amines and phosphines may also may be utilized for the difference in their inversion barriers. Referring to Figure 2A again, when the energy gap δE between the HOMO and the LUMO of the planar geometry is made smaller, the difference in energy between a₂″ of the planar geometry and 2a₁ of the pyramidal geometry is increased thus increasing the inversion barrier.[4] Again it may be incorrect to ascribe these changes solely to the electronegativity change since such change inevitably accompanies the change to lower group on the periodic table. In support of these arguments Epiotis and Cherry[117] and Levin[118] have shown that there is relationship between barrier increase and HOMO–LUMO splitting in the D₃h transition state and Dougherty *et al.*[177] have shown that π-acceptor groups lower the barrier. On the other hand Jolly *et al.*[123] in more recent calculations found a linear relation between the differences in the energies of the HOMO's in the planar and pyramidal forms and the calculated inversion barriers in H₃P, Me₃P, and Ph₃P. Thus the larger the destabilization of the HOMO in the planar form, the higher the inversion barrier.[123]

However in the last few years some important new work[148,160,178,179] has shown that there is an inversion mechanism other than the commonly accepted pyramidal–planar trigonal process; namely inversion via a T-shaped transition state.[178] It turns out that Y₃A molecules fall into two groups—one inverting via the classical D₃h transition state and the other by the C₂ᵥ T-shaped transition state. In the former group are, for example, H₃N, H₃P, H₃As, F₃N, and Cl₃N while the latter group contains, for example, F₃P, Cl₃P, Br₃P, and F₃As. A consequence of these new findings is that many previous calculations of inversion barrier which were done on the assumption of a D₃h transition state may need to be reexamined. For example, the difference in energy between the two transition states[148] in the case of F₃P is approximately 132 kJ mol⁻¹. Also, some of the previous calculations did not optimize the geometry of the planar transition state, and it is now well known[126,133,160] that the bond length is shorter in that transition state.

Bader *et al.*[161] in calculations at the 6-311G**+ D+P+CI level confirmed that the barrier to inversion

in phosphine and ammonia is of the *repulsive-dominant* type.[175] Thus it is a consequence of an increase in repulsive nuclear–nuclear interactions as internuclear separation decreases in the planar transition state which outweighs an accompanying decrease in the attractive nuclear–electronic potential energy. They attributed the larger barrier in the third row compound as being due to the larger size of phosphorus, the decrease in A–H bond length on attaining the planar geometry being largest in PH_3.

C. Summary of the Bonding in Phosphines

On examination of the results of the calculations for phosphine and referring again to Figure 2A, it can be seen that (i) the $1a_1$ and $1e$ orbitals provide the bonding by virtue of their overlap population being positive, (ii) $2a_1$ is nonbonding because the bonding of the p orbital contribution to it is exactly balanced by the antibonding of the s orbital contribution, (iii) the contribution of the s electrons to chemical bonding is zero overall, this being achieved by their bonding in $1a_1$ being balanced by antibonding in $2a_1$, (iv) all the bonding is done by p orbitals, including the bonding by p_z in $2a_1$ and $1a_1$, (v) the lone nonbonding pair is located in $2a_1$ (which is the HOMO) and therefore has the observed directional properties, and (vi) the LUMO may be $3a_1$ or $2e$ and this is not yet settled by the calculations and also it will depend upon the phosphine substituents (section III.B.6).

In this way the s electrons do not contribute to bonding, and yet the nonbonding electrons are not in the s orbital! This is a paradox only if one forgets that there is no phosphorus s orbital in H_3P only the utilization of the phosphorus s orbital in various MO's of H_3P. Ammonia can be compared to phosphine using the same procedure again referring to Figure 2A: (i) again the bonding is provided by the $1a_1$ and $1e$ orbitals, (ii) the $2a_1$ orbital is still nonbonding but its character is different from the same orbital in phosphine in that there is a lower contribution to it by s electron density, (iii) the important difference is that the s electrons are bonding to a certain extent, this being caused by their lower contribution to antibonding in $2a_1$ and their higher contribution to bonding in $1a_1$ and this change is due to the higher symmetry (larger bond angle) in ammonia, (iv) the bonding is done by a combination of s and p orbitals but not the 25%/75% split as suggested by the directed valence approach (the s contribution being less than expected), (v) the HOMO is again $2a_1$ (the lone pair of electrons), and (vi) the LUMO is presumed to be $3a_1$ or $2e$.

The differences between phosphine and ammonia can be understand if one takes the view: either (a) that it is bond angle which controls the utilization of central atom s and p orbitals in bonding and in turn the bond angle is dictated by steric factors—it cannot go below 107° in ammonia because there is not enough room around nitrogen—or (b) that it is the utilization of central atom s orbitals in bonding which controls the bond angle, where s orbitals are available for use, as in nitrogen, the angle will be wider.

Indeed a picture emerges[4] that the second row of the periodic table is the anomalous one—whether this be because the atoms are smaller or because the 2s and 2p orbitals have similar radial extent or that these amount

to the same thing remains to be determined. In any event size is important in chemical bonding!

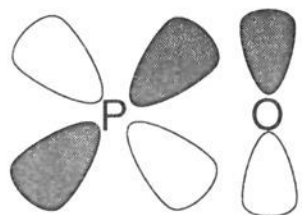## IV. Phosphine Oxides

A. Introduction

Simple qualitative arguments work rather well in predicting the bonding in phosphine oxides. Phosphorus has five electrons available for bonding, so five bonds to phosphorus are possible, while oxygen is normally divalent and double bonds are allowed. So, if we ignore the octet rule, there is no problem predicting the correct structure: phosphorus will have four ligands via three single bonds and one double bond to oxygen, with all electrons used. From VSEPR theory[48] the four ligands are expected to have tetrahedral geometry with the angle to oxygen wider. The bond to oxygen would also be predicted to be stronger than the rest and rather polar because of the difference in electronegativity between oxygen and phosphorus. These predictions are in fact borne out completely by measurement of the bond lengths and angles and many other physical properties.

The typical PO bond length probably[180] lies in the range 147.6–148.9 pm. This PO distance is fairly insensitive to molecular environment[2] and may be compared with those in HPO^{182} (151.2 pm), diatomic PO^{182} (147.6 pm), and a typical PO single bond (160 pm, bridging bond in P_4O_{10}).[183] Clearly the PO bond has high multiple character. Similar comments may be made about the PS (194–195 pm) and PSe (209–211 pm) bond lengths,[2] although to a lesser degree. Phosphine chalcogenides have also been studied with respect to their bond energies and dipole moments, and by, among others, the techniques of infrared, nuclear magnetic resonance, and photoelectron spectroscopy. The combined experimental evidence (summarized in ref 2) is that the phosphoryl bond is strong, short, and polar and while the sulfur and selenium analogues are similar, they are not quite as strong and are more polar. Most estimates of bond order give the PO bond as greater than two and the PS and PSe bonds as somewhat less than two.[2]

Much of the previous discussion of the bonding in phosphine oxides (and sulfides and selenides) has centered on how to overcome two problems in connection with the straightforward analysis presented above: how to overcome the octet rule and secondly, on the LCAO-MO model there are, on first sight, not enough orbitals on phosphorus. Thus the standard discussion of the PO bond in previous reviews[20,21,103–108,184–186] of this topic has been in terms of a combination of two different descriptions, often via a resonance between structures like 1A and 1B:

$$R_3\overset{+}{P}-\overset{-}{O} \longleftrightarrow R_3P=O$$

1A 1B
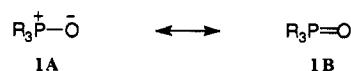
Structure 1A avoids the problem of violation of the octet rule but there is evidence[2] that there is not a full positive charge on phosphorus or negative on oxygen, so structure 1B is allowed to contribute. The conventional phrase is often used:[20,21,103–108,184–186] "there is expansion of the octet on phosphorus to allow back-bonding from oxygen lone pairs into low-lying empty

Figure 6. The now outdated and misleading view of the π-type orbital overlap in phosphine oxides.

d orbitals", a euphemism for saying that the octet rule is broken by these compounds. Also, up until recently, there was a smoothly made connection[20,21,103–108,184–186] that this indicated that "the low-lying atomic d orbitals are involved in hybridisation at phosphorus", in an overlap scheme like the one in Figure 6.

Work over the last 10–15 years has rendered this description untenable. First we have already seen in section II that the d-orbitals concept is now redundant at best, inaccurate and misleading at worst. Secondly, at a deeper level, doubt has been cast on the description of the PO bond as a single bond with some backbonding, the rival description being a formal triple bond. As we shall see in section IV.E.3, this latter issue is not yet settled and is part of a developing general controversy about the nature of multiple bonding.

Aside from the d orbitals question, there is a further problem with a description based on structures **1A** and **1B**. This is because they are not mutually exclusive. For example, consider the overlap of oxygen lone pairs with suitable receiving orbitals on phosphorus. No matter what receiving orbitals are envisaged (either the d orbitals or some other combination—*vide infra*) the overlap would be highly unsymmetric with most of the electron density near oxygen.[27] So the double-bond structure **1B** would necessarily lead to a polar molecule anyway. Alternatively one could consider that the PO bond is a pure σ single bond formed by donation of the phosphine lone pair into a vacant p orbital on O (preserving the octet at phosphorus). Then the phosphorus carries a full positive charge and the oxygen a full negative one. The proximity of these two opposite charges must surely lead to a strengthening of the PO link via an ionic type of attraction. It is often implied,[187] but has not been shown explicitly, that this does not account fully for the shortened PO distance and the increased bond strength. A final difficulty is that there may be more than one way of having a π-type back-bonding interaction from oxygen to phosphorus. In the case of d orbitals it was always recognized that this was the case,[10,76,188] because there are two d orbitals of appropriate symmetry which could overlap with two oxygen lone pairs. This is obscured by the double-bond formula **1B** and so a triple-bond formula naturally arises.[76] An alternative description is as a resonance between structure **1A** and a triple bond.[189] The description "partial triple bond" is also reasonable[10,76] on the basis that the bond order is between two and three. This latter view involves one σ bond and two half π bonds and has become common recently.[10,13] Note that a formal triple bond from oxygen to phosphorus in these compounds would imply that phosphorus carries a negative charge and oxygen a positive charge, perhaps providing a qualitative rationalization of the fact that the PO bond moment is less than expected.[2]

Studies of the bonding in phosphine oxides, sulfides, and selenides therefore have naturally concentrated
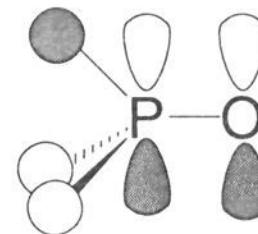
Figure 7. Description of the P=O bond as a σ bond and two π bonds (one shown) formed by back-bonding of two electron pairs on oxygen into two orbitals of e symmetry on the phosphine moiety. (Adapted from ref 2. Copyright 1992 Wiley.)

on the nature of the PO bond, and to a lesser extent the PS and PSe bonds. Particular issues which have been of concern are (i) the great strength of the PO bond, (ii) the exact distribution of the electron density in the PO bond especially if it can be classed as a multiple bond, (iii) the difference between the PO bond in phosphine oxides and the NO bond in amine oxides, and (iv) the difference between the oxides and the sulfides and selenides.

B. Acceptor Orbitals for Back-Bonding

Now that we have discarded d orbitals we must find a set of acceptor orbitals on phosphorus if back-bonding is to be significant. In fact there is a perfectly reasonable alternative set of such orbitals available—the LUMO of the phosphine moiety which is of σ* type.[5–7,147,198] These are the orbitals labeled 2e in Figure 2A and in the case of Me_3PO, H_3PO, and F_3PO are the 7e, 3e, and 7e sets respectively shown in Figure 5. Figure 7 shows this overlap scheme which is simply another example of negative hyperconjugation (see section III.B.3).

Both theoretical[121,147] and physical[5–7,190] methods confirm that back-bonding is likely to be into these σ* orbitals. Trogler, Ellis, and co-workers,[147] in the empirical calculations described above (section III.B.6), found that the LUMO of the phosphines studied mostly consisted of phosphorus p character, consistent with the 2e orbitals of Figure 2A. In a later study Marynick,[121] using both empirical and *ab initio* calculations, confirmed that phosphine ligands could be π accepting without involving d orbitals on phosphorus and that the σ* orbitals were indeed the acceptor orbitals. This conclusion was confirmed by Tossell and co-workers[190] who examined the LUMO of H_3P by electron transmission spectroscopy and found it to be of σ type.

However, the most significant contribution has been by Orpen and co-workers[5–7] initially in application to transition metal complexes[6,7] and later to all Y_3PZ derivatives.[5] Exactly the same arguments concerning the nature of back-bonding arise in the case of transition metal phosphine complexes[1] and in their initial elegant study Orpen and Connelly[6,7] examined the metal–phosphorus and the phosphorus–substituent atom bond lengths in the crystal structures of a series of 24 transition metal complexes, Y_3PM, related by formal redox couples. The idea was that if the back-bonding is occurring into σ* orbitals, then the bonds to the phosphorus substituents should be weakened[7] and they found that indeed there was a correlation between MP bond strengthening and PY bond weakening as measured by bond length. Thus metal phosphorus bond lengths increase on oxidation of the metal, consistent

with the presence of MP π back-bonding. At the same time, there is a decrease in average PY bond lengths, consistent with the acceptor orbital on phosphorus having antibonding character.[6,7] Extension of these arguments by Orpen and co-workers[5] to the wider study of all Y_3PZ compounds is discussed below (section IV.C.2).

