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73

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Penta- and Hexacoordinate Phosphorus Derivatives

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Contents

Stereochemistry of Penta- and Hexacoordinate Phosphorus Derivatives

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Table of Contents

1. Introduction

Phosphorus is a stereochemically versatile element. It may be found coordinated to between one and six ligands in various compounds, but the vast majority of known phosphorus derivatives have coordination numbers of [3] and [4]. In contrast to nitrogen, the chemistry of phosphorus is characterised by higher coordination numbers [4–6], and is, therefore, in this respect more analogous to that of the heavier Group V elements, arsenic and antimony. The tricoordinate derivatives of phosphorus constitute a large class of compounds with nitrogen counterparts. However, the bond configuration around tricoordinate nitrogen may vary between trigonal pyramidal (*e.g.* NH_3, NMe_3) and planar [*e.g.* $N(SiH_3)_3$]1). On the other hand, the analogous phosphorus derivatives are exclusively trigonal pyramidal, with valence angles normally in the range 90–100°. In spectroscopic studies of members of the series, $M(SiH_3)_3$, M = P, As, Sb, the inference was drawn that the molecular skeleton is planar, as in the nitrogen analogue2, 3). However, subsequent electron diffraction studies have shown these molecules to have the expected pyramidal structure4, 5). The stereochemical insensitivity of tricoordinate phosphorus to the chemical nature of its substituents may be ascribed to the fact that, in contrast to nitrogen, it shows no tendency to form multiple bonds in which its p_π orbitals are involved.

A coordination number of [4] is most characteristic of the phosphorus atom. It is displayed in naturally occurring phosphates and nucleotides, and in the numerous coordination complexes of phosphine ligands, characterised over the last 20 years. According to classical valence theory the pentavalent phosphorus in the former class of tetracoordinate derivatives must be formally double bonded to one ligand (usually oxygen) in non-ionised structures. The distribution of the substituents at phosphorus is basically tetrahedral but, owing to the presence of bonds of differing nature and multiplicity within an individual structure, the valence angles can vary within wide limits (100–120°). The importance of π-bonding involving the phosphorus $3d$-orbitals in PO_4^{3-} ions has been discussed by Cruickshank6).

The existence of two possible geometrical configurations of very similar energies, namely the trigonal bipyramid and the square (or rectangular) pyramid, bestows the stereochemistry of pentacoordinate phosphorus with a particular fascination. The stereochemical and electronic structural aspects of pentacoordination in both main group elements and in transition metals have been the subject of a number of reviews7–9). Both of the possible geometries are characterised by non-equivalent bonding; in the former there are three equatorial and two axial, and in the latter one apicel and four basal substituents. Theoretical considerations based on molecular orbital and electrostatic calculations have consistently predicted that the trigonal bipyramidal configuration should be energetically slightly more favourable (ca. 5–10 kcal/mol) for acyclic pentacoordinate phosphorus derivatives, and these findings have been borne out by electron and X-ray diffraction studies. However, in view of the relatively small energy difference between the two modifications, it is possible that a particular arrangement of ligands of differing electronegativities or the inclusion of phosphorus in a strained small 4–5 membered ring can lead to a relative stabilisation of the square (or rectangular) pyramid. Rectangular pyramidal structures have indeed been confirmed by X-ray diffraction for a number of spirobicyclic der-

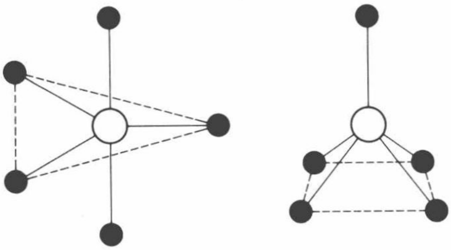


Fig. 1.1. Trigonal bipyramidal and square pyramidal geometries

ivatives of pentacoordinate phosphorus. The significance of the $3d$-orbitals in the bonding of pentacoordinate phosphorus is still contested. The general features of molecular geometry can be explained in a qualitative manner without consideration of these orbitals, and their absolute role will only be better understood as more structural parameters become available.

