

# Pentacoordinated AB<sub>5</sub>-Type Main Group Molecules Favorably Adopt sp<sup>2</sup> Hybridization in the Central Atom: Bonding without d-Orbital Participation

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**Abstract:** The pentacoordinated AB<sub>5</sub>-type main group molecules have long been thought to have sp<sup>3</sup>d hybridization of the central atom, accounting for their oxidation state and molecular geometry; however, this does not explain the difference in axial and equatorial bond distances within these molecules. In addition, d-orbital participation in bonding for nonmetals is energetically unfavorable because it requires a  $np \rightarrow nd$  excitation energy. In this paper, we have proposed that the sp<sup>2</sup> hybrid orbitals are formed on the central atom, overlapping with ligand orbitals in the equatorial positions. The longer axial bonds are formed via the overlap of the unhybridized p orbital on the central atom and the two terminal ligand orbitals, resulting in a three-center, four-electron bond. Examining the partial charge on the central atom using relevant electronegativity values supports this model without a d component in bonding. The model explains well the structure and bonding in pentavalent molecules. We believe that the results will be useful in updating chemistry texts.

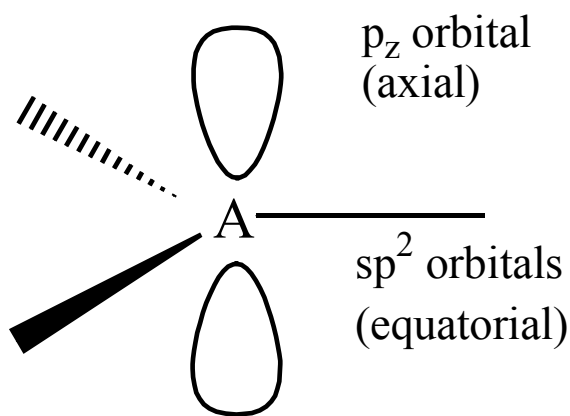
## Introduction

The Valence Shell Electron Pair Repulsion (VSEPR) model has long been used successfully to predict the geometry of various main group molecules [1–3]. According to this model, the pentacoordinated AB<sub>5</sub>-type molecules possessing five electron pairs (electron domains [1, 4]) are predicted to have trigonal bipyramidal structure, consistent with experimental observations. In order for the central atom to be coordinated by five ligands, the predominant understanding is that a d orbital is required to participate in bonding. As a result, one electron in the s or p subshell is promoted to a higher-level d orbital forming five sp<sup>3</sup>d hybrid orbitals in the central atom. However, the sp<sup>3</sup>d hybridization does not provide the best explanation to the fact that in most of the AB<sub>5</sub>-type and AB<sub>5-n</sub>E<sub>n</sub>-type (E represents a nonbonding pair) compounds, the A–B<sub>ax</sub> axial bond distance is constantly significantly greater than the distance of the A–B<sub>eq</sub> equatorial bond. For example, in phosphorus pentahalides PX<sub>5</sub> (X = F, Cl), P–F<sub>ax</sub> = 1.58 Å and P–F<sub>eq</sub> = 1.52 Å; P–Cl<sub>ax</sub> = 2.14 Å and P–Cl<sub>eq</sub> = 2.02 Å [5a]. In SF<sub>4</sub>, which contains a nonbonding pair, S–F<sub>ax</sub> = 1.65 Å and S–F<sub>eq</sub> = 1.55 Å [6]. An intrinsic problem for sp<sup>3</sup>d hybridization is that it would involve the energetically unfavorable  $s^2p^n d^0 \rightarrow s^2p^{n-1}d^1$  [ $n = 3(\text{P}), 4(\text{S}), \text{ or } 5(\text{Cl})$ ] excitation, which requires a promotion energy. In addition, d orbitals in nonmetals are heavily shielded by the more penetrating s and p electrons and extremely diffuse. As a result, they have poor overlap with the orbitals of neighboring atoms. These two factors disfavor the utilization of d orbitals and have made d-orbital participation in bonding in main group compounds a controversial issue [7]. The characterization of hypercoordinated compounds of the second period elements, such as BH<sub>5</sub> [8] and NF<sub>5</sub> [9], and recent discovery of the linear trifluoride anion F<sub>3</sub><sup>–</sup>, the analog of the previously known X<sub>3</sub><sup>–</sup> (X = Cl, Br, or I) [10], have implied that an unanticipated high degree of coordination