The energies of these antibonding acceptor orbitals are also interesting and we refer again to those derived from SCM-Xα-DV calculation[147] detailed in Figure 5. In H_3P, the 3e orbital is the LUMO at 0.88 eV while in F_3P the 7e orbital is the LUMO at -1.05 eV but in Me_3P the lowest unoccupied orbital of e symmetry is the 7e orbital which is the NLUMO at 0.85 eV, the LUMO being $9a_1$ at 0.43 eV. Thus the appropriate acceptor orbital for the F_3P moiety of F_3PO is at significantly lower energy than that in H_3PO and Me_3PO in agreement with greater back-bonding leading to a stronger PO bond in F_3PO.

As an aside we note that this analysis solves one other outstanding difficulty in bonding theory. The structure of F_3NO was always very inconvenient for those who advocated the involvement of d orbitals to explain the structure of phosphine oxides. The NO distance in this molecule is extremely short (see Table 2) in comparison to that in trimethylamine oxide which is close to the NO single bond length in hydroxylamine[182] (145.3 pm). Thus it must be accorded the status of a double bond and "rightly or wrongly, few chemists would invoke the 3d orbitals of nitrogen to explain the bonding".[191] Thus its stability was "somewhat surprising".[192] Now that back-bonding does not have to be into d orbitals there is no problem. Indeed the NF bond is lengthened (see Table 2) consistent with population of the antibonding orbitals. The orbitals of F_3NO were analyzed in detail by Grein and Lawlor[93] who concluded that the 3e orbital of F_3N was the suitable acceptor orbital.

There is one further qualitative insight which is of value. There is a formal analogy between the semipolar bond e.g. in H_3PO and the bonding situation in phosphoranes like H_3PF_2, just as H_2CO and H_2CF_2 are formally related.[10,13] In this way the PO bond can be viewed as analogous to the three-center, four-electron bond developed by Rundle[37] to explain the bonding in phosphoranes. Note that this three-center, four-electron bond model is not incompatible with some degree of back-bonding.

C. Structure Correlations in Comparisons of Y_3PZ

It has been found that useful chemical insights can be derived from an examination of trends in the published structures of tetracoordinate phosphorus compounds. We discuss below some of the recent conclusions of such correlations and the relevant data are collected in Table 2.

At the outset it must be stressed that comparisons must be done very carefully because much reported data is unreliable due to R factors which, although they might have been considered adequate at the time, are now known to be too high. For example, a selection of reported X-ray crystal structure determinations on triphenylphosphine oxide[25,33-35] is included in Table 2. Note the fairly large changes in structural parameters

as the R value falls from 7.8 to 3.5. Thus the figure of 146 pm for PO length, derived from the first study[210] on triphenylphosphine oxide, which was widely quoted[194,199] into the mid-1980s is in error, our best present estimate[2,229] being 149.1–149.4 pm. Similar difficulties were encountered in the study of phosphorus ylides (see Table 2). Thus a recent study[223] on $Ph_3P=CH_2$ which was done at -100 °C and with a high order data refinement found a value of 169 pm for $r(P=C)$. The previous study on this molecule by Bart[224] had acceptable precision even by today's standards[230] but again the P=C distance was 3 pm shorter. A similar lengthening of $r(P=C)$ by about 3 pm on reduction of R was found for hexaphenylcarbodiphosphorane.[227]

1. Correlations Derived from Phosphine Chalcogenides and Analogues

Notwithstanding the difficulties concerning R values, the following observations have been made[2,181] on phosphine chalcogenides and their analogues:

i. There is a consistent deviation of the bond angles from the tetrahedral values with CPZ higher (112–114°) and CPC lower (104–107°). However there is no significant change of CPC angle with change in chalcogen i.e. there is no correlation of PC bond length and CPC bond angle in these cases.

ii. The PC bond length decreases on formation of the chalcogenide and the extent of reduction is in the order O > S > Se. Thus the PC bond length in phosphine oxides is normally in the range 179–181 pm (see item iv, below), while that in the sulfides is longer (181–182 pm), and the selenides may be longer again (181–184 pm). There are similar decreases in the PF and PCl bond lengths in the series $F_3P > F_3PS > F_3PO$ and $Cl_3P > Cl_3PS > Cl_3PO$. Most interestingly, the only exception to this observation (and which is strongly in the other direction) is for the PC bond to an alkyne carbon (see Table 2). However the PC distance to the alkyne carbon is already very short indeed in the parent phosphine.

iii. There is a consistent variation in PO and PS bond lengths in that they decrease over the series $Me_3PO > Cl_3PO > F_3PO$ and $Me_3PS > Cl_3PS > F_3PS$. At the same time there is decrease in APA bond angle.

iv. The PC_{alkyl} bond length is less than the PC_{aryl} case for all the chalcogenides and the parent phosphines. Thus Allen et al.[181] determined the mean PC_{alkyl} distance in phosphines to be 185.5 pm compared to a PC_{aryl} distance of 183.6 pm. The same distances in the phosphine oxides were found to be 181.3 pm and 180.1 pm, respectively.

v. There is a much larger decrease in NO distance from the trimethyl to the trifluoro compound than in the analogous PO distance.

vi. There is an increase in both NC and NF on formation of the oxide. This is the opposite of the trend noted above for the phosphine oxides.

2. Correlations Found by Orpen and Co-Workers

A major contribution to this area has been made by Orpen and co-workers[5-7] through studies of the geometry of Y_3PZ compounds obtained from the Cambridge Crystallographic Database. We have already referred to their early study[6,7] of some transition metal phosphine complexes (section IV.B). Recently Dunne, Morris, and

Table 2. Structural Data[a] for Some Y₃Pn and Y₃Pn=Z Molecules

molecule	method[b]	r(Pn=Z), pm	r(Pn—Y), pm	∠ZPnY, deg	∠YPnY, deg	R[c]	ref(s)
Me₃P	E		184.7		98.6		150
Me₃PO	E	147.6	180.9	114.4	104.1	5.2	193
Me₃PO	X	148.9	177.1	113.1	105.9	6.5	194
Me₃PS	E	194.0	181.8	114.1	104.5	4.8	193
Me₃PS	X	195.9	179.8	113.2	105.8	5.0	195
Me₃PSe	E	209.1	181.6	113.8	104.8	9.1	196
Me₃PSe	X	211.1	178.6	113.1	105.7	4.8	197
Buᵗ₃P	X		191.9		109.9		198
Buᵗ₃PO	E	159.0	188.8	106.1	112.9	9.7	199
Buᵗ₃PTe	X	236.8	189.6	108.7	110.2	6.9	200
Ph₃P	X		182.8		103.0		201
Ph₃PO	X[d]	148.4	180.3	112.3	106.6	4.5	202
Ph₃PS	X	195.0	181.7	113.1	105.7	4.6	203
Ph₃PSe	X	210.6	183.0	113.1	106.0	7.0[e]	204
(2-MeC₆H₄)₃P	X		183.5		101.7	4.5	205
(2-MeC₆H₄)₃PO	X	147.4	181.0	112.9	106.0	7.5	205
(2-MeC₆H₄)₃PS	X	194.8	181.9[f]	112.6	106.1[g]	9.0	205
(2-MeC₆H₄)₃PSe	X	211.6	183.4	112.7	106.4	6.7	205
Ph₂PC≡CPPh₂	X		176.5		100.2	6.1	206
			183.2[h]		102.8[j]		
Ph₂P(O)C≡CP(O)Ph₂	X	148.1	179.4	114.4	103.7	3.9	207
			180.8[h]	112.9[i]	108.5[j]		
Ph₂P(S)C≡CP(S)Ph₂	X	192.3	176.3	113.8	101.8	4.0	208
			179.5[h]	114.9[i]	108.3[j]		
Ph₂P(Se)C≡CP(Se)Ph₂	X	209.7	178.3	112.7	102.6	6.3	209
			183.2[h]	114.5[i]	108.8[j]		
Ph₃PO	X[k]	146	176	111.7	107.1	7.8	210
Ph₃PO	X[l]	148.3	179.2	112.3	106.5	6.0	211
Ph₃PO	X[d]	148.4	180.3	112.3	106.6	4.5	202
Ph₃PO	X[d,m]	149.4	180.0	112.4	—	3.6	212
Me₃PO	E	147.6	180.9	114.4	104.1	5.2	193
Cl₃PO	E	144.9	199.3		103.3		213
F₃PO	E	143.6	152.4		101.3		213
Me₃PS	E	194.0	181.8	114.1	104.5	4.8	193
Cl₃PS	E	188.5	201.1		101.8		213
F₃PS	E	186.6	153.8	117.9	99.6		214
H₃N			101.2		106.7		215
H₃P	M		141.15		93.36		146
Me₃N	M		145.1		110.9		216
Me₃NO	X	138.8	147.7	110.0	109.0	7.4	217
F₃N	M		136.5		102.4		218
F₃NO	E/M	115.9	143.2	117.4	100.5		219
F₃P	E		157.0		97.8		149
F₃PO	E	143.6	152.4		101.3		213
F₃PS	E	186.6	153.8	117.9	99.6		214
Cl₃P	E		203.9		100.3		220
Cl₃PO	E	144.9	199.3		103.3		213
Cl₃PS	E	188.5	201.1		101.8		213
Me₃As	E		196.4		96.0		196, 221
Me₃AsO	E	163.1	193.7	112.6			193
Me₃AsS	E	205.9	194.0	113.4			193
R₃P	X		185.5 alk				181
			183.6 aryl				
R₃P=O	X	148.9	181.3 alk				181
			180.1 aryl				
R₃P=S	X	195.4					181
X₃P=Se	X	209.3					181
Me₃P=CH₂	E	164.0	181.5	116.5	101.6	10	222
Ph₃P=CH₂[m,n]	X	169.3	182.0	112.2	103.8	4.3	223
			183.3u	116.3u	105.8u		
Ph₃P=CH₂	X	166.1	182.3	113.5	105.0	6.4	224
Fc₃P=CH₂	X	162.9	180.4	115.3	103.1	3.4	223
Prⁱ₃P=CMe₂	X	173.1	183.4	108.1	114.9	4.9	225
				117.5u	104.2u		
Me₃P=C=PMe₃	E	159.4	181.4	116.7	101.4	6.6	226
Ph₃P=C=PPh₃[k]	X	161.0	185.3			5.9	227
Ph₃P=C=PPh₃[k,o]	X	163.5	183.1			4.1	227
Ph₃P=C=PPh₃[p]	X	163.1	183.5	114.7	104.0	8.9	228

[a] Mean values are quoted; u refers to the unique substituent on phosphorus in the ylides (see Figure 13). [b] E: electron diffraction. X: X-ray crystallography at room temperature unless indicated otherwise. M: microwave spectroscopy. [c] R: reliability index = 100 × conventional R for both X and E unless indicated otherwise, see original papers for definitions. [d] Monoclinic, space group P2₁/c. [e] R = Rw. [f] d(P–C) range: 177.3–187.0 pm. [g] ∠CPC range: 101.5–110.6°. [h] r(P–C_Ph). [i] ∠ZPC_Ph. [j] ∠C_PhPC_Ph. [k] Orthorhombic. [l] Monoclinic, space group P2₁/a. [m] Performed at 100 K. [n] With high order data refinement. [o] Performed at 113 K. [p] Monoclinic, two molecules in unit cell, averages given.

Orpen[5] have brilliantly extended this early study to nearly 1300 crystal structures containing the Ph_3PZ unit and statistically examined the symmetrical (C_{3v}) distortions of the C_3PZ moieties. A preliminary analysis of a further 1200 structures containing Y_3PZ units was also given. Z now may be a transition metal, or a main group metal or nonmetal. The following is a resume of their results. Aside from confirmation of points i–iii above, they report three other much more powerful correlations.

a. Correlations of bond lengths and bond angles.

i. There is a strong negative correlation between the mean CPC bond angle and the mean PC bond length in all Ph_3PZ. The majority of other phosphine classes show the same marked negative correlation. One notable exception is the case of F_3PZ complexes, where no such correlation is observed, perhaps because of the systematic errors associated with the high librational motion often seen in these complexes.[5]

ii. Where Ph_3P is bonded to a nonmetallic element, the substituents C (sp^3), N, O, OX, and S all show positive correlations between the PZ bond lengths and the mean CPC bond angle in Ph_3PZ.[5]

b. Geometry dependence on Z.

i. Strongly σ-bonding Z (e.g. H, R, O) are associated with smaller PC bond length (179–180 pm) and larger CPC bond angle (107–110°). Structures in which Z is a transition element show larger PC bond length (183 pm) and smaller CPC bond angle (102–104°) i.e. Ph_3P geometries close to that of triphenylphosphine itself. Broadly speaking, as the substituent Z becomes more electronegative the Ph_3P unit tends to flatten out (the CPC angles increase) and the PC bonds become shorter.[5]

ii. Complexes of the early transition elements (e.g. Cr) show mean Ph_3P geometries more pyramidal than that of free triphenylphosphine. The central elements of the series (e.g. Os) are characterized by geometries near that of the free ligand, while those of late and post transition series metals (e.g. Au, Ag, Hg, Sn) are less pyramidal than the free ligand. Furthermore mean CPC values rise monotonically in the series from Cr to Zn, Ru to Cd, and Re to Hg; correspondingly the mean PA values fall monotonically across this series.[5]

Two other useful observations were extracted from their data by Orpen and co-workers.