The dynamic stereochemistry of pentacoordinate phosphorus has received very considerable recent interest in view of the role of transitory pentacoordinate species in mechanisms advanced to account for the hydrolysis of phosphate esters10) or nucleophilic displacements in phosphonium systems11). Rapid intramolecular ligand exchange takes place readily in many phosphoranes. The ^{19}F NMR-spectrum of PF_5 contains, for instance, only one fluorine resonance12), indicating that the non-equivalent axial and equatorial sites are scrambled by molecular inversions during the relatively long time scale of the NMR-measurements. Mechanisms involving the rearrangement of the substituent ligands in the trigonal bipyramid by internal rotation (the so called turnstile rotatiom mechanism13)), or by a pseudorotation pathway through an intermediate of C_{4v} symmetry as suggested by Berry14), have been advanced to account for such phenomena.

Phosphorus may make use of its $3d$-orbitals, to some extent, to increase its coordination number from five to six, as for instance in the adducts of PF_5 with nitrogen bases (*e.g.* $PF_5 \cdot$ pyridine) or in anions of the type PF_6^-. The neutral complexes display a distorted octahedral geometry with a very long coordinate bond. Regular octahedral geometry with equivalent bond distances is observed in the PF_6^- anion, for which the hybridisation may be described as sp^3d^2.

The most interesting recent developments in the structural chemistry of phosphorus have involved penta- and hexacoordinate derivatives. Little structural information was available until recently owing, in the main, to the instability and volatility of many of these compounds. In the last decade improved methods of analysis by electron and X-ray diffraction and the availability of increasing numbers of phosphoranes, which owe their stability to the inclusion of phosphorus in one or two small rings, have led to a substantial growth in the fund of determined structures. At the end of 1976 more than 50 diffraction studies of pentacoordinate phosphorus derivatives had been published, 14 of these being for acyclic molecules. This information has in its turn led to a better theoretical understanding of the nature of pentacoordination at phosphorus. The present state of knowledge of the static stereochemistry of penta- and hexacoordinate phosphorus derivatives as determined by diffraction methods will be discussed in this review. Although a detailed consideration of the dynamic stereochemistry of pentacoordinate phosphorus is outside the scope of this article, it is nevertheless self-evident that many of the factors governing the stability of trigonal bipyramidal species, which may be inferred from studies of static geometries, are of immediate relevance to the development of ligand exchange mechanisms and to proposed reaction mechanisms involving transitory pentacoordinate intermediates. Furthermore, distortions in the regular trigonal bipyramidal geometry at phosphorus have been interpreted as providing evidence for the onset of just such a ligand exchange. The stereochemistry of tri- and tetracoordinate phosphorus derivatives have been extensively reviewed elsewhere[15-17].

2. Stereochemistry of Pentacoordinate Phosphorus Derivatives

2.1. Static and Dynamic Configurations

Before we proceed to a detailed discussion of the significance of individual structural studies, it is apposite to summarise those features which characterise the stereochemistry of the simplest class of compounds containing pentacoordinate phosphorus, namely the acyclic derivatives. In the later sections we shall see how the inclusion of phosphorus in one or more strained small ring system (4–5 atoms) may lead to a modification of these structural principles. Structural data on compounds containing acyclic pentacoordinate phosphorus are however relatively limited, owing to the high volatility and reactivity of these species. Therefore, of particular relevance to the development of bonding theory has been the determination of accurate structural parameters by electron diffraction for the series of methyl substituted fluorophosphoranes $PF_{5-n}Me_n$, $n = 0$–3[18-20]. Previously the structure of PF_5 had been the subject of some controversy as a result of early electron diffraction studies carried out in 1937–38, which had suggested that the PF_5 molecules are trigonal bipyramids in which the axial and equatorial P-F bonds are equal in length[21,22]. A similar analysis on the related molecule PCl_5, carried out two years later demonstrated, however, that the P-Cl axial bonds are significantly longer than the equatorial bonds (0.15 ± 0.06 Å) in this likewise trigonal bipyramidal molecule[23]. The situation was finally clarified in 1965 when Hansen and Bartell[18] were able to demonstrate, using modern electron diffraction techniques, that the P-F bond distances in PF_5 actually are significantly different. They obtained values of 1.577(5) for the axial and 1.534(4) Å for the equatorial bonds (see Fig. 2.1.1.). Any theory of bonding should be capable of explaining, at least in a qualitative manner, the stereochemical features observed in the fluorophosphorane series (Fig. 2.1.1.), which are representative for all acyclic derivatives:

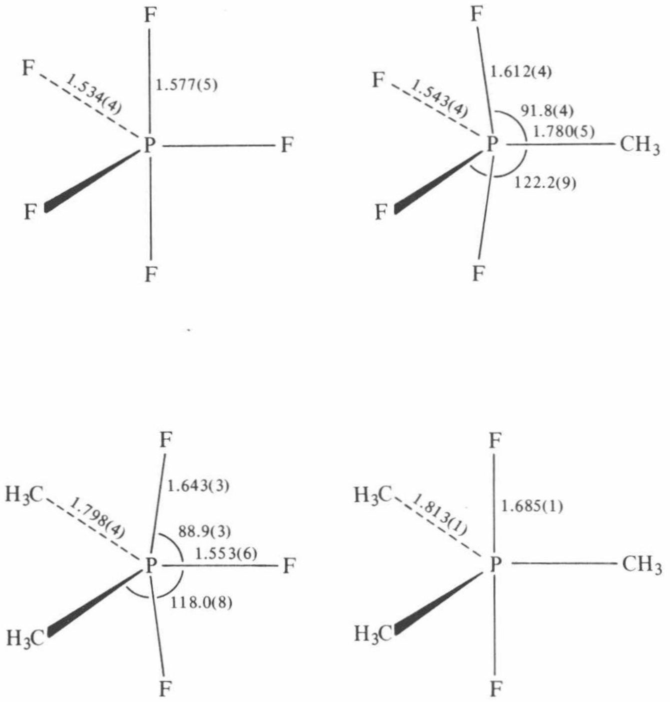


Fig. 2.1.1. Results of electron diffraction studies on the series $PF_{5-n}Me_n$, $n = 0-3$

1. The molecules are trigonal bipyramids or distorted trigonal bipyramids rather than the alternative square pyramid.
2. The more electronegative substituents (fluorine) preferentially occupy the axial sites in the trigonal bipyramid.
3. Axial bonds are longer than the corresponding equatorial bonds.
4. All the corresponding bond lengths and the ratio of the length of the axial bonds to that of the equatorial bonds, r_{ax}/r_{eq}, increase, the former linearly, as the number of methyl substituents increases.
5. Methyl substitution causes the P-F bonds to be bent away from the methyl groups [*e.g.* C_{eq}-P-F_{ax} = 91.8(4) in $MePF_4$].

The preferential occupation of axial sites by more electronegative substituents had also been anticipated by Muetterties *et al.*$^{24,25)}$ on the basis of IR and NMR studies. The observation of axial bonds which are significantly longer than the corresponding equatorial bonds suggests that the former are weaker than the latter. This has been confirmed for phosphorus and other analogous non-transition metal derivatives by investigation of vibrational stretching frequencies. These have been shown to be 100–200 cm^{-1} higher for equatorial bonds$^{26)}$. The stretching force constants are correspondingly lower for axial as compared to equatorial bonds$^{27,28)}$.

The NMR-equivalence of all fluorine atoms in PF_5 at temperatures above −100° implies very rapid interchange of axial and equatorial ligands. This phenomenon, which has since been observed for numerous acyclic and cyclic phosphoranes prompted Berry in 1960 in propose the pseudorotation exchange mechanism, which has since been named after him[14)]. He suggested that a pairwise exchange of the two axial ligands with two equatorial ligands may take place through synchronous vibrational motions, as illustrated in Fig. 2.1.2. mechanism 6. The third equatorial ligand (3), which may be regarded as functioning as a pivot, is not involved in the exchange retains its original position. As may be seen from mechanism 6, molecular C_{2v}- symmetry isretained throughout the exchange pathway, which also passes through a C_{4v} square pyramidal intermediate state.