about a particular central atom does not necessarily require a d orbital in bonding. In fact, the central atoms of these molecules lack d orbitals. An alternative approach excluding the utilization of d orbitals has been employed [5b, 7] to account for bonding in the uncommon highly coordinated xenon hexafluoride XeF<sub>6</sub>, namely, the molecule forms three linear three-center, four-electron bonds via the overlap of F(2p<sup>1</sup>)–Xe(5p<sub>x</sub><sup>2</sup>, 5p<sub>y</sub><sup>2</sup>, or 5p<sub>z</sub><sup>2</sup>)–F(2p<sup>1</sup>). The full-blown molecular orbital treatment has been used in studying bonding in other main group hypercoordinated compounds [11]; however, the method is quite complicated. As a result, spd hybridization is still being continuously employed for describing bonding in main group hypercoordinated compounds in most chemistry textbooks. In this paper, we use electronegativity as a powerful tool to analyze bonding in the pentacoordinated AB<sub>5</sub>-type main group molecules and related species. This approach supports a new model for bonding that only involves participation of s and p orbitals on the central atom. This model avoids the full-blown molecular orbital treatment and is more readily understood by undergraduate students. The understanding of bonding in this class of molecules is essential in undergraduate chemical education.

## sp<sup>2</sup> Hybridization in the Central Atom of the AB<sub>5</sub>-Type Molecules

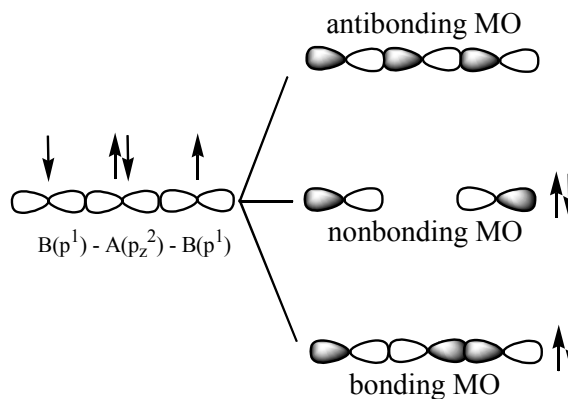
The unnecessary involvement of d orbitals in bonding in the pentacoordinated AB<sub>5</sub>-type main-group molecules is best demonstrated by examining the orbital hybridization in the hypercoordinated compounds of the second-period elements such as BH<sub>5</sub> [8] and NF<sub>5</sub> [9] in which the central atoms lack d orbitals. Theoretical work has shown that nitrogen can possibly form the structurally stable pentacoordinated NF<sub>5</sub> containing five pure N–F σ bonds and that its molecular geometry optimized as trigonal bipyramidal [9], consistent



**Figure 1.** The  $sp^2$  hybridization in the central atom of the  $AB_5$ -type main group molecules. The angle between any two equatorial  $sp^2$  orbitals is  $120^\circ$ . The unhybridized axial  $p_z$  orbital is perpendicular to the equatorial plane.

with the VSEPR prediction. Conceivably, the central nitrogen atom would best adopt the  $sp^2$  hybridization with the unhybridized  $p_z$  orbital (axial) perpendicular to the equatorial plane defined by the three  $sp^2$  orbitals (Figure 1). Thus, each of the three equatorial  $N-F_{eq}$  bonds is formed by  $sp^2-2p$  overlap; and the linear axial  $F_{ax}-N-F_{ax}$  bonds are formed by the  $F_{ax}(p^1)-N(p_z^2)-F_{ax}(p^1)$  overlap resulting in a three-center, four-electron delocalized  $\sigma$  bond (Figure 2). The hypervalency of nitrogen is achieved by dispatching one electron from the nitrogen valence shell to the axial ligand orbitals. This electron transfer is driven by the large electronegativity of fluorine. This model fully accounts for the computed trigonal bipyramidal structure of  $NF_5$  in which the distance of the  $N-F_{ax}$  bonds (1.55 Å) is greater than that of the  $N-F_{eq}$  bonds (1.41 Å) [9a]. The difference in bond distances originates from the different types of bonding in equatorial and axial positions. The longer axial bond is reasonably due to the existence of nonbonding electrons in the three-center, four-electron bond (Figure 2) that lowers the bond order and energy of this bond relative to those of a localized  $N-F$  bond. The existence of pentacoordinated  $BH_5$  has been evidenced experimentally [8a]. Theoretical optimization has revealed several possible structures including those with  $D_{3h}$ ,  $C_{nv}$  ( $n = 2, 3, 4$ ), and  $C_s$  symmetries [8b]. The hypervalency on electron-deficient boron is achieved by transferring one electron from the hydrogen atoms to the boron valence shell via formation of the three-center, two-electron  $H-B-H$  bond. For the  $D_{3h}$  trigonal bipyramidal structure, the central boron atom adopts  $sp^2$  hybridization, the same as in  $NF_5$ . The unhybridized axial  $p_z$  orbital is empty; thus, the three equatorial  $B-H_{eq}$  bonds are formed by  $sp^2-1s$  overlap, and the linear axial  $H_{ax}-B-H_{ax}$  bonds are formed by  $H_{ax}(s^1)-B(p_z^0)-H_{ax}(s^1)$  overlap, resulting in a three-center, two-electron bond (with empty nonbonding MO).