The angular symmetric deformation coordinate $S4'$ (defined as the sum of ZPY angles minus the sum of the YPY angles) correlates surprisingly well with the cone angle of the phosphine. The correlation is negative, meaning that large cone angles tend to give small $S4'$, corresponding to a small sum of ZPY angles and a large sum of YPY angles i.e. the phosphine is considerably flattened.

The grand mean of the $C_{ipso}C_{ortho}$ bond lengths is 138.9 pm while that of the $CC_{ipso}C$ bond angles is 119.260°. These may be compared with the values of 139.5 pm and 120° used when constraining a phenyl group to fit a rigid regular hexagon in the SHELXTL program and suggest that there should be some modification of the latter.

3. Anomalous Structure of Very Bulky Phosphine Chalcogenides

The reported structure[199] of tri(*tert*-butyl)phosphine oxide is totally anomalous (see Table 2). The remark-

able features of the structure of Bu^t_3PO are (i) the much greater length of the PO bond (159.0 pm) compared to all other oxides, making it essentially a single bond length, (ii) the greater length of the PC bond (188.8 pm), and (iii) the reversal of the angle deviation from tetrahedral (CPC is greater). Obviously the great bulk of the *tert*-butyl groups may be at least partly responsible for this anomalous structure. For example, the CPC angles in the parent phosphine[198] (109.9°) are already one of the highest known and could hardly be expected to decrease on oxidation. But it should be pointed out that there is no steric requirement for the PO bond to be so long because the oxygen atom is well separated from its neighboring carbon atoms and from the methyl group atoms.[199] *So there must be a suspicion that this very long PO bond report is due to the very high R value (9.7).* We have already noted (section IV.C) that reduction of R values from 6–7 to 3–4 can cause reduction of PZ bond length by 3 pm. On the other hand the structure of the fairly bulky tricyclohexylphosphine sulfide[2] shows, to a lesser extent, the same trends of longer bond lengths and equalization of bond angles. Similar is the structure of tris(2,4-dimethoxyphenyl)phosphine selenide,[2] again to a lesser extent. However in the tris(trimethoxyphenyl)phosphine selenide crowding is avoided by a marked asymmetry of the substituents.[2]

The uncertainty in the exact nature of the PO bond in tri(*tert*-butyl)phosphine oxide is unfortunate because to date there are structural data for only one tertiary phosphine telluride—the tri(*tert*-butyl) case.[200] Comparison of the two (Table 2) shows that the same unusual structural characteristics are present in the telluride as in the oxide. Thus the CPC angle is greater than the TePC angle and the PC bond length is very long (same length as in the oxide), in contrast to all other tertiary phosphine chalcogenides. There must then be a strong suspicion that the PTe bond length of 236.8 pm is not typical of tertiary phosphine tellurides. On the other hand there is some other evidence to the contrary[2] and anyway the data for the oxide are not satisfactory. Even with this uncertainty, it should be noted that a PTe bond length of 236.8 corresponds[200] to a bond order of 1.5 using the covalent radii of Schomaker and Stevenson.[19] However no evidence for multiple bonding to tellurium in R_3PTe was found by ^{125}Te NMR or Mössbauer spectroscopy.[231]

D. Explanations of Structure Correlations

There are two possible approaches to the explanation of the structure correlations described in the previous section. First, we may say that the correlations appear to powerfully vindicate the use of the Walsh correlation diagram analysis using, for example Figure 2A. This analysis which was described by Orpen and co-workers[5] is summarized first. However in the following section it is shown that arguments based solely on size may account for all of the observations. This reviewer is inclined toward the orbital viewpoint because it has already proved itself for the phosphines as described earlier and because it is more amenable to analysis and prediction. But it has to be said that the alternative remains to be disproved. On the other hand, Orpen and co-workers[5] refer briefly in their paper to a

correlation which cannot be explained purely on steric grounds.

1. Orbital View—Walsh Diagram Explanation

Referring to Figure 2A, reduction of the YPY angle on pyramidalization results in destabilization of the PY σ-bonding orbitals (1e). This loss of PY bonding accounts for the negative correlation between mean CPC bond angle and PC bond length in Ph_3PZ.[5]

Depopulation of $2a_1$ occurs on coordination to a σ-acceptor Z, such as H^+. The driving force toward pyramidalization is thus reduced, resulting in increased YPY angles and hence shorter PY bonds. This is the situation observed for Z = H, C, N, O, and other main group substituents where the PZ σ bonding is undoubtedly very strong.[5]

Coordination of the phosphine to a π-donor species Z will partially populate the Y_3P LUMO (2e) i.e. the π-accepting function. This level becomes increasingly stabilized as Y_3P pyramidalization increases. It follows that an increase in PZ π bonding should lead to a decrease in the mean YPY angle coupled with a longer mean PY distance. In addition population of the 2e orbitals directly weakens the PY bonds since they are PY antibonding. Phosphine complexes of transition series elements do indeed exhibit geometries with smaller YPY angles and longer PY distances than complexes with strongly σ-bonding p-block substituents. Most significant are the trends found in Ph_3P unit geometry from left to right across the transition series wherein the unit progresses from more pyramidal than the free ligand to less pyramidal than it. These trends are consistent with decreasing importance of π bonding and enhanced importance of σ-bonding effects on moving from left to right across the d block and are to be expected if left to right progression across the periodic table decreases π-back-bonding ability, due to the metal d electrons becoming increasingly tightly bound.[5]

An interesting viewpoint advanced by Orpen and co-workers[5] concerns the nonmetallic elements Z = C, N, O, OX, S. Here the observed positive correlation between PZ bond length and CPC angle can be extrapolated to the conclusion that on extension of the PZ bond to infinity (i.e. PZ bond cleavage) the Ph_3P fragment progresses toward planarity at phosphorus. This is consistent with heterolytic PZ bond cleavage yielding e.g. O^{2-} from Ph_3PO along with hypothetical Ph_3P^{2+}. This latter possesses two fewer electrons than the neutral species and on the above qualitative molecular orbital grounds would be expected to favor the planar geometry.

A measure of the importance of σ donation of the phosphorus lone pair would be that increasing the electronegativity of Z should enhance σ donation (and reduce π back-donation) and, from the above arguments, drive the phosphine toward planarity. While a correlation was found[5] between CPC and Pauling electronegativity of the Z atom in Ph_3PZ species, it was not strong. This might have been expected however because the use of electronegativity of attached atom is a crude approximation here. On the other hand data on phosphine chalcogenides alone do not show any similar correlation (section IV.C.1).

Orpen and co-workers[5] concluded that the geometry of the Ph_3P fragment may be primarily determined by the σ interactions with the substrate Z when Z is from the first two short periods. For transition elements, however, σ and π effects on Ph_3P geometry are approximately in balance.

2. Steric View—Bond Length/Bond Angle Relationship Explanation

There is a simple steric idea that bond length and bond angle are naturally related. It is especially useful in the case of a tetrahedral disposition of ligands around a central atom where most of the space around that atom is occupied. Then the introduction of either bulky or more electronegative groups will lead to a change of both bond angle and bond length. Thus, for example, the bond angle between bulky groups will have to be larger, so all ligand(s) will not be able to get as close to the central atom and their bond length will be larger. On the other hand, a more electronegative group will require a shorter bond length to the central atom forcing the other ligand(s) closer together and reducing their bond angle. The structure of the molecule then reflects the balance between these two effects.

Used carefully the concept can reduce the number of experimental correlations that have to be explained, but obviously, there are limitations on its use. First, if the space around the central atom is not fully occupied, then the bond angle can increase while maintaining bond lengths and it has been noted that there is no evidence for a bond length/bond angle relationship in the tricoordinate phosphines.[1] Similar conditions would perhaps apply in the later rows of the periodic table where the central atom is relatively large. Secondly, if the space around the central atom is already very crowded as in tetrahedral derivatives of the small second row atoms, then the size effect may be more dominant.

First the basic structural details of Y_3PZ (Z = O, S, Se) are noted to be consistent with VSEPR theory which predicts multiple bonds to take up more room than single bonds.[48] Also the fact that the YPY bond angles are larger than in the parent phosphines is attributed in the new version of VSEPR theory[48] to the greater space requirements of the lone pair than the oxo, sulfido, or seleno ligand. Then, a negative correlation of YPY bond angle and PY bond length is predicted in Y_3PZ compounds because as the PY bond length gets smaller, the Y groups would be forced closer unless the YPY angle gets larger. Similarly as PZ gets larger, there is more room, so the YPY bond angle can increase. Introduction of more electronegative Z increases the effective electronegativity of P, strengthening the PY bond and decreasing its length. Similarly more electronegative Y leads to shorter PZ and wider YPY.

The much larger decrease in NO distance from the trimethyl to the trifluoro compound than in the analogous PO distance is undoubtedly due both to the increased electronegativity and a strong steric effect at the small nitrogen atom. That both NC and NF increase on formation of the oxide (the opposite of the case for phosphine oxides) has to be attributed again to the small size of the first row atom. Thus as the ligands are already close together, the additional oxygen means they have to move apart.

Table 3. Results of Calculations on Phosphine and Amine Oxides $Y_3P=Z$ and on Methylenephosphorane

molecule	calculation[a]	energy[b]	r(P=Z), pm	r(P—Y), pm	∠YPZ, deg	μ,[c] debye	ref(s)
H_3PO	3-21G	−415.0830	157.9	140.5	117.2	4.60	232
	3-21G#	−415.2070	147.0	139.1	117.5		233
	3-21G*	−415.2961	146.0	139.3	117.8	3.46	232
	4-31G*	−416.8795	146.0	139.8	117.4		144, 234
	6-31G*	−417.3068	146.4	139.3	117.0	4.18	13, 232, 235, 236
	DZ	−417.1831	160.5	140.5	116.0		237
	DZ+P	−417.3342	147.4	139.3	115.8	5.14	232
	TZ+P		145.6	139.2	116.0	4.22	238,239
	>DZ+P+C[d]	−417.5378					76
	TZ+P[e]+C[f]	−417.7140				3.87	239
F_3PO	3-21G*	−710.4446	142.7	152.7		1.75	77
	6-31G*		142.5	152.6	117.2		236
	>DZ+P[g]	−714.0301	145[h]	157[h]			240
	GVB-SOPP		147				14
	EXPT		143.6	152.4	116.8	1.74	213
Me_3PO	3-21G*	−531.8002	147.8	180.5		4.41	77
	6-31G*		147.4	182.0	113.8		236
	DZ+P[i]	−534.1679	148.0	180.0	114.4		237
	EXPT		147.6	180.9	114.4	4.29	193
H_3NO	4-31G	−130.7596	153.1	101[h]	109.5[h]		241
	4-31G+BF	−130.8057	140.0	101.0	111.0		93
	6-31G	−130.8937	152	101[h]	109.5[h]	5.8	241
	6-31G*	130.9339	137.7	100.9	111.6	5.6	13,241
	GVB-SOPP[j]		142				14
F_3NO	4-31G	−426.7288	118.7	141.2	117.2	0.88	242
	4-31+BF	−426.9059	117	136	116.6	1.20	93
	6-31G*		117.2	135.0	116.3		13
	DZ+BF	−427.4232	118	136	116.9	1.23	93
	DZ+BF+CI	−427.7633	116	143	117.4	0.52	93
	GVB-SOPP		120				14
	EXPT		115.8	143.1	117.1	0.04	219,243
Me_3NO	4-31G	−247.6864	146.6	147[h]	109.5[h]	5.2	241
	EXPT		138.8	147.7		5.0	217,244
H_3PCH_2	3-21G*	−379.5494	164.9	141.4u	126.6u	2.4	245,246
				139.1	113.5		
	4-31G*	−380.9968	165.2	142.8u	128.8u		8
				139.8	112.8		
	6-31G*+D	−381.3975	167.2	141.4u	127.5u		247
				138.9			
	DZ+P+D	−381.4025	167.5	141.4u	127.7u	2.86	248,249
				138.9	112.1		
	GVB-SOPP[k]	−381.4351	166.8	140.1	118.6u		170
					117.7		
	6-31G*+MP2	−381.6470	167.4	144.0u	127.2		139
				140.4			

[a] All self-consistent field, contracted Gaussian-type basis sets and geometry optimized by the gradient method, unless noted otherwise; u refers to the unique substituent on phosphorus (see Figure 13); symbols 3-21G, 4-31G, 6-31G, DZ and TZ have their usual meanings:[96] *, a set of six d-type polarization functions added to basis set; #, set of five d-type polarization functions added; P, other combinations of polarization functions added; BF, bond functions as polarization functions; D, diffuse functions added to the basis set of the anionic carbon; CI, with electron correlation by configuration interaction; C, with correlation by other methods; MP2, with correlation by second-order Møller–Plesset perturbation theory; GVB-SOPP, generalized valence bond calculation employing the strong orthogonality and perfect pairing approximations. [b] Total electronic energy in hartrees; 1 hartree = 27.2 eV = 2625 kJ mol⁻¹. [c] Dipole moment. [d] CEPA-PNO method: coupled electron pair approximation with pair natural orbitals. [e] Two uncontracted d sets on P and one on O, one p set on H with added diffuse functions. [f] Double substitution coupled-cluster method–ACCD form. [g] Two d sets on P. [h] Assumed. [i] Single d function on P. [j] At the geometry found for F_3NO by GVB-SOPP method. [k] Using HF geometry determined at the DZ+P+D level.