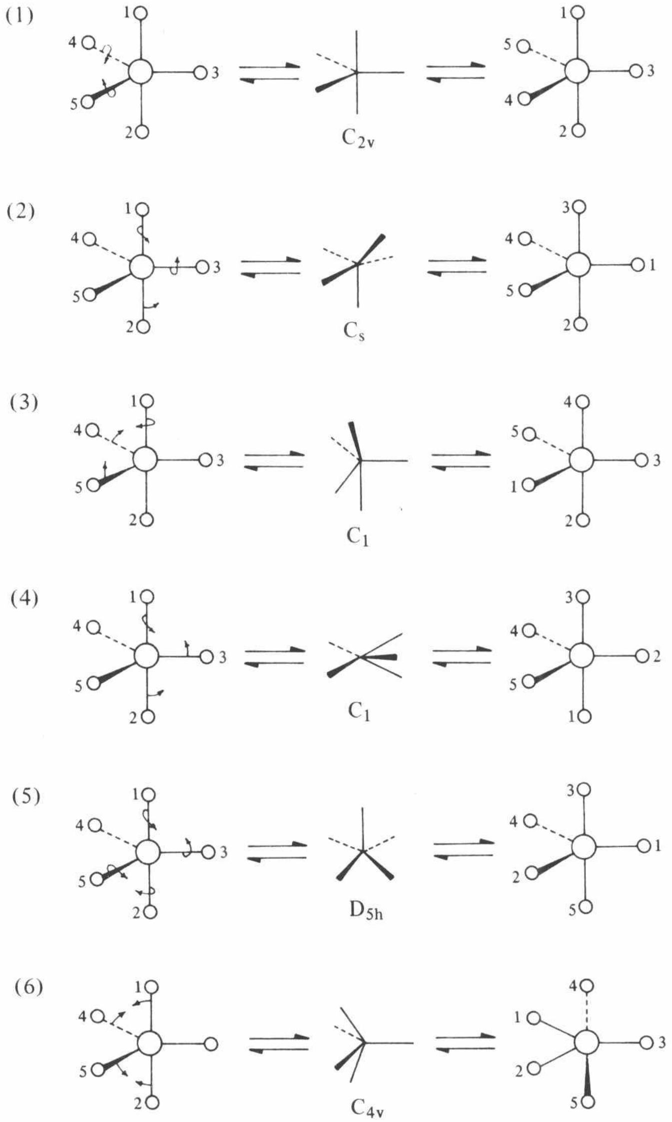


Fig. 2.1.2. Possible mechanisms for the isomerisation of trigonal bipyramidal molecules as proposed by Mutterties[29, 30)]

Muetterties attempted to symbolise the conceivable mechanisms and symmetries of intermediate states for the regular pentatopal isomerisation of trigonal bipyramidal molecules [Fig. 2.1.2. mechanisms (1)–(6)]29, 30). A further physically reasonable model, which was not discussed by Muetterties, is the turnstile rotation mechanism developed by Ugi, Ramirez *et al.* 31–33), which is depicted in Fig. 2.1.3. This mechanism corresponds to an internal rotation of one axial and one equatorial ligand with a pair angle α_2 about an approximate local C_2 axis, combined with a simultaneous opposite rotation of the three remaining ligands (trio angle α_3) about an approximate local C_3 axis. It has been envisaged as involving the pathway illustrated in Fig. 2.1.3. As a prerequisite to internal rotation, the diequatorial angle (4)-P-(5) contracts from

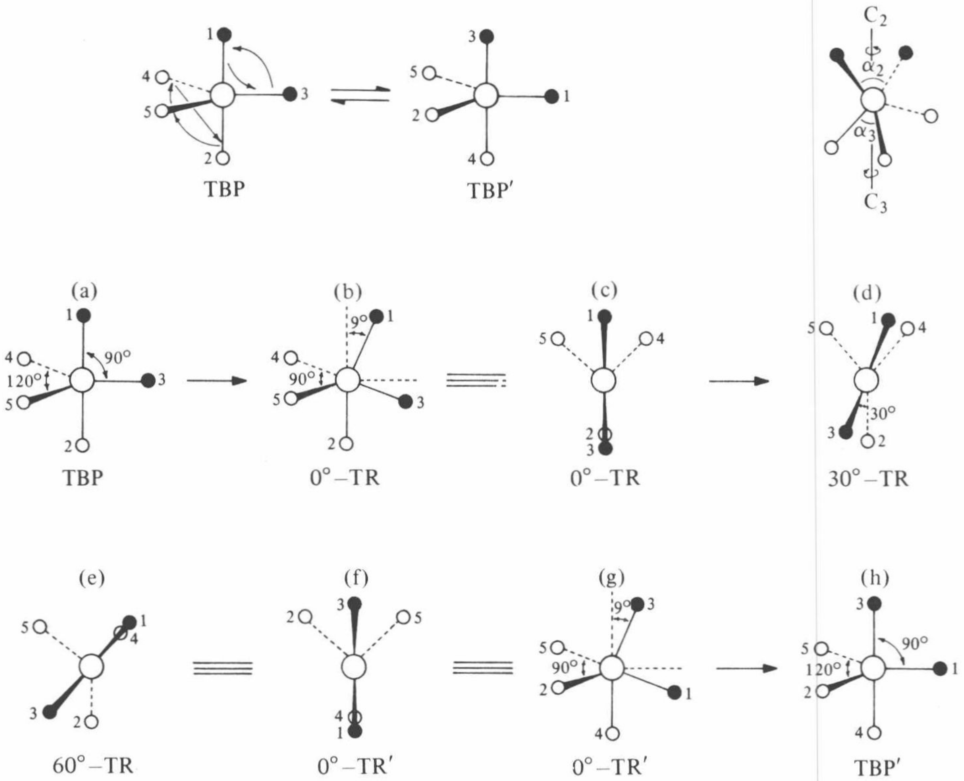
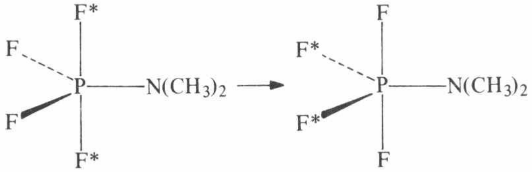