The same approach can be employed in the analysis of bonding in  $PX_5$  ( $X = F, Cl$ ), namely, the central phosphorus atom adopts the energetically favorable  $sp^2$  rather than  $sp^3d$  hybridization with the unhybridized  $p_z$  orbital (axial) perpendicular to the  $sp^2$  equatorial plane (Figure 1). Each of the three equatorial  $P-X_{eq}$  bonds is formed by  $sp^2-np$  overlap [ $n = 2(F)$  or  $3(Cl)$ ]; and the linear axial  $X_{ax}-P-X_{ax}$  bonds are formed by  $X_{ax}(p^1)-P(p_z^2)-X_{ax}(p^1)$  overlap resulting in a three-center, four-electron bond (Figure 2), the same as in  $NF_5$ . As a result, the energetically unfavorable  $sp^3d$  hybridization



**Figure 2.** The three-center, four-electron delocalized  $\sigma$  bond formed in axial positions of the  $AB_5$ -type molecules via the  $B(p^1)-A(p_z^2)-B(p^1)$  orbital overlap. The linear combination of the three  $p$  orbitals in the axial orientation gives three molecular orbitals (bonding, nonbonding, and antibonding MOs). The bonding and nonbonding MOs are occupied, and the antibonding MO is unoccupied.

involving a high-energy  $s^2p^3d^0 \rightarrow s^1p^3d^1$  excitation is effectively avoided. The high oxidation state in phosphorus (+5) is achieved by partial electron transfer from the phosphorus  $3s3p$  subshells to the ligand  $p$  orbitals. Both  $2p(F)$  and  $3p(Cl)$  are lower in energy than  $3p(P)$ . Although the energy of the  $3d$  orbitals in  $PF_5$  is substantially lower than the  $3d$  orbitals in a free phosphorus atom, presumably due to the partial positive charge on phosphorus induced by the electronegative fluorines, the  $3d$  orbitals in  $PF_5$  are still higher in energy than its  $3p$ . Therefore, electron transfer from the  $3p$  orbitals of phosphorus to ligand orbitals is expected to be energetically favorable while promotion of these same electrons to  $3d$  orbitals of phosphorus is not.

The absence of  $d$ -orbital participation in bonding is further supported by examining the partial charge on the central phosphorus atom by using Allen's partial charge formula for  $AB_n$ -type compounds [12], eq 1, which accounts for the effect of the electronegativity (EN) difference in Allen's scale [4, 13, 14].

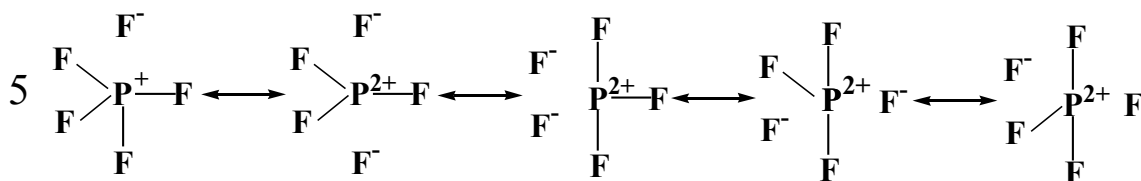
$$\delta_A = (\text{group number of A}) - (\text{number of nonbonding electrons on A}) - 2 \sum [EN_A / (EN_A + EN_B)] \quad (1)$$

The last term in eq 1 is twice of the sum of the electronegativity weighting  $EN_A / (EN_A + EN_B)$  over all the  $A-B$  bonds. This method has been well reviewed in a journal article [3] as well as in a recently published general chemistry textbook [4].