E. *Ab Initio* Studies of the Bonding in Phosphine Chalcogenides

We have already discussed (section III.B) how calculations on phosphines have become reliable only in the last few years. The factors responsible for this (basis set inadequacy and lack of geometry optimization) apply with increased force to calculations on phosphine chalcogenides and an additional consideration is the increased need for polarization functions, due to the charge differences within the molecule. Also we require more from the calculations because an understanding of the nature PO bond is not a comparative problem (unlike the investigation of the possible geometries of H_3P) and therefore is more difficult.

Table 3 gives the results (total energy, geometry, and dipole moment) of selected calculations on phosphine oxides and amine oxides. The unsubstituted phosphine oxide was unknown until quite recently and the only data we have about it is the infrared spectrum.[250] Therefore we consider in some detail below the adequacy of the calculations on it. Note that once again, as in the calculations on phosphines, only a limited number include correlation corrections in MO treatments, even for H_3PO. Note also that in this case the absence of polarization functions has a much more deleterious effect on the results of the calculations, especially on PO bond length (e.g., cf. results at 3-21G/ 3-21G*/3-21G# and DZ/DZ+P levels for H_3PO). This

Table 4. Comparison[a] of Experimental and Calculated Vibrational Frequencies (cm⁻¹) in the Infrared Spectrum of H₃P=O

mode		expt[b] ν_E	6-31G*[c] ν_C	Δ	Δ_{SC}	6-31G**[d] ν_C	Δ	Δ_{SC}	TZ+P+A[e] ν_C	Δ
PH	a₁	2359	2694	335	46	2647	288	23	2500	141
PH	e	2372	2666	294	7	2618	246	-16	2490	118
PO	a₁	1240	1397	157	16	1389	149	10	1341	101
HPH	a₁	1144	1284	140	11	1282	138	10	1245	101
HPH	e	1114	1246	132	-22	1238	124	0	1213	99
HPO	e	853	958	105	-13	959	106	7	922	69

[a] ν_E: experimental vibration frequency. ν_C: calculated harmonic vibration frequency at the indicated level of theory. $\Delta = \nu_C - \nu_E$ and $\Delta_{SC} = \nu_C - \nu_E$ after scaling of the calculated value (see section IV.E.1). [b] From ref 250. [c] From ref 236. [d] From ref 251. [e] With anharmonicity correction, from ref 238.

latter observation is not surprising because the PO bond is very polar, hence the increased need for polarization functions.

It can be seen from Table 3 that the best split-valence and double-ζ calculations are only just about adequate to describe consistently the geometric parameters of these molecules. Notwithstanding that, we may say with reasonable confidence that if the structure of phosphine oxide is determined in the future, the values will be $r(PO) = 146.0 \pm 0.5$ pm; $r(PH) = 139.4 \pm 0.2$ pm, and $\angle HPO = 116.5 \pm 0.5°$. Similar predictions can be made for other unknown species in Table 3. The bond length of 146 pm for H₃PO may be compared with those in HPO[182] (151.2 pm), diatomic PO[182] (147.6 pm), and a typical single PO bond (160 pm, bridging bond in P₄O₁₀).[183] Also the PO length in H₃PO is about 2 pm shorter than in substituted phosphine oxides (section IV.C.1 and Table 2) which could be either a steric or electronic bond length/bond angle effect (see section IV.D).

1. Infrared Spectrum of Phosphine Oxide

The only experimental study that has been reported on H₃PO is the infrared spectrum of the matrix-isolated species.[250] Two groups have attempted to calibrate the theory with this experimental.[236,238,251]

Table 4 shows the comparison of experimental and the best calculated wavenumbers in the infrared spectrum of H₃P=O.[252] As can be seen from Table 4, after scaling[253] the predicted frequencies are accurate to about 20 cm⁻¹ in most cases. Schneider, Thiel, and Komornicki[236] were noncommittal about the quality of the scaled 6-31G* results, being fairly content with the PO modes but less than satisfied with the PH stretching modes (2359 and 2372 cm⁻¹), whereas Person, Kwiatkowski, and Bartlett[251] considered that the scaled 6-31G** results were spectacularly good. However it can also be seen from Table 4 that there is still a substantial difference in absolute terms between theory and experiment because, even after including a correction for anharmonicity, the calculated wavenumbers at the triple-ζ plus polarization level are still approximately 5-10% higher than the experimental. This reviewer concludes that better than TZ+P and substantial consideration of correlation effects will be necessary for satisfactory agreement between experiment and theory for the infrared spectrum of H₃P=O. However this should not discourage us from using the geometries derived from the present calculations.

The PO force constant derived from the infrared spectrum[250] is 9.53×10^2 N m⁻¹. This may be compared[250] with the force constants for the PO bonds in H₂POH (4.39×10^2 N m⁻¹), HPO (8.67×10^2 N m⁻¹), and diatomic PO (9.24×10^2 N m⁻¹). This confirms that the PO bond is stronger than a single or double bond and is comparable with, or greater than, the bond strength in diatomic PO.

2. Usefulness of the Present Calculations for the Study of Bonding

The results in Tables 3 and 4 do not lead to confidence in the usefulness of the calculations for the elucidation of the nature of the PO bond. They are only just about able to predict geometries with confidence but, more seriously, all theoretical studies so far on the nature of the PO bond have used either the 6-31G*, DZ+P or inferior levels of calculation and most have been on phosphine oxide. From Table 3 it can be seen that the lowest energy achieved so far for phosphine oxide is about 0.4 hartree below that at the 6-31G* or DZ+P levels. This is about twice the energy of the PO bond and was achieved by electron correlation. Thus, again, it is legitimate to feel uneasy as to whether the electron distribution in the PO region is adequately described at these levels.[256] Even with correlation, the computed PO strengths are significantly low; for example Schmidt and Gordon[189] estimated the PO bond strength in F₃-PO to be 467 kJ mol⁻¹ (at the 6-31G* level with correlation by third-order Møller–Plesset theory using the 6-31G* geometry), whereas the experimental value[257] is 542 kJ mol⁻¹, an error of about 14%.

Given these comments, the reader will not be surprised that a single picture has not yet emerged of the nature of the PO bond. That is not to say, however, that there are not definite statements in the literature on this topic. In fact, as intimated in the introduction to this section, the debate on the nature of the PO bond has recently been rather vigorous with two apparently contradictory viewpoints being proposed. These may be termed the σ/π-bond description and the Ω-bond description, neither of which, of course, involves much discussion of the involvement of d orbitals.

Indeed phosphine oxide calculations are a very good example of the trend mentioned in section II whereby the significance of d orbitals appeared to change during the 1970s.[2] In 1970 three sets of calculations reported that d orbitals were significant in the electronic description of phosphine oxide.[75,258,259] By 1979, the situation had changed, even though the calculations were quite similar,[2] and in an influential paper, Wallmeier and Kutzelnigg[76] showed (i) that d functions make up deficiencies in the sp basis, (ii) that they are essential as polarization functions to get an accurate description electronic description of phosphine oxides because the PO bond is so polar so that there is a rapidly varying potential between the nuclei, not adequately described using only atom-centered s and p functions, and (iii) that the d functions used were not true valence orbitals. These conclusions have been confirmed in detail by the later studies. For example, Magnusson[18] included calculations on phosphine oxides in his general study of hypercoordinate molecules (described in section II) and they followed the same general pattern whereby there is no role for valence d orbitals. Reed and

Schleyer[13] addressed the same problem in their recent study of hypervalent molecules (discussed further in section IV.E.3.a). They showed that the depletion of the Z lone pair orbital population in Y_3AZ systems was not matched by a corresponding increase of the central atom d orbital population.

Finally an interesting psychological observation can be made about the influential paper by Wallmeier and Kutzelnigg.[76] Although they demonstrated that there is no valence role for d orbitals in phosphine oxides, nevertheless they used arguments based on them, in the same paper, to explain several aspects of the bonding. This reluctance on their part to abandon the concept, even though they had disproved it, shows how convenient the idea had been up to that time. Reed and Schleyer also displayed this ambivalent attitude.[2,13]

3. The Three Alternative Views of the Bonding in Phosphine Oxide

All of the detailed theoretical studies of the PO bond to date show, in agreement with experimental observation, that the PO bond has high multiple-bond character and is highly polarized.[13,14,74–76,187,189,232,233,235,258–261] From Table 3, the optimized PO bond length for H_3PO (146 pm) is in good agreement with the experimental value for the substituted compounds. This is less than the bond length in the PO molecule (147.6 pm) or the HPO molecule (151.2 pm), both of which must have multiple character, and is distinctly shorter than a PO single bond (160 pm). Also from Table 3, there is a significant calculated dipole moment.

From population analyses[162] phosphorus has a net charge near 1.0 while oxygen has charge of about -1.0,[2] consistent with the picture that about one electron is transferred from phosphorus to oxygen. So the PO bond is strongly polarized, its polarity being significantly larger in, for example, H_3PO than in H_2POH where it is only determined by the difference in electronegativity. Also there is significant PO overlap as measured by overlap populations. There is no problem reconciling these population results because if there was overlap of oxygen lone pairs with suitable receiving orbitals on phosphorus it would be highly unsymmetrical with most of the electron density near oxygen, as discussed in section IV.A. In fact the detailed studies (references given at start of this section) show that the presence of back-bonding does not attenuate the charge-transfer characteristic of a semipolar bond and that back-bonding means that the π AO's of oxygen are strongly polarized toward the H_3P moiety.

Although we know that the PO bond is multiple and highly polar, there is still strong disagreement about the exact electron distribution in it. There are three viewpoints, described below. It turns out that phosphine oxides are part of the overall dichotomy between the σ/π and the bent-bond descriptions of multiple bonds.[97]

a. One σ Bond and Two π Back-Bonds (Negative Hyperconjugation). This, the now more traditional view, has been discussed qualitatively in section IV.B. The bond is viewed[189,233] as a donor–acceptor or Lewis acid–base interaction with back-bonding superimposed. The lone pair of electrons from phosphorus forms a σ-bond to oxygen which completes its octet. The resulting extra charge density on oxygen may go into
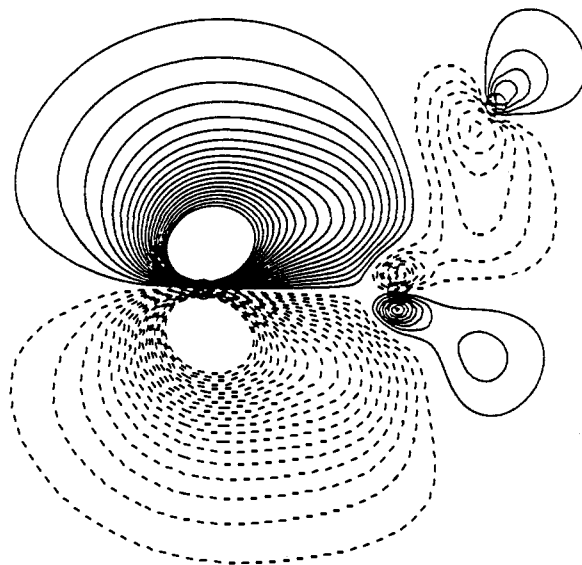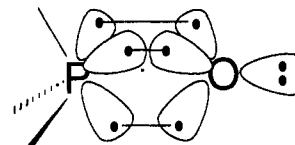

Figure 8. Contour plot of the natural localized molecular orbital for the delocalization of the oxygen lone-pair orbital that is coplanar with one of the fluorine atoms of F_3PO, corresponding to the description in Figure 7, at the 6-31G* level, with oxygen atom at the left. (Adapted from ref 13. Copyright 1990 American Chemical Society.)

suitable acceptor orbitals on phosphorus, forming a double bond (or rather a partial triple bond) by a π-type interaction i.e. back-bonding,[10,13,76] as shown in Figure 7. The suitable orbitals are now known[13,18,76] not to be d orbitals but a set of antibonding orbitals of e symmetry on the R_3P moiety (see section IV.B). This can be viewed as a resonance between singly and triply bound structures.[189] Reed and Schleyer[13] did a broad general study of the bonding in Y_3AZ species in the context of their wider studies of negative hyperconjugation (see section III.B.3). They used calculations at the 6-31G* level and population analyses using the natural population method and found that the back-bonding is indeed into empty σ^* orbitals on the R_3P moiety as shown in contour plot form for F_3PO in Figure 8.

b. One σ Bond and Three π Back-Bonds. An alternative possibility to that in the preceding section[187,232] is that the two opposite charges on adjacent atoms interact in an ionic bond and strengthen the PO link so that it is multiple (essentially structure 1A with some polarization of the charges toward each other). Now, there has never been any doubt, from the earliest to the most recent calculations, that there is a polarization of the charge at oxygen (the lone pairs) toward phosphorus.[10,13,75,76,187,189] It is the interpretation of this polarization which has proved difficult because, as already pointed out, any double bond between phosphorus and oxygen must be highly polar, so that it has been particularly difficult to distinguish between ionic and covalent binding here. Most workers have interpreted the polarization as indicating back-bonding, but others, for example Streitwieser and co-workers[187,232] took the view that it is nothing more than the polarization of the charges in an ionic bond. They asserted, but did not show quantitatively, that this view was consistent with the reduced dipole moment because the charges are not spherically symmetric about the nuclei.[232] Wallmeier and Kutzelnigg[76] argued similarly at one point in their paper.
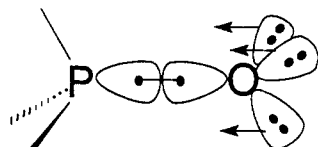
Figure 9. Description of the P=O bond as a σ bond and three π back-bonds (arrowed). (Adapted from ref 14. Copyright 1991 American Chemical Society.)