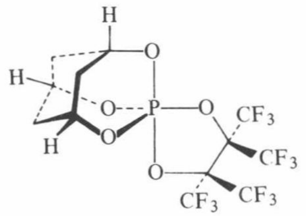
Fig. 2.1.3. The turnstile rotation mechanism for pentatopal isomerisation

120° to 90° and the ligand pair (1)(3) tilts 9° in the plane P(1)(3)(2) towards the axial ligand (2) to yield (b), which is termed the 0°-TR configuration (TR = turnstile rotation). The ligand pair (1)(3) rotates against the trio (2)(4)(5) leading to the 30°-TR configuration (d), which is the halfway intermediate between the two isomeric trigonal bipyramidal geometries. Further rotation leads to the 60°-TR configuration (e), which through tilting of the pair (3)(1) and expansion of the angle (5)-P-(2) generates the new trigonal bipyramidal geometry TBP′. It should be noted that ligand (5) retains an equatorial position in the new trigonal bipyramid. Assuming a staggered 30°-TR configuration, optimisation of the angles α_2 and α_3 for PF_5 has been carried out by CNDO/2[31, 32], extended Hückel[34] and *ab initio*[35] MO-calculations. The lowest barrier for a turnstile rotation was found by all these methods for values of $\alpha_2 \approx 85°$ and $\alpha_3 \approx 95°$.

The mechanistic alternatives 1–5 considered by Muetterties have since been demonstrated to be in disagreement with experimental evidence and have therefore been discarded. This may be illustrated by reference to an elegant study by Whitesides and Mitchell[36] of the temperature dependence of the ^{19}F-NMR spectrum of the substituted fluorophosphorane $(CH_3)_2NPF_4$. At temperatures below –100°



there is no exchange of equatorial and axial fluorines. Above –50° all four fluorines are NMR-equivalent, but there is an intermediate temperature range in which the equatorial fluorine pair replaces the axial pair *via* a single concerted step. F* and F do not, however, exchange with one another. Only the Berry pseudorotation and turnstile rotation mechanisms are capable of explaining this phenomenon. MO-Calculations (to be discussed in Section 2.2.) indicate that the Berry pseudorotation mechanism is energetically more favourable than the turnstile rotation mechanism for the regular pentatopal isomerisation of acyclic phosphoranes. Extended Hückel[34] and *ab initio*[35] MO-calculations on PF_5 have produced energy barriers of 1.4 and 4.8 kcal/mol for the pseudorotation and 10.0 and 18.1 kcal/mol for the turnstile rotation mechanism. The high values for the latter energy barrier would seem to rule out turnstile rotation as a possible mechanism for the interconversion of PF_5. On the basis of CNDO/2 calculations, however, which yield respective barriers of 3.5 and 9.1 kcal/mol for the two mechanisms in discussion, Ugi, Ramirez *et al.*[31, 32] concluded that neither of the mechanisms is quantum mechanically impossible. They also pointed out that, as there are four possible turnstile rotation pathways which lead to the same isomerisation as one Berry pseudorotation, the involvement of the former mechanism in interconversion processes becomes relatively more likely from a statistical point of view. Furthermore, in some cyclic oxyphosphoranes. for which pentatopal isomerisation has been confirmed by NMR spectroscopy there may be very high energy barriers to Berry pseudorotation. Variable temperature NMR studies[37] on a polycyclic oxyphosphorane derived from a phosphatrioxaadamantane serve to illustrate such a state of affairs. From the ^{19}F- and ^{1}H-NMR data, it would appear that there is a permutational isomerisation in this molecule. Solvent dependent ^{31}P-NMR data indicate that this isomerisation is regular *i.e.* it occurs without bond breaking and re-formation. Examination of molecular models reveals that any pentatopal isomerisation by Berry pseudorotation must traverse a prohibitively high energy barrier, but that the experimental data may be nicely explained by the turnstile rotation mechanism. This may be readily appreciated



by observing that the five-membered ring oxygens may provide the pair and the adamantoid oxygens the trio for such a process. Therefore, in conclusion, it seems probable that isomerisation of acyclic phosphoranes involves a pseudorotation process, but that for some cyclic derivatives simple or multiple turnstile rotations must be invoked to explain experimental observations.