For  $PF_5$  in which  $EN_P = 2.25$  and  $EN_F = 4.19$  [Allen's scale (4,13,14)], the partial charge on phosphorus is calculated as

$$\delta_P(PF_5) = 5 - 0 - 2 \times 5 [2.25 / (2.25 + 4.19)] = +1.51$$

This shows that in  $PF_5$  more than one electron (c.a. a  $-1.5$  charge) on phosphorus has been dispatched to the fluorine valence shell due to the large difference in electronegativities between fluorine and phosphorus, suggesting that  $d$ -component in bonding is zero.  $PF_5$  can be characterized by nine prevalent resonance structures (Figure 3) including five monocationic  $PF_4^+ F^-$  structures and four dicationic  $F^- PF_3^{2+} F^-$  structures. The average charge on phosphorus of these



**Figure 3.** Resonance structures of the trigonal bipyramidal  $\text{PF}_5$ . In the postulated  $\text{PF}_4^+$  and  $\text{PF}_3^{2+}$  the positive charges reside in phosphorus. In the monocationic  $\text{PF}_4^+\text{F}^-$ , the  $\text{F}^-$  anion can possibly occupy five different positions giving five structures. Both of the  $\text{F}^-$  anions in each of the structures containing  $\text{PF}_3^{2+}$  occupy either two equatorial or axial positions in order to minimize the electrostatic repulsion.

resonance structures is +1.45, very close to the calculated  $\delta_p(\text{PF}_5) = +1.51$  by eq 1. The agreement in these values indicates that the postulated  $\text{PF}_4^+$  monocation and  $\text{PF}_3^{2+}$  dication do not have a d-component in bonding.

The partial charge on phosphorus of  $\text{PCl}_5$  in which  $\text{EN}_{\text{Cl}} = 2.87$  [Allen's scale (4, 13, 14)] is calculated as

$$\delta_p(\text{PCl}_5) = 5 - 0 - 2 \times 5 [2.25/(2.25 + 2.87)] = +0.61$$

The possible resonance structures of  $\text{PCl}_5$  have been previously proposed [7] to involve the neutral  $\text{PCl}_5$  and five  $\text{PCl}_4^+\text{Cl}^-$  ion pairs, showing minimal importance in d-orbital participation. The calculated  $\delta_p(\text{PCl}_5) = +0.61$  in this work indicates that the d-orbital contribution in the  $\text{PCl}_5$  molecule, if there is any, should be smaller than 9% [15] (20% d-component in  $\text{sp}^3\text{d}$  hybridization). Although d-orbital participation in  $\text{PCl}_5$  cannot be ruled out completely by this calculation, the electronegativity argument disfavors the existence of the  $\text{sp}^3\text{d}$  hybridization on phosphorus. Energetically favorable, in  $\text{PCl}_5$  a small negative charge (-0.61) is transferred to the valence shell of the chlorine atoms from the central phosphorus atom making phosphorus partially positively charged (+0.61). This partial electron transfer occurs especially via the p-orbital delocalization in the axial orientation. That is because on the central phosphorus atom the axial p orbital is less electronegative than that of equatorial  $\text{sp}^2$  orbitals. Apparently, this is the case for both  $\text{PCl}_5$  and  $\text{PF}_5$ . This model not only accounts for the bond angles in a trigonal bipyramidal structure as expected by employing  $\text{sp}^3\text{d}$  hybridization but also better accounts for the greater axial bond distance than that of the equatorial bonds (due to the nonbonding electrons lowering the bond order and energy) as mentioned earlier ( $\text{P}-\text{F}_{\text{ax}} = 1.58 \text{ \AA}$  and  $\text{P}-\text{F}_{\text{eq}} = 1.52 \text{ \AA}$ ;  $\text{P}-\text{Cl}_{\text{ax}} = 2.14 \text{ \AA}$  and  $\text{P}-\text{Cl}_{\text{eq}} = 2.02 \text{ \AA}$  [5a]).

### Bonding in $\text{AB}_{5-n}\text{E}_n$ -Type Molecules

Bonding in  $\text{AB}_{5-n}\text{E}_n$ -type (E represents a nonbonding pair) molecules can also be characterized by the model depicted in Figures 1 and 2, which excludes d orbital participation. These compounds include  $\text{AB}_4\text{E}$ -type (seesaw-shaped; e.g.,  $\text{SF}_4$ ),  $\text{AB}_3\text{E}_2$ -type (T-shaped; e.g.,  $\text{ClF}_3$ ), and  $\text{AB}_2\text{E}_3$ -type (linear; e.g., the trihalide anions). Each of the nonbonding pairs would preferably reside in an equatorial  $\text{sp}^2$  orbital in accordance with VSEPR theory. The equatorial and axial bonds in each compound are formed via the available  $\text{sp}^2$  orbitals and the three-center, four-electron bonding, respectively. This is best demonstrated by examining bonding in the recently observed linear trifluoride  $\text{F}_3^-$  [10]. This molecular anion belongs to the  $\text{AB}_2\text{E}_3$ -type, the same as  $\text{X}_3^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ). Fluorine does not have any d orbitals and bonding occurs only in its 2s2p subshells; therefore, the central fluorine atom in  $\text{F}_3^-$  would