Figure 10. Contour plots of the energy-localized bonding orbitals of H_3PO, corresponding to the description in Figure 9: (a) one of three PH bonds; (b) the PO σ bond; (c) one of three oxygen lone pairs which is back-bonding toward phosphorus (at the 3-21G# level). (Adapted from ref 233. Copyright 1984 American Chemical Society.)

A more precise version of this description was produced by Schmit, Yabushita, and Gordon[233] for H_3-PO at the 3-21G# level using the energy localization procedure. This is shown in bond orbital form in Figure 9 and in contour plot form in Figure 10 as given in their paper. There are three equivalent PH bonds, one strong


Figure 11. Description of the P=O bond as three Ω (banana) bonds. (Adapted from ref 14. Copyright 1991 American Chemical Society.)

PO σ bond, and three equivalent orbitals on oxygen whose character is principally lone pair. This is similar to a representation using structure 1A except that each of the lone pairs possesses some tendency to back-donate electron density to phosphorus. This viewpoint is in accord with the picture of the PO bond as arising from strong σ donation enhanced by some degree of π back-bonding, except that the back-donating lone pairs are staggered with respect to the PH bonds, which would be inimical to negative hyperconjugation. However, this was not the description given by the Boys procedure for this molecule at the same level (see next section). On the other hand this description also arises in the GVB-SOPP calculations of F_3NO, which are described in section IV.E.4.

c. Three Ω Bonds (Banana Bonds/Bent Multiple Bonds). This might be termed the unorthodox view. There is neither a σ nor a π bond. The PO bond is a formal triple bond with the three curved regions of electron density disposed between P and O in a symmetrical fashion at 120° to each other in Newmann projection along the PO coordinate as shown in bond orbital form in Figure 11 and contour plot form in Figure 12. This description arises in both the MO and VB theoretical analyses of phosphine oxides as described below. In both cases the electron density of the bonds is found to be strongly displaced toward oxygen and the remaining lone pair on the oxygen atom is found to be directed away from phosphorus along the PO axis.

These curved bonds have been termed "bent multiple" bonds[19] or "banana" bonds[97] while more recently the terms "τ bond" and "Ω bond" have been coined by VB workers.[170,262] Since the term Ω bond has been used in connection with phosphine oxides already, and since the Greek letter is reminiscent of their shape, we shall use it in the following discussion. The term τ bond has been used for the specific case where the banana bonds occur in pairs, as in alkenes[97] and phosphorus ylides[170] (see section V.E.2).

i. Boys Localization. In SCF-HF/LCAO-MO calculations, the Boys localization procedure for phosphine oxides give the Ω-bond description, shown as a contour plot in Figure 12, at all levels of theory studied. Guest et al.[261] were the first to describe banana bonds for H_3PO, Me_3PO, F_3PO, Cl_3PO, and F_3PS at the STO-3G* level. Then Wallmeier and Kutzelnigg[76] found the same at the >DZ+P level, after noting that there was no natural choice of a plane of symmetry to impose a σ/π separability. Recently, Molina et al.[235] found the same result at the 6-31G* level. Schmidt, Yabushita, and Gordon[233] also found that the Boys procedure gave an Ω-bond description at the 3-21G# level. But, more interestingly this result was different from the energy localization procedure at the same level which is described in the previous section. Even starting each
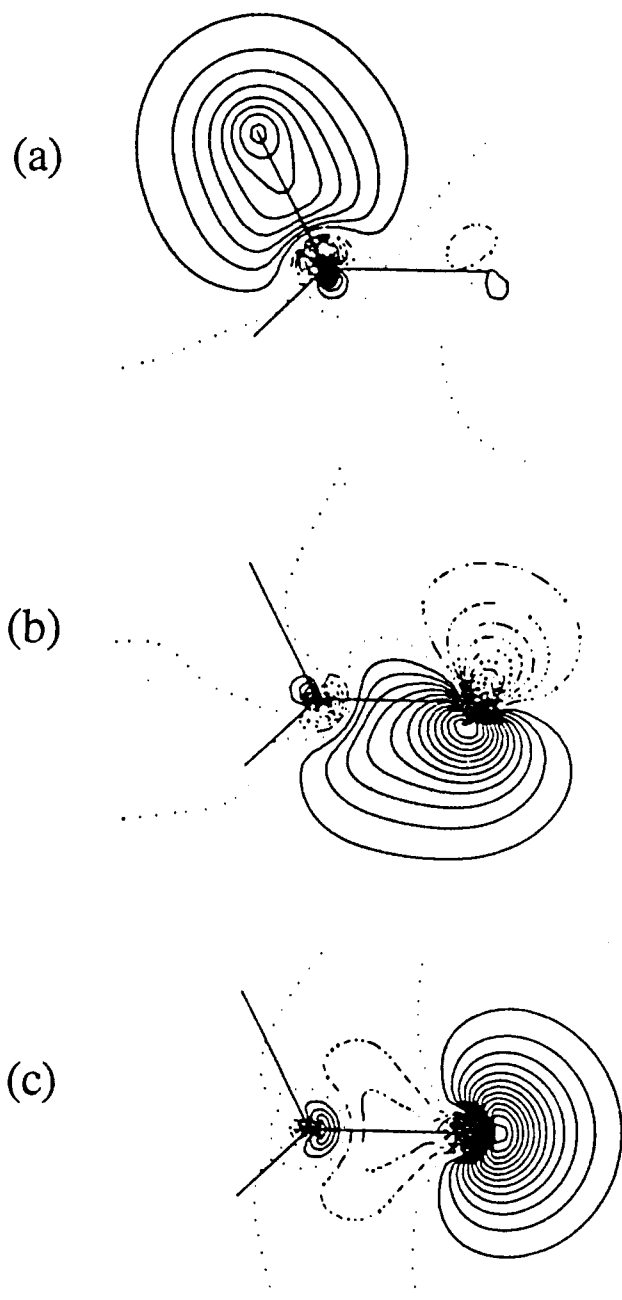
Figure 12. Contour plots of the Boys localized bonding orbitals of H_3PO, corresponding to the description in Figure 11: (a) one of three PH bonds; (b) one of three Ω (banana) bonds (strongly polarized toward oxygen); (c) the single oxygen lone pair (at the 3-21G# level). (Adapted from ref 233. Copyright 1984 American Chemical Society.)

procedure with the localized orbitals from other procedure gave the same end result.[233]

It is noticeable that whenever a localization procedure gives banana bonds, the result is not taken seriously.[97] This is not reasonable, since it has the same energy as a σ/π description, but it is understandable, because it is outside the familiar realm of textbook chemistry. In just the same way, those workers who got this result for phosphine oxide were often reluctant to take it fully on board; some comments were "should not be taken too literally",[76] "overly complicated",[233] and "a very peculiar electronic distribution".[235] Most notable was the reaction of Schmidt, Yabushita, and Gordon[233] who had performed both localization procedures and chose to reject the banana-bond description without any jus-

tification other than to say that they favored the alternative. This was in spite of the fact that on increasing fluorine substitution the energy localized orbitals reverted to the banana-bond description (see section IV.E.5).

ii. Generalized Valence Bond Calculations. Very recently a new approach to the bonding in these compounds has been published[14,263,264] based on the generalised valence bond (GVB) method.

The GVB method was developed from about 1970 by Goddard and co-workers.[265] The GVB wave function is much simpler than a VB wave function and so easier to calculate. However it is still computationally difficult and, as usual, approximations have to be made. There are two such approximations, called the strong orthogonality (SO) and the perfect pairing (PP) restrictions. Usually they are both applied (SOPP). The method is claimed to be a substantial improvement beyond Hartree–Fock theory in that it is the most general independent particle model and provides a unique set of localized orbitals with which to interpret the bonding.[14,265] There are very few valence bond studies of hypervalent molecules.[68,87,170]

Recently Messmer and co-workers[14,262-264,266-270] have started to explore the utility of GVB methods on simple systems, both with and without the SOPP restrictions. In most cases they find that the description of multiple bonds is in terms of Ω bonds. For example, in the description of acetylenes the three Ω bonds may be thought of as the overlap of three sp^3 hybrids on each of the carbons.[263,266] These Ω bonds are very similar to the banana bonds often given by localization procedures in MO theory, except in this case they are the only result which minimizes the energy of the system.[14,263] One interesting aspect of these studies is that the GVB-SOPP results give different results from the full GVB method. For example ethylene is described by the traditional σ/π representation in GVB-SOPP but by a two Ω-bond representation (τ bond) in the full GVB treatment.[263] It turns out that the SO restriction is the one which makes the difference because it militates against the bent-bond description, whereas the PP case is a relatively benign approximation in this context.[263]

Recently, these studies using the GVB-SOPP method have been applied to main group (N, S, and P) oxides.[14,269,270] It is found that in F_3PO the oxygen forms a triple bond to the phosphorus atom using three Ω bonds; very similar to the Boys localization results from MO theory shown in Figures 11 and 12. The phosphorus atom assumes a pseudo-octahedral distribution of orbitals about its core, and the orbitals are strongly polarized toward the surrounding atoms.

iii. Notes on the Bent Bond Description. It should be noted that, although the idea of Ω bonds now appears unorthodox, it is not at all new. In fact, Pauling introduced it in 1931[23] to explain E/Z isomerism in alkenes in the same paper which developed the sp^3 model and it is discussed at length in the third edition[19] of *The Nature of the Chemical Bond*, where he notes that the description was used by nineteenth century chemists to explain why the carbon–carbon double bond is not fully twice the energy of the single bond. However, the σ/π representation predominated later because it could be quantified fairly easily through MO theory.[97] One very attractive feature of the bent-bond model,[14]

emphasized recently by Gillespie,[48,49] is that it enables a very satisfactory rationalization of the detailed geometry of multiply bonded compounds by the VSEPR method.

The triple-bond description for the PO bond is very convincing and appealing but a few reservations do have to be entered. First, an examination of Table 3 shows that the few results available from GVB-SOPP calculations do not compare favorably with those from other calculational methods. For example, for F_3PO, the predicted PO bond length is 147 pm compared with the experimental result of 143.6 pm while the 6-31G* value was 142.5 pm. Secondly, the other ligands on phosphorus have a significant effect on the energy difference between the σ/π and bent-bond representations; fluorine in particular stabilizing the bent-bond description, relative to hydrogen.[263] Also the actual energy differences are quite small; the stabilization of the bent-bond model is about 4 kJ mol^{-1} for C_2H_4, rising to about 15 kJ mol^{-1} for C_2F_4 at the full GVB level.[263] It is in this context that the only other recent study of bent versus σ/π bonds by Gerratt and co-workers[271] is most relevant. They used the spin-coupled (SC) method which should in principle be equivalent to a full GVB calculation. Once again the bent-bond description is found to be the favored one but the energy differences are even less, about 2 kJ mol^{-1} for C_2H_4, rising to about 9 kJ mol^{-1} for C_2F_4.[271] Since these energy differences are smaller than between the SC and complete active space (CAS) SCF wave function, Gerratt and co-workers concluded that both the bent-bond and σ/π constructions provide equally good starting points for the treatment of correlation effects beyond the one-configuration approximation.[271] However Murphy and Messmer[262] have recently addressed just this question at near the CASSCF level. They do indeed find that relaxation of the restriction that the wave function be either the bent-bond or σ/π description gives a function which comes even closer to the CASSCF limit. But the σ/π component contributes a very small amount (<2%) to the wave function.[264]

The last point mentioned above leads on to a further consideration which is that a number of theoretical workers,[124,271] including Messmer,[263] have pointed out that in the limit of full configuration interaction the bent-bond and σ/π descriptions are indistinguishable and therefore not distinguishable experimentally. As Messmer[263] points out; the potential value of making any such distinctions lies in the utility, applicability, and economy of the concepts which emerge. In this context we note that none of these workers have addressed the "evidence" which Pauling[19] adduced for the bent-bond description in *The Nature of the Chemical Bond*. He cited the ready explanation of the bond angles in alkenes and, much more significantly, the potential energy function for the restricted rotation of methyl groups adjacent to double and triple bonds, which should be different in the bent-bond and σ/π cases.[19]

A final point is that both the Boys localization results and the GVB-SOPP results for F_3PO are again inconsistent with negative hyperconjugation. Examination of Figures 11 and 12 shows that the three Ω bonds are staggered with respect to the other phosphorus–ligand bonds, giving an octahedral disposition of electron pairs

around phosphorus. This is the arrangement expected on the basis of the Pauli exclusion principle, but it would minimize the overlap of the orbital interaction required for negative hyperconjugation.