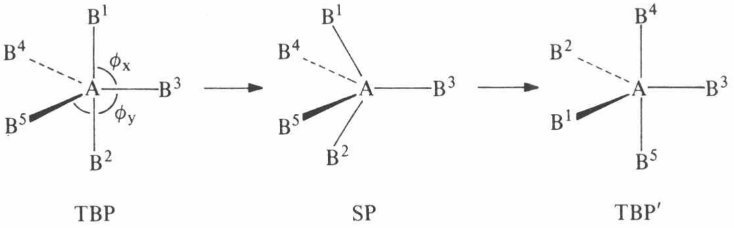
As mentioned previously, it is outside the scope of this review to pursue this topic in detail. Its relevance to an appreciation of the static stereochemistry of pentacoordinate phosphorus derivatives lies in the fact that, as will be seen in later sections, deviations from idealised trigonal bipyramidal (and square pyramidal) geometries in cyclic derivatives have often been interpreted as being in accordance with a partial pseudorotation or turnstile rotation of the molecule in question. For instance, Ramirez has interpreted X-ray analyses of caged adamantoid polycyclic oxyphosphoranes as supporting the latter mechanism for the permutational isomerisation of such species37). He has incorporated the turnstile rotation mechanism in its turn into his "oxyphosphorane concept", which proposes that metastable oxyphosphoranes are intermediates in the nucleophilic displacement reactions of tetracoordinate phosphorus compounds37). This concept has been invoked in the design of new types of phosphorylating agents suitable for the synthesis of oligodesoxyribonucleotides.

2.2. Theories of Bonding

Many theories of bonding of pentacoordinate phosphorus have been advanced over the last 20 years, which purport to explain, at least in a qualitative manner, those features of molecular geometry, which have been characterised by recent structural investigations using spectroscopic and diffraction techniques. One of the most fascinating aspects of this area of bonding theory is how models which start from totally opposite conceptual standpoints give rise to closely parallel predictions for the external aspects of molecular structure. For instance, as will be discussed subsequently, a simple Hückel model38), which altogether neglects explicit electron repulsions, explains the experimentally observed trends in molecular geometry of the trigonal-bipyramidal series $PF_{5-n}Me_n$, $n = 0–3$, which are also unambiguously predicted by the valence shell electron pair repulsion model (VSEPR), which has been developed by Gillespie39).

The shape of AB_5 complexes with fixed A-B distances of equal length has been investigated in terms of electrostatic repulsion forces40). It was found that the trigonal bipyramid is energetically slightly more favourable than an optimised square pyramid with a B_{ap}-A-B_{ba} (ap = apicel, ba = basal) angle of 104.1 and B_{ba}-A-B_{ba}

angles of 86.6 and 151.9°. Variation of the angles ϕ_x and ϕ_y, whilst preserving local C_{2v}-symmetry along the axis A-B^3, showed that the two equivalent trigonal bipyramids TBP and TBP′ ($\phi_x = 90$, $\phi_y = 120$ and $\phi_x = 120$, $\phi_y = 90°$) lie at opposite ends of a trough in the potential energy diagram of AB_5, which has an intermediate square pyramidal form SP ($\phi_x = \phi_y = 104.1°$) at a flat minimum. This is, of course, exactly the proposed pathway for molecular inversion between trigonal bipyramids by the Berry pseudorotation mechanism[14)].



Analogous results were obtained by Foppl[41)], who investigated the optimum arrangement of 2–9 particles on the surface of a sphere (equivalent to introducing fixed bond lengths in an AB_n system, $n = 2$–9) for an inverse square force law. Zeman[40)] also found that the introduction of non-Coulombic repulsion terms into his calculations served to further increase the relative energetic stabilisation of the trigonal bipyramid.