most reasonably adopt  $\text{sp}^2$  hybridization leaving the unhybridized  $\text{p}_z$  orbital perpendicular to the three  $\text{sp}^2$  orbitals. The linear  $\text{F}-\text{F}-\text{F}$  bond is formed via axial three-center, four-electron bonding and the three nonbonding pairs reside on the three equatorial  $\text{sp}^2$  orbitals. This bonding gives rise to a trigonal bipyramidal electron pair (electron domain) geometry as predicted by the VSEPR model. The uncommon hypercoordination to the central fluorine in  $\text{F}_3^-$  is achieved by dispatching some electron density to the terminal atoms via the p-orbital delocalization in the axial orientation. Similarly, this type of electron transfer can also reasonably occur in other trihalide anions by forming a three-center, four-electron bond in the sp subshells rather than adopting the energetically unfavorable  $\text{sp}^3\text{d}$  hybridization in the central atom.

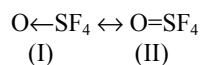
The partial charge on sulfur (containing two nonbonding electrons) in  $\text{SF}_4$  in which  $\text{EN}_{\text{S}} = 2.59$  (Allen's scale) [4, 13, 14] is calculated by eq 1 as

$$\delta_s(\text{SF}_4) = 6 - 2 - 2 \times 4 [2.59/(2.59 + 4.19)] = +0.94$$

In  $\text{SF}_4$ , approximately one electron in sulfur has been dispatched to the fluorine valence shell. The  $\text{SF}_4$  molecule can be considered to resonate among four  $\text{SF}_3^+\text{F}^-$  ion pairs in which  $\text{F}^-$  occupies four possible, different axial and equatorial positions. Apparently, the postulated  $:\text{SF}_3^+$  (containing one nonbonding pair) cation does not have a d component in bonding. By adoption of  $\text{sp}^2$  hybridization and three-center, four-electron bonding, the difference in axial and equatorial bond distances ( $\text{S}-\text{F}_{\text{ax}} = 1.65 \text{ \AA}$  and  $\text{S}-\text{F}_{\text{eq}} = 1.55 \text{ \AA}$  [6]) in  $\text{SF}_4$  can be best accounted for in terms of different bonding types in the equatorial and axial positions. The longer axial bond is presumably due to the electrons assigned to a nonbonding molecular orbital (Figure 2) lowering the bond order and energy as discussed earlier. This difference in bond distances has been previously explained by VSEPR theory: the large effective size of the lone-pair domain in the equatorial plane repels the two axial fluorine-atom bonding pairs to a greater extent than it repels the two equatorial fluorine-atom bonding pairs [3]. We believe that the different bonding, including the fashion of orbital hybridization and overlap in equatorial and axial positions, exerts a greater influence on the bond distance than electron repulsion would.

### Multibond Electron Domain

Bonding in compounds containing multiple bonds is more complicated. For example,  $\text{SOF}_4$  possesses trigonal bipyramidal structure with the oxygen atom occupying an equatorial position [1]. Its bonding may be described by the following resonance structures



Structure (I) contains a coordinate  $\sigma$  bond between sulfur and oxygen. Its central sulfur atom may well adopt  $sp^2$  hybridization as depicted in Figure 1. The coordinate  $\sigma$  bond is formed via overlap between a filled  $sp^2$  orbital in sulfur and an empty p orbital in oxygen; however, structure (II) contains a double-bond electron domain between sulfur and oxygen, and d orbitals on sulfur may participate in bonding, forming a  $\pi$  bond.  $\text{H}_2\text{C}=\text{SF}_4$  also possesses trigonal bipyramidal structure and the  $\text{CH}_2$  group is located in an equatorial position [1]. The  $\text{C}=\text{S}$  double bond is very likely formed via sulfur d-orbital participation. In both cases, the energy required for the  $3p \rightarrow 3d$  excitation may be compensated by the  $\pi$ -bond energy. This paper will not discuss extensive details about compounds containing a double-bond electron domain. The  $sp^2$  hybridization and related orbital overlap without d-orbital participation as depicted in Figures 1 and 2 are mostly applicable to purely  $\sigma$ -bonded species.

### References and Notes

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- Phosphorus in  $\text{PCl}_5$  ( $\delta_p = +0.61$ ) carries a net  $-4.39$  charge in its valence shell. Assuming that a d orbital participates in bonding and adopting the  $-0.39$  negative charge,  $d\% = (0.39/4.39) \times 100 = 8.9\%$ .