4. Comparison of Phosphine Oxides and Amine Oxides

Table 3 also includes for comparison results from calculations on ammonia oxide and other amine oxides. It is to be hoped that differences between these results and those for phosphine oxides should reflect fundamental differences between second and third row elements and many phosphine oxide studies[13,14,76,189,235] have addressed the issue. Phenomena to be explained include[2] the lower dipole moment of phosphine oxides, the greater strength of PO bonds, the difference between H_3NO and F_3NO, and the fact that the NY lengths in Y_3NO are longer than in Y_3N, unlike the analogous phosphorus compounds (section IV.C.2).

First we note that most of the calculations on F_3NO are hopelessly inaccurate with the single GVB-SOPP result being particularly bad. The worst predictions are for the NF bond length and the dipole moment and only when correlation is included are the results reasonable, although the NO bond length is still overestimated. Indeed, we can be much less confident in predicting the geometry of ammonia oxide than we were above for phosphine oxide.

Population analyses from MO calculations[2,10,76,189] show that ammonia oxide and tertiary amine oxides are singly bound with a semipolar bond and no back-bonding, equivalent to the representation R_3N^+—O^-. The presence of back-bonding in the phosphine oxides and its absence in the amine oxides then explains the lower than expected dipole moment in phosphine oxides. There is back-bonding in the fluoro derivatives however, explaining the difference between H_3NO and F_3NO. As observed in section IV.B, now that back-bonding does not have to be into d orbitals there is no problem about it for nitrogen compounds. The likely acceptor orbitals for back-donation in F_3NO were analyzed by Grein and Lawlor[93] who concluded that the 3e orbital of F_3N was the most suitable. Thus the difference between F_3NO and H_3NO is for the same reason that F_3P is a better ligand than H_3P (see section IV.B). A similar picture was found in the Boys localized molecular orbitals of H_3NO at the 6-31G* level,[235] which were found to be composed of one centroid along the NO bond with the remaining ones around oxygen, in contrast to the result found by the same workers[235] for phosphine oxide outlined in the previous section.

Similar results were obtained from GVB-SOPP calculations[14] on F_3NO and H_3NO, which gave results different from each other and from F_3PO. We have seen in section IV.E.3.c that the result for F_3PO was three Ω bonds. The result for F_3NO was different, it was the one σ-bond and three π-back-bonds model described in section IV.E.3.b above. The result for H_3-NO was different again.[14] This time there is again a σ bond but the lone pairs on oxygen are not polarized toward nitrogen; there is no back-bonding, in agreement with the longer bond lengths in substituted amine oxides. It should be mentioned that the concept of back-bonding used here is somewhat different from the same idea in MO theory. This is because it is not based on atomic orbitals.[14] Thus in order for electrons on

one atom to back-bond to another atom there is no need to invoke vacant atomic orbitals on the acceptor atom. The only requirement, for example for the oxygen lone pairs in F_3NO to back-bond to nitrogen, is that there be sufficient space for them, provided by the polarization of the NF bond orbitals toward fluorine.[14] In the case of H_3NO the NH bond orbitals are not polarized toward the ligands as in F_3NO and so there is not room for back-bonding electron density. Note again that this back-bonding model is inconsistent with negative hyperconjugation.

Messmer[14] contends that the fundamental difference between second and third row atoms is reflected in these different results from the GVB-SOPP calculations on F_3PO and F_3NO, described above. The nitrogen atom in F_3NO prefers to form four primary bonds (the back-bonding is regarded as secondary), whereas the phosphorus atom in F_3PO forms six. This is a direct consequence of the greater core size in the second row.

5. Bonding in Substituted Phosphine Oxides and Sulfides

Parent phosphine oxide is known only in matrix-isolation experiments,[250] and yet the formation of the PO bond drives the synthetically useful Wittig and Arbusov reactions and some of the processes of life itself. The most obvious question to be answered here then is why do carbon, oxygen, and fluorine substituents stabilize phosphine oxide? The obvious answer is that decomposition by tautomerism of a hydrogen atom is prevented by any substitution. However calculations have shown that the answer is more subtle than that, because there is a general effect of substitution to increase the PO bond strength.[10,76,189,236,240,272] The effect increases with the electronegativity of the substituent but there is a limit to the ability of increasing electronegativity to increase bond strength.[189]

It is likely that stabilizations by, for example, fluoro and methyl substituents are caused by different mechanisms.[2,76,236] Thus fluorine increases π back-bonding by electron withdrawal from phosphorus, which becomes more positive, giving more opportunity for electron donation from oxygen lone pairs. On the other hand, methyl groups stabilize the partial positive charge on phosphorus in Me_3PZ so that we must look for another effect. A possibility is that steric hindrance destabilizes Me_3P relative to H_3P to a higher extent than Me_3PZ relative to H_3PZ, because of the change in the angles at phosphorus.[1,2] Thus, since PO bond dissociation in Me_3PO leads to R_3P, this gives a higher bond dissociation energy for the methyl-substituted compound.

Schmidt and Gordon[189] found a very interesting result of substitution on energy-localized orbitals. Methyl- and silylphosphine oxides still have the three lone pair orbitals on oxygen and one PO σ-bonding orbital as described in section IV.E.3.b above for parent phosphine oxide. For hydroxy- and fluorophosphine oxides, the lone pair orbital *trans* to the substituent becomes so involved in back-bonding that it tips inward and the localization procedure leads to the formation of two banana bonds from it and the σ bond. For the trifluoro compound two lone pairs tip in, leading to three banana bonds.

Some of the studies of phosphine oxides have included phosphine sulfides for comparison.[2,13,189,261] It is found that the sulfides are qualitatively similar to the oxides, except that they have a relatively weaker PS bond and are less polar. Boys localization at the STO-3G* level on F_3PS gave the same result as for F_3PO, namely a description in terms of banana bonds.[261]

F. Summary of Bonding and Comments on the Formula of Phosphine Oxides

Previous general discussions[20,21,103-108,184-186] of the bonding in phosphine oxides have been couched in terms of a resonance between two possible limiting structures H_3P=O and H_3P^+—O⁻. This view will have to be given up. It is too simplistic because, as we have seen, the presence of a multiple bond between phosphorus and oxygen is not inconsistent with a high degree of polarity. More importantly this view reduces the significance of the P=O formulation without conveying in return the true complexity of the bonding. A subsidiary point is that if the Ω-bond description (section IV.E.3.c) turns out to be the correct one the formula R_3P^+—O⁻ would be misleading because it implies that there is a σ bond between P and O.

Even the representation of the bond from oxygen to phosphorus in tertiary phosphine oxides is contentious. Practical chemists usually just write a double bond, R_3P=O, but a number of other descriptions and representations have been advocated as the following chronological list illustrates: "somewhere between a single and triple and only by chance it happens to be a double bond";[158] "a partial triple bond";[76] "a resonance between single and triple bond structures, the double bond being rejected on symmetry grounds";[189] "the dipolar structure dominates and the double bond structure contributes but little";[187] "a formal triple bond".[14]

The satisfactory formulation of the PO bond is difficult because we are more accustomed to formulae from the second row of the periodic table. In the second row there is a fortuitous correspondence among bond strength, number of electron pairs, and valence. This is one of the indirect consequences of the small size of these elements. Thus for the common multiple bonds of organic chemistry, C=C, C≡C, and C=O, the 2 (or 3) lines carry three different implications at the same time: (i) that the bond is twice (or thrice) the strength of a single bond between the elements concerned, (ii) that there are two (or three) electron pairs in the region between the elements, and (iii) that it is possible to have an addition reaction wherein one (or two) ligand-(s) are added to each of the atoms involved in the bond.

This all breaks down in the third and higher rows. In the case of PO, we have a double-strength, highly polar bond composed of three (or maybe even four) electron pairs. So the PO bond can be viewed as either a double bond P=O or a triple bond P≡O. If we wish to have one formula to represent the PO bond, we must choose which information is the most important to convey. If we consider that it is more important to convey the information that the PO bond contains three electron pairs then we should use the P≡O formula. But if we consider that it is more important that the strength of the bond be specified then we should use P=O formula. This reviewer proposes that a utilitarian view be taken. Strength and valence are the things that matter in practical chemistry (i.e. how much energy will be

required for the bond to react and how many things can be attached to it in an addition reaction). So the formula $R_3P{=}O$ is the most useful. In addition it also has the merit that it is presently in common use. However, up until now, practical chemists have been made to feel uneasy about its correctness. The new analyses outlined in this review show that their instincts were correct.

Sometime in the future, better calculations will determine the electronic distribution in the PO bond. For now, the best we can say is that the PO bond is a double strength bond with its electron density strongly skewed toward O so that there is a high degree of positive charge on P and negative on O. It is formulated as $P{=}O$ and this representation also imples either (a) that there are three electron pairs between P and O composed of a σ bond between P and O and two π back-bonds between lone pairs on O and acceptor orbitals on P which are antibonding in character with respect to the other ligands on P as shown in Figure 7 or (b) that there are four electron pairs between P and O composed of a σ bond between P and O and three back-bonds from lone pairs on O to the P atom as shown in Figure 9 or (c) that there are three electron pairs between P and O composed of three Ω bonds from P to O as shown in Figure 11.

A most important point is that, at the present time, it seems extremely likely that the calculations are only just at the edge of being able to provide a correct description of the bonding these molecules (see section IV.E.2). Thus slight changes in difficulty or structure of the molecule being studied leads the calculations to give different results. This is definitely the case in the GVB-SOPP versus GVB calculations (section IV.E.3.c) and in the energy localization and Boys localization procedures (section IV.E.3.b and c). Thus it seems that *these three descriptions are not equally valid alternatives*. It is not the case that there is no single correct representation; rather, right now, we do not know which of the three, if any, is correct. Ultimately one of these descriptions may be found to be appropriate in all cases. However the most likely outcome is that one description will be found correct for one class of molecules while another description will be best for a different class. We will need to be very confident of the quality of the calculations before this is finally settled.

Recent work reported by Burford et al.[273] on the coordinative bonding modes of phosphine chalcogenides may be relevant here. They have classified these bonding modes into σ and π types depending on the PZM bond angle. It is found that phosphine oxide complexes exhibit bond angles at phosphorus of 140–180° with few exceptions, corresponding to a σ-donor complex. In contrast the angles at the chalcogen in complexes of phosphine sulfides and selenides are more restricted and are substantially smaller (91–117°) consistent with π-donor complexes. This suggests an important electronic control of molecular geometry, and Burford et al.[273] conclude that the potential for σ complexation of the oxides is a consequence of effective π bonding between the phosphorus and oxygen centers. As we have seen (section IV.A) this π bonding is less effective in the thio and seleno analogues, so that the electrons in π-type orbitals on sulfur and selenium may be considered more available for donation. Now a linear

geometry for phosphine oxide complexes would be predicted by cases a and c above but not by case b which would be more consistent with a bent geometry.

It can be seen that the investigation of the bonding in phosphine oxides (and sulfides and selenides) calls for an examination of some of the most basic concepts in valency and bonding theory in the context of one of the most important bonds in practical chemistry and the processes of life.

Finally, is the octet rule broken by phosphine oxides? The following quotations are from two recent papers and illustrate the controversial nature of the subject:

These studies emphasize the importance of partial ionic bonding in second row hypervalent species... Due to the ionic character of the bonding, the electronic octet rule is far from being violated. This emphasizes the robustness of the Lewis octet concept.

*A. E. Reed and P. v. R. Schleyer[13]*

Contrary to much previous discussion based on molecular orbital theory, generalized valence bond calculations exhibit *six bonds* to P and S atoms in the presence of electronegative ligands. One must conclude that this is strong evidence that such molecules violate the Lewis–Langmuir Octet rule.

R. Messmer[14]

As these quotations above imply, the answer is yes and no. This reviewer would argue that it may not be broken technically because the electron density is skewed toward O so that P is not receiving a full half share of each electron pair. Reed and Schleyer,[13] for example, are careful to say that the *electronic* octet rule is not broken and Cioslowski and Mixon[50] provide a rigorous interpretation of this in terms of atomic charges, localized orbitals and covalent bond orders. However, there is a strong case that it is broken in spirit because phosphorus is participating in more than four electron pair bonds.

V. Phosphonium Ylides

For reasons similar to the oxides (section IV.A), studies of the bonding in phosphonium ylides have concentrated on the nature of the $P{=}C$ bond and, again as in the oxides, all previous discussions,[21,103,104,106–108,274–279] except the most recent,[280] of the PC bond have been in terms of a resonance hybrid between a dipolar form **2A** and a double bond form **2B**:

$$R_3\overset{+}{P}{-}\overset{-}{C}R_2 \quad \longleftrightarrow \quad R_3P{=}CR_2$$

$$\textbf{2A} \qquad\qquad\qquad \textbf{2B}$$
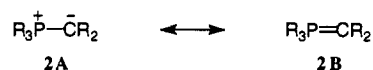
For the purposes of chemical reactivity, the dipolar form **2A** is considered the more important.[274,281] Previously structure **2B** was meant to indicate $d\pi$–$p\pi$ bonding involving back-donation of electron density from a doubly occupied 2p orbital of the ylidic (anionic) carbon into vacant phosphorus 3d orbitals in an overlap scheme such as that for the oxides shown in Figure 6. This $d\pi$–$p\pi$ bonding had been invoked to explain a number of the properties of phosphonium ylides,[3] particularly the fact that they are more stable than their nitrogen analogues for which such a stabilizing interaction is not possible, nitrogen not having the requisite low-

energy vacant orbitals.[274,281,282] Contrariwise, many authors had also taken these properties as evidence for dπ–pπ bonding so that the structure and bonding of phosphonium ylides was part of the general controversy about dπ–pπ bonding (see section II). For these reasons, many studies in the past 20 years have addressed the two fundamental problems associated with phosphonium ylides, namely the extent (if any) of the contribution of structure **2B** and the related question of the geometry (i.e. configuration) at phosphorus and the anionic carbon.