According to the VSEPR model of Gillespie[39, 42–47)], which has augmented and developed the original simple electrostatic model of Sidgwick and Powell[48)], pairs of electrons in a valence shell, irrespective of whether they are bonding or nonbonding, are always arranged so as to minimise the repulsions between themselves. Gillespie demonstrated that the mutual interactions of the valence shell electrons arising from the Pauli exclusion principle are, in general, more important than those due to electrostatic repulsions. The magnitude of this Pauli exchange force increases rapidly with increasing overlap of the orbitals of two electrons with the same spin and may be represented as being proportional to $1/r^n$, where n is large. The optimum arrangement of particles on the surface of a sphere under such a force law has been investigated by Shutte and Van der Waerden[49)]. They obtained the same results as had been given by Foppl for an inverse square law[41)] in all cases ($n = 2$–9) except that of seven particles. Thus for AB_5 systems a trigonal bipyramidal rather than a square pyramidal shape was found to be most favourable under any inverse force law.

The VSEPR model provides an unambiguous explanation of all the trends observed in the trigonal bipyramidal methyl-substituted fluorophosphoranes (see Fig. 2.1.1.). Because an axial bonding electron pair has three nearest neighbouring pairs at 90°, while the equatorial pairs have only two such neighbours, minimisation of the repulsions can only be attained if the axial pairs are at a greater distance from the nucleus than the equatorial pairs. Therefore, axial bonds in a trigonal bipyramid must be longer than the corresponding equatorial bonds. Now electron pairs bonding electronegative ligands must be drawn further away from the central nucleus than those bonding less electronegative ligands, and as a consequence will take up less space on the surface of the central atom. Thus electronegative ligands with small electron pairs will tend to occupy the axial positions in order to minimise interactions with other electron pairs, while the larger electron pairs will occupy the equatorial positions where there is more space available for them. Substitution of an equatorial fluorine by a methyl group leads to a decrease in the effective electronegativity of the phosphorus and allows all the bonding pairs to move away from the phosphorus slightly, thereby increasing all the bond lengths. At the same time, there will be increased axial-equatorial repulsions, because of the size of the electron pair bond to carbon, and this will lead to the $P-F_{ax}$ bonds being both further lengthened and bent away from the methyl groups. Thus the VSEPR model is capable of accounting for all the observed structural features of the methyl-substituted fluorophosphoranes without having to make any arbitrary assumptions about the atomic orbitals which take part in the bonding (*e.g.* the role of the phosphorus 3*d*-orbitals). The success of such an inherently simple model hints at an underlying simplicity in nature. It cannot, however, tell us anything about the geometrical preferences of π-electron donors and acceptors, independent of their electronegativities, which we shall see are predicted for pentacoordinate phosphorus derivatives by a recent MO-description.

The earliest descriptions of the hybrid orbitals for PF_5 always assumed significant involvement of the phosphorus 3*d*-orbitals, which are of low energy and about the same size as the 3*s* and 3*p*. Cotton[50)] constructed an orthonormal set of trigonal bipyramidal hybrid orbitals from an sp^3d set of orthonormal atomic orbitals in order to investigate the relative strengths of the axial and equatorial bonds in PF_5 and PCl_5, using the overlap integral criterion of Mulliken[51)]. Calculations, using overlap integrals computed from the Slater orbitals, over the entire range of distribution of *s*- and *d*-character between the axial and equatorial bonds, showed the latter to be stronger over wide ranges and particularly at values corresponding to greatest total overlap. Another model based on overlap considerations, due to Craig *et al.*[52)], which also assumed that a least one 3*d*-orbital was of low enough energy to participate in the bonding, showed that the maximum overlap of a substituent orbital with an equatorial orbital of the central atom occurs at a smaller internuclear distance than for an axial orbital.

In total contrast to these approaches was that of electron-rich three-centre bonding proposed by Rundle[53–56)], which suggests that a good first order representation of the structures of PX_5 species may be constructed without an appreciable contribution from the phosphorus 3*d*-orbitals. The equatorial P–X bonds may be regarded as normal in this model, while the delocalised three-centre orbitals are constructed for the axial P–X bonding from the phosphorus $3p_z$ and the axial ligand *s*- and *p*-functions. The interaction diagram for the construction of such molecular orbitals for the unknown model compound PH_5 is shown in Fig. 2.2.1. The non-bonding a_1' orbital of this three-centre set is localised on the axial hydrogens. Upon mixing with the equatorial P–H σ and σ^* levels, this a_1' orbital transfers a small but significant part of its electron density onto the equatorial atoms. The P–H axial bonds will naturally be longer than the P–H equatorial bonds in this interpretation, as the linear H–P–H bonds contain one bonding and one non-bonding pair, whereas the latter are electron pair bonds. The character of the non-bonding orbital favours increasing the electron density on the axial atoms, thereby explaining why electro-

