

Re-examining Fluxions and Pseudorotation—Why Hepta-Coordinated Compounds Are Not Well Represented as a Pentagonal Bipyramid

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A much simpler and mathematically more precise explanation for the concept of “pseudorotation” as well as the closely-related class of “fluxional molecules” is supplied by noting that there are only five regular polyhedra and by postulating that a static, stable orientation of a molecule with formula AB_n can be achieved only by positioning the n like ligands at the vertices of one of these five polyhedra. In the absence of such “libration points”, molecules will shift around their ligands in order to minimize intramolecular forces. This can be explained from a strictly geometric perspective—without the need for consideration of the shape of orbitals, etc. From this reinterpreted perspective, one may make the qualitative conclusion that the equilibrium which best approximates the desired equidistance between ligands in pseudorotation will be a dynamic, in contradistinction to a static, one; i.e., a fluxional one. Furthermore, the trigonal and pentagonal bipyramidal models that are traditionally used to describe molecules of coordination five and seven, respectively, are shown to be based on a bias toward modified octahedral orientation and that, for the case of hepta-coordination, better sets of libration points are predicted using the largest (in number of vertices) of the regular polyhedra (the dodecahedron). Additionally, a speculation about the quantitative nature of pseudorotation is supplied using “Schaeffli” angles.

1. INTRODUCTION

The ideas referred to as “pseudo-rotation”¹ and “fluxions”² or “fluxional molecules”² have been explained by many different authors in many ways.³ Two of the first major summaries of these phenomena were provided by Cotton and Westheimer, respectively, in the same volume, but different issues, of *Acc. Chem. Res.*⁴ Cotton described fluxional molecules as those which “have more than one thermally accessible structure and which, under conditions (especially temperature) of interest, pass from one to another of these structures fairly rapidly”, while Westheimer asserted the following: “Pseudo-rotation for compounds of pentavalent elements is defined as the intramolecular process where a trigonal-bipyramidal molecule is transformed by deforming bond angles in such a way that appears to have been rotated by 90° about one of the interatomic bonds”. In other words, one may consider pseudorotation as a proper subset of fluxions and that the primacy of the “simplest” static three dimensional polyhedron having the appropriate number of vertices is assumed.

This bias has been buttressed by much, possibly irrelevant, physics such as Bader, Gillespie, and MacDougall⁵ concluding “that the Laplacian of the charge density provides the physical basis for the Lewis and VSEPR