As outlined in section II, we now know that d orbitals are not involved in the bonding and that the appropriate acceptor orbitals are the LUMO pair on the phosphine moiety. Also as pointed out in section IV.A, structures **2A** and **2B** are not mutually exclusive because any back-bonding that occurs will still lead to a highly unsymmetrical charge distribution. As we shall see recent ideas concerning the bonding in ylides are similar to those described in section IV.E.3 for the oxides.

A. Structure

Structural data for some ylides are included in Table 2. Unfortunately bond length data are unsatisfactory for the length of the P=C ylidic bond and it can be seen from Table 2 that it varies from 163 to 173 pm for unstabilized ylides. Our best guess must be the value of about 169 pm reported recently by Schmidbaur and co-workers[223] for Ph_3P=CH_2 although the same workers also reported a value of 163 pm for the trisferrocenyl derivative.[223] Now a value of 164 pm was found for r(P=C) in Me_3P=CH_2 by electron diffraction,[222] although this study had a rather high R value (leads to smaller r(P=Z)—see section IV.C), C_3 symmetry was imposed in the analysis and anyway we expect a smaller value for the methyl analogue (see section IV.C.1). Indeed a similar 4–5 pm difference in r(P=C) between trimethyl and triphenyl derivatives was seen for carbodiphosphoranes (see Table 2), so this is probably a *bona fide* effect. The only isopropylidene ylide reported has a P=C length of 173 pm but this is may be anomalous because of the hindered nature of the substituents (see section IV.C.3) which cannot easily be varied because of proton-transfer isomerization problems.[3] Despite these difficulties, we may still say that r(P=C) is considerably shortened with respect to r(P—C) (180–183 pm—see Table 2) and is in the range expected for a double bond between phosphorus and carbon. Thus, for example, the P=C bond length in phosphaalkenes[1,283] can vary between 161 and 171 pm with an average of 167 pm while P≡C in phosphaalkynes[1] is <154 pm. Pauling[19] predicts 166.5 pm for a P=C double bond which includes the Schomaker–Stevenson correction.[264] The P–C_{phenyl} bond length of 181–182 pm is definitely longer than in phosphine oxides (179–180 pm), about the same as in the few phosphine sulfides/selenides and shorter than in phosphines (183–184 pm) (see Table 2).

From Table 2, it can be seen that there is the expected tetrahedral arrangement about phosphorus. Again just as in the phosphine chalcogenides (section IV.C.1), the bond angles to the ylide carbon are normally wider than those to the other carbons which can again be rationalized as a bond length/bond angle relationship or in orbital terms (section IV.D.2). Consistent with this,
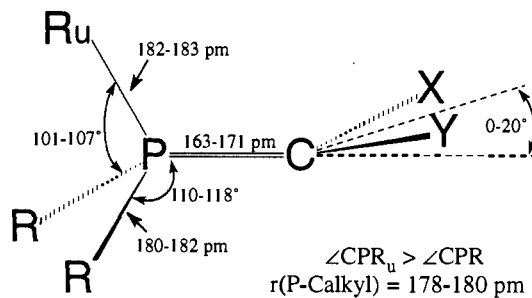
Figure 13. Structure of a typical phosphonium ylide. (Reprinted from ref 3. Copyright 1993 Wiley.)

the bond angles at phosphorus in a stabilized ylide are nearer to regular tetrahedral than in unstabilized ylides.[3] Note that in trisisopropylphosphonium isopropylide this normal disposition of angles around phosphorus is inverted just as in highly hindered phosphine chalcogenides (section IV.C.3). It has been commonplace in the past[21,103,104,106–108,274–276] to state that the ylide carbanionic carbon is planar and that, since this is counter to VSEPR expectations for an isolated carbanion in an sp^3 orbital on carbon, this is evidence for back-bonding from carbon to phosphorus. In fact there are small but definite deviations from planarity for many ylides.[3,281] This is quite strikingly so for the most careful study[223] on Ph_3P=CH_2 where the angle sum at carbon is only 349° (*vide infra*).

Two structural observations on sp ylides are noteworthy and have been discussed.[3] There is a reduction of about 5–6 pm in r(P=C) in the sp ylide relative to the sp^2 ylide, and the angle at carbon may be significantly less than 180°. Note that hexamethylcarbodiphosphorane has r(P=C) significantly less than the hexaphenyl derivative consistent with the same observation for the sp^2 analogues.

B. Conformation

Liu and Schlosser[285] have recently shown convincingly by ^{13}C NMR that in solution there is free rotation about the P=C bond in unstabilized triphenylphosphonium ylides. This was because they failed to find any evidence for nonequivalence of the *ipso*-carbon signals down to temperatures as low as –105 °C.

However there does appear to be a preferred conformation in the solid state which is shown in Figure 13. Thus it is frequently observed in X-ray studies that the carbanion substituents tend to take up an orientation at right angles to the plane of one of the P-substituent bonds, referred to[3] as the *unique* substituent and labeled u in Table 2 and Figure 13, and the conformation is usually referred to as *perpendicular*. The conformation resulting from a 90° rotation of the carbanion substituents is called *parallel* or *eclipsed*. The perpendicular conformation has also been found by electron diffraction.[286] Also, where a deviation from carbanion planarity is found, it is commonly toward this unique substituent and, in those cases where a difference can be discerned, the bond angle to the unique substituent is increased somewhat compared to that to the other substituents and the PC_u bond length is increased. These generalizations are still somewhat tentative because the data set is not large but there does appear to be a definite effect, so that we may

give the overall solid-state structure of a typical phosphonium ylide as that shown in Figure 13.

In those cases where there is a deviation from carbanion planarity the resulting structure is called the *trans*-bent conformation. This is a known phenomenon for other double bonds and cumulenes containing second or higher row atoms and has been treated theoretically.[287,288] A simple rule has been devised to predict when this distortion will occur in any given system based on the singlet–triplet separation of the constituent carbenoid fragments.[288] However in this case it might be argued that it is a simple steric effect which operates once negative hyperconjugation is invoked. In those cases where there is significant pyramidalization of the carbanion, there is also rapid carbanion inversion at room temperature which can be detected by NMR[289] and by the relatively large displacement parameters for the substituents in X-ray crystal studies e.g. the hydrogen atoms of $Ph_3P=CH_2$.[223]

The *trans*-bent conformation is not the preferred conformation in those ylides where the carbanion bears a substituent with a lone pair of electrons.[3,223]

C. Stability

It is often loosely stated that phosphorus ylides are more stable than nitrogen ylides. However in comparing stabilities we must be particularly careful to define the sort of stability referred to. Thus it has been well established[274,281,282,290] that ylides become less reactive (due to decreased basicity) as more powerfully electron-withdrawing groups are substituted on the ylide carbanion. Thus $Ph_3P=CH_2$ is very reactive while $Ph_3P=CHC(O)OMe$ and cyclopentadienylidenetriphenylphosphorane are quite stable. However in this context stable means both capable of isolation and handling in the atmosphere and slow rates of Wittig reaction. If precautions are taken to exclude air, water, and light, the reactive ylides are just as long-lived as the stable ones.

Similarly the presence of such electron-withdrawing groups on a potential ylide carbon facilitates the formation of that ylide from its conjugate acid (the phosphonium salt) and this in turn correlates with the strength of base required in the Wittig reaction.[281,291] Likewise, a comparison[292] of the acidity of fluorene (pK_a = 22.6), fluorenylammonium salts (pK_a = 17.8), and fluorenylphosphonium salts (pK_a = 6.6) shows that the effect of an ammonium group does not alter the stability of the fluorenyl anion very much, whereas the presence of a phosphonium group stabilizes it considerably. Since a purely electrostatic stabilization has been estimated[293] to be 30% stronger for nitrogen, some additional stabilization in the case of phosphorus is suggested. Extension to other main group onium centers gives Se $\approx$ S > P > As > Sb as the stability order.[294,295] However this order does not parallel the reactivity of these ylides with, for example, aldehydes or nitrosobenzene, since the phosphonium ylide is less reactive than the others[295] and anyway, rather than showing a special stabilization in third row ylides, these results may suggest a special destabilizing effect for nitrogen ylides.

It is worth recording that in no meaning of the term stability have phosphorus and nitrogen ylides been directly compared experimentally. This is because their reactivities are rarely comparable since there are few reactions which both nitrogen and phosphorus ylides undergo to give analogous products. The main difficulty is that nitrogen ylides readily undergo Stevens rearrangement.[296,297] Now in fact, contrary to what was believed until fairly recently, phosphorus ylides do undergo a Stevens rearrangement process,[298,299] and indeed this requires temperatures in the range 100–200 °C while the Stevens rearrangement occurs at room temperature. However this qualitative observation may merely reflect the relative strengths of PC and NC single bonds.

D. Calculations

Table 3 includes the results of some calculations on methylenephosphorane. As previously noted for the phosphine oxides (section IV.E) we seek, as a minimum, two related objectives from calculations such as these: an understanding of the bonding in these unusual systems and prediction of the structure and properties of unknown species. Difficulties similar to those noted for the oxides attend these objectives using the calculations reported to date on ylides. Thus little data are available on any of the molecules studied so that we cannot calibrate these calculations against experiment and few of the calculations reach the standards required (see section IV.E.2) for confident prediction of the exact electron density in these systems. Most reported calculations are for methylenephosphorane which has been detected by neutralization–reionization mass spectrometry[300] as predicted by calculation[301] but no data are yet available for it. Thus we may only tentatively say that if the structure of H_3PCH_2 is ever determined it will be similar to the results obtained at the DZ+P+D[248,249] or 6-31G*+MP2[139] levels shown in Table 3.

In the best calculations the geometry at phosphorus is found to be tetrahedral and that at carbon approximately planar but almost always with slight pyramidalization toward the *trans*-bent conformation of Figure 13. Almost free rotation is found about the ylide bond[8,235,247] with barriers in the range 4–5 kJ mol^{-1}. The derived valence MO energies give a low HOMO energy, consistent with the first ionization potentials determined for substituted ylides which are in the range 6–7 eV.[3] Population analyses show that there is a build up of electron density on carbon, with a corresponding decrease of electron density at phosphorus.[3] There are relatively few reported calculations on substituted ylides[3] but one useful study was reported by Bestmann and co-workers[247] who showed that σ-donor, π-acceptor substituents stabilize the P=C bond, for example Li, BeH, and BH$_2$, whereas π-donor substituents destabilize it, for example OH and NH$_2$. Similar observations were made by Dixon and Smart[248] who also found the spectacular destabilizing effect of two fluorine substituents so that H_3PCF_2 is really just weakly interacting H_3P and CF_2.[248]

The last point above leads to a useful viewpoint, developed in detail in studies by Trinquier and Malrieu,[302] Bestmann and co-workers,[247] and Dixon[280] which considers the construction of the ylide bond by interaction of a phosphine and a carbene. This is allowed if a non-least motion pathway is adopted[280,302] and the triplet carbene would give rise to a pyramidal carbanion while the singlet gives the planar. This is related to the
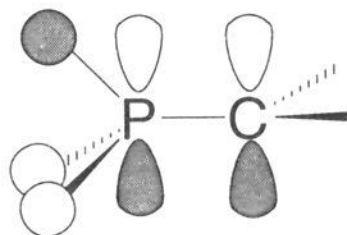
Figure 14. Description of the P=C bond as a σ bond and a π bond formed by back-bonding into an orbital of e symmetry on the phosphine moiety. (Reprinted from ref 8. Copyright 1981 National Research Council of Canada.)

general discussion of the *trans*-bent conformation of multiple bonds[287,288] (section V.B); the likely occurrence of which may be predicted by a consideration of the singlet/triplet separation in the carbene components of the bond concerned.[288] The binding energy of $H_3P=CH_2$ with respect to H_3P and CH_2 is found to be about 225 kJ mol^{-1} at the 6-31G*/MP2[139] and DZ+P+D[248] levels rising somewhat to 256 kJ mol^{-1} at higher levels,[139] while the use of isodesmic equations at the 6-31G*/MP2 level[247] gives a value of 286 kJ mol^{-1}. The H_3PCH_3 isomer was found to be 236 kJ mol^{-1} more stable at the 6-31G*/MP2 level[139] falling slightly at higher levels.[139]

E. The Two Alternative Views of the Bonding in Phosphorus Ylides

The bond length data, although not satisfactory, do suggest that the P=C bond has multiple character with a bond order of about two. Other physical measurements including bond energies, dipole moments, infrared, ultraviolet/visible, nuclear magnetic resonance, and photoelectron spectroscopy support this and show that the ylide bond is highly polar.[3] In agreement with experimental observation, all of the detailed theoretical studies of the P=C bond show that it has multiple character and is highly polarized.[8,139,170,187,235,245–249,302–307] However, again just as in the phosphine oxides (section IV.E.3), there is disagreement about the exact electron distribution in the P=C bond with one view corresponding to the σ/π description of multiple bonds and the other a bent (banana) bond description. These are discussed further below. There is a further alternative which cannot yet be ruled out, namely that structure 2A is the best description with the strengthening of the P=C link being due to an ionic interaction. This would be the equivalent of the triple-back-bond description of phosphine oxides (section IV.E.3.b). In support of this Whangbo et al.,[308] in an MO study, found that the CX bond length in the CH_3X (X = O, S) radicals, cations, and anions could not be correlated with overlap populations but instead correlated linearly with ionic bond order, and Glidewell[309] has rationalized the planarity of the ylide carbon purely on the basis of nonbonded interactions.