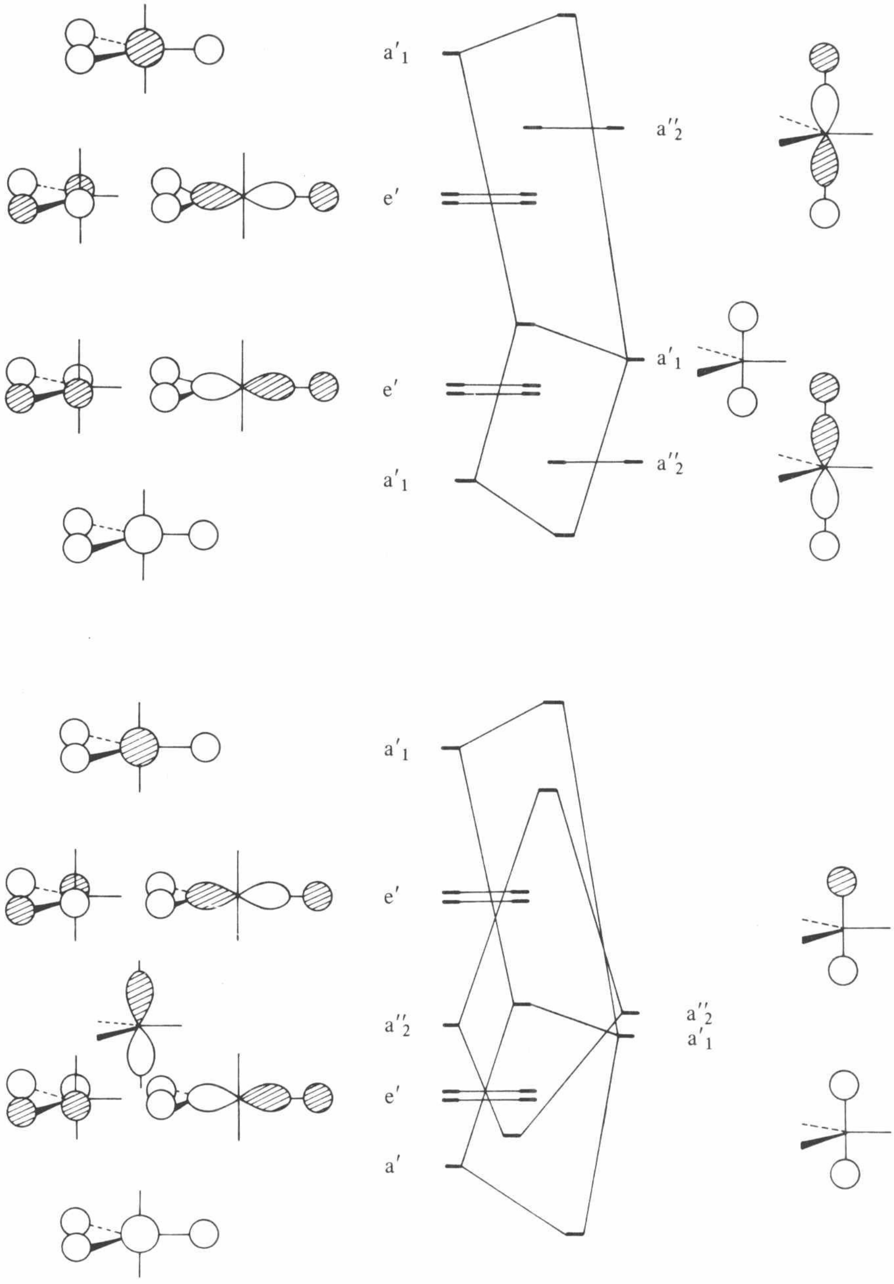


Fig. 2.2.1. Interaction diagrams for the construction of the molecular orbitals of trigonal bipyramidal PH_5.
(a) Semilocalised orbitals as calculated using Rundle's electron-rich three-centre bonding model.
(b) Fully delocalised orbitals as calculated using a semiempirical extended Hückel model (after Hoffmann *et al.*[34])