1. Back-Bonding/Negative Hyperconjugation

The lone pair of electrons from phosphorus forms a σ bond to carbon which completes its octet. The extra charge density on carbon is in a p orbital which forms a back-bond by overlap with the σ* LUMO of the phosphine moiety as shown in Figure 14. Thus the back-bonding in phosphorus ylides can be considered exactly analogous to that in phosphine oxides and in transition metal phosphine complexes which has been
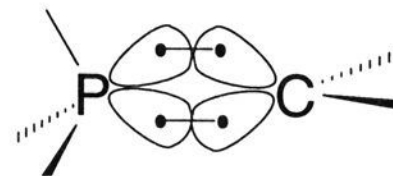
Figure 15. Description of the P=C bond as two Ω bonds. (Reprinted from ref 170. Copyright 1983 American Chemical Society.)

termed negative hyperconjugation (section IV.E.3.a). Actually phosphorus ylides were one of the first systems whose bonding was explicitly described in this way in a paper by Bernardi and co-workers[304] and the description is now fairly commonplace.[3,4,8,187,247]

Very strong support for this model of the bonding in ylides is provided by their overall structure, shown in Figure 13. The model envisages back-bonding as being from a p orbital on the anionic carbon into an antibonding orbital on the R_3P moiety as shown in Figure 14. The putative p orbital on carbon would be eclipsed by the unique substituent (R_u) and so would be best placed to back-bond into a π-type antibonding orbital lobe on phosphorus collinear with PR_u, thus lengthening PR_u to a greater degree than the other PR bonds. Further support comes from a recent remarkable study reported by Grützmacher and Pritzkow[9] on $^tBu_2ClP=CPh_2$. The bond to a halogen has σ* lower in energy than to carbon so we may expect halogen to be the unique ligand. Grützmacher and Pritzkow reported that this was indeed the case, but better still, there were three independent molecules in the unit cell, all with slightly different dispositions of the CPh_2 group and as this group becomes more nearly perpendicular to the PCl bond that bond is lengthened the most.[9]

Mitchell et al.[8] have analyzed this bonding model in detail. In a very full and clear discussion they show, for example, that there can be back-bonding to antibonding orbitals in both the perpendicular and parallel conformations, hence explaining the low barrier to rotation in phosphorus ylides.[8] Also secondary interactions with the other lobes of the σ* orbital favor the perpendicular conformation, there being one extra antibonding interaction in the eclipsed form.[8] Similarly, minimization of unfavorable secondary interactions in the perpendicular conformation would also lead to a lengthening of the PC_u bond and a wider $C_{ylide}PC_u$ angle, thus explaining the overall *trans*-bent conformation shown in Figure 13.[8]

2. Two Ω Bonds (τ Bonds/Banana Bonds)

This is again analogous to the oxides (section IV.E.3.c). However in this case all *ab initio* calculations so far of the electron density result in two banana bonds, depicted in Figure 15. This was found using the Boys localization procedure in MO calculations by both Molina et al.[235] and Lischka.[307] Similar was the single GVB calculation on ylides by Dixon et al.[170] who used the term τ bond for these regions of electron density. Furthermore in both the MO and VB calculations the two banana bonds are not quite equivalent. The Boys localized MO's have both bond pairs near carbon but one is slightly closer to phosphorus than the other,[235] and the GVB bond pair which is in the plane of the unique PH is more diffuse.[170] The GVB calculation also compared the phosphorus ylide with H_3NCH_2 which was found to have an anionic carbon with no

backbonding.[170] Finally we noted in section IV.E.3.c that often when a localization procedure leads to banana bonds the result is not quite taken seriously. A similar comment can be made about the reaction to his results by Lischka.[307]

F. Summary of the Bonding in Ylides

Phosphorus ylides have been succinctly described[223] as an easily pyramidalized carbanion stabilized by an adjacent tetrahedral phosphonium center. They usually adopt the trans-bent conformation of Figure 13 but the barrier to rotation about P=C is very low (4–5 kJ mol^{-1}). The P=C bond is highly polar and multiple. It is significantly stronger and shorter than a PC single bond, so it may be referred to as a double bond, although the actual order may be less and anyway such terms may have a different meaning in third row compounds than in second row compounds (see section IV.F). The actual electron-density distribution in the P=C bond is still a matter of debate with two possible descriptions in both of which it is strongly skewed toward carbon: **either** (a) there are two electron pairs, composed of a σ bond between P and C and a π back-bond between a filled p orbital on C and one of two possible acceptor orbitals on P which are antibonding in character with respect to the other ligands on P as shown in Figure 14 **or** (b) there are two electron pairs, composed of two Ω bonds (banana bonds) from P to C as shown in Figure 15.

Finally, again as in the phosphine oxides (section IV), we note that there is an analogy between the bonding in ylides and the three-center, four-electron bonding in phosphoranes[3] (section II). This has been formally stated by Musher[44] thus: "an ylide is a hypervalent molecule in which a three-center bond is reduced to a two-center bond using a single orbital from the hypervalent atom and formally transferring one electron from the main group atom to the ylide carbon".

VI. Summary and Outlook

Three levels of progress may be identified in the understanding of the issues involved in the bonding of these compounds. There are those issues which are settled, those which are in an advanced state of understanding but which remain to be confirmed and those issues which are still wide open.

In the first category we find mostly discarded concepts: the involvement of d orbitals in main group bonding; the directed valence approach to the explanation of bond angles in phosphines and amines; and the description of the PO bond in oxides and the PC bond in ylides as resonance hybrids of the double bonded and charge separated forms shown in structures **1A/1B** and **2A/2B**. On the positive side though, we do at least know the quality required for calculations and structure determinations to be useful in the study of bonding in these molecules. Thus we know that calculations which use better than double-ζ basis sets with plenty of polarization functions, full geometry optimization, and some sort of electron correlation will give results which are just on the edge of being reliable for the electron distributions in these systems. We note that such calculations are presently on the point of becoming routine so that, although the calculation of electron density for these systems is still somewhat precarious, useful results are just around the corner.

For structure determinations we now know that many previous results are unreliable because of the realization that previously acceptable R values yield bond length data more than 3 pm in error. Thus it must be borne in mind that structural comparisons using older data will be precarious unless all $R \leq 0.05$ and even this may be too high considering the observations in made in section IV.C. One other helpful result is that the double-bonded formula for phosphine oxides ($R_3P=O$) has been shown to be perfectly reasonable, despite the uncertainties in our knowledge of its electron distribution.

In the second category, we have to place the Walsh diagram analysis of bonding in these compounds. We have seen throughout this review that Walsh's rule is a very powerful hypothesis for the explanation of bonding. Highlights of its success in our realm are (i) the simple and elegant explanation of the peculiar sequence of bond angles in phosphine, ammonia, and their trifluoro derivatives, (ii) the explanation and prediction of a series of bond length and angle correlations across a very large number of $Y_3P=Z$ derivatives, and (iii) the preferred conformation of phosphonium ylides (trans-bent) which perfectly matches expectation based on the model. However, it still remains a hypothesis to be fully tested. Thus, although some calculations support it (the HOMO energies in phosphines), others deny it completely (the disposition of back-bonding electron pairs found to be inimical to negative hyperconjugation). There are alternative explanations (mostly steric—vide infra) of some of the observations and in addition its use to explain the variation in the heights of inversion barriers is complicated (but not frustrated) by the discovery of the new inversion mechanism via a T-shaped transition state.

Lastly, we come to those issues which are far from resolution. There are two, and they are paradigms for some of the major issues in bonding theory today. We have seen that the Walsh diagram of orbital energies can be used to explain well the geometries of some molecules. However the argument can be turned on its head, and we could equally say that the sequence of orbital energies is the result of the molecular geometry. Precisely the same quandry exists within the two alternative explanations of the observed structure correlations in Y_3PZ molecules. At its simplest we seek to know if the bond angle in ammonia is dictated by the availability of s orbitals or if the usage of s orbitals is dictated by the bond angle which in turn is set by steric requirements. These two viewpoints might be caricatured as being typically inorganic (orbital) and typically organic (steric) respectively. Despite his background, this reviewer leans toward the dominance of the orbital viewpoint because of its proven greater power of prediction and because of its great success across a wide range of different areas of chemistry as described comprehensively in the book by Albright et al.[4] However these matters remain to be demonstrated unequivocally by calculation. We note that both viewpoints can be said to ascribe the effects as being due to the anomalously small size of second row atoms, a point which has been made many times now.[10-12]

The other great unresolved issue derives from the uncertainty about nature of multiple bonding in general.

Its manifestation here is that there are three possible electron distributions in the PO bond of phosphine oxides, two of which involve the location of electron density along the PO internuclear axis while the other does not. It seems to this reviewer that this is a dramatic dichotomy. Especially so because it is likely that only one of these descriptions will be eventually be found to be the correct one at least for any particular substitution pattern on phosphorus. A final twist is that these two big unresolved issues are linked because only one of the three possible electron distributions in the PO bond is compatible with the Walsh diagram analysis of phosphine oxides.

To end we have to try to see all of these issues in a wider context. Throughout the review the approach has been taken that chemical bonding can be understood qualitatively from an atoms-in-molecules perspective and in particular that bonds are to be understood as overlaps of atomic orbitals of the constituent atoms. However many theoretical chemists[124] consider that is important to find the electron distribution in the molecule of interest which is fully satisfied by a solution of the Schrodinger equation as a series of orbitals and associated energies but they are not as interested, considering it unphysical, in trying to partition this electron distribution into separate pieces which could be associated with the atoms and bonds which make up the molecule.[310] However all practical (especially synthetic) chemists wish just such a partition because it is their everyday experience that an atom brings with it to a molecule something constant and quantifiable.[311] We are still not able to fully reconcile these views although Bader[312] has gone a long way toward trying to rigorously and sensibly partition the electron density. Ironically the single issue which we are happy to have settled after a lot of work, the noninvolvement of d orbitals, would be quite irrelevant if atomic s and p orbitals have no special significance for bonding themselves. Also the whole question of bent versus σ/π bonds would be irrelevant if they really are equivalent at a higher level.

Thus it can be seen that, notwithstanding the great progress in our understanding of bonding concepts in the main group, much work still remains to be done. We can look forward eagerly to the prospect of the resolution of these great issues in the near future.

Note Added in Proof. Some of the issues discussed in this review are treated in a very recent paper by Cooper et al.[313] In a full GVB study they confirm that the d orbital concept is redundant, they propose that less emphasis be placed on the octet rule and they assert a new *democracy principle* which anthropomorphically allows every valence electron the right to take part in chemical bonding if it wants!

VII. Acknowledgments

VIII. References and Notes

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(230) Allen *et al.*,[181] in their compilation of organic bond lengths, defined acceptable precision on the basis of either (a) crystallographic *R* factor ≤0.07 with reported mean estimated standard deviation (esd) for C–C bond lengths ≤0.010 Å or (b) crystallographic *R* factor ≤0.05 with unreported esd. Orpen and co-workers[5] in their survey of phosphine metal complexes used similar criteria but allowed *d*(C–C) esd ≤ 0.030 Å.
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(252) Note that there is inevitable uncertainty as to the frequency of the PO stretch in H₃PO due to strong mode mixing[251] from the H₃P bending mode (both a₁ modes). Ironically, Schmidt, Yabushita, and Gordon[233] used their calculated value of 1287 cm⁻¹ which they assigned to the PO stretch to argue that the PO bond fell far short of a double bond in comparison to the calculated value of 1498 cm⁻¹ for the PO bond in the HPO molecule. With a revised assignment of this value to the H₃P bend, the PO stretch now occurs at 1437 cm⁻¹ and their argument would then lead to the opposite conclusion.
(253) Usually computed wavenumbers are considerably higher (10–15%) than experimental values and this can be seen clearly in Table 4 at all levels of theory studied. Traditionally this difficulty has been addressed by using a scaling procedure; one compares theoretical and experimental values for related species for which data is available (e.g. PH₃ and F₃P=O in this case) and computes scale factors with which one adjusts the theoretical wavenumbers for the unknown species. Scaling procedures attempt to remove systematic errors which may be due, for example, to basis set incompleteness, neglect of electron correlation or neglect of anharmonicity considerations.[251,254,255] Table 4 includes scaled values for two of the theory levels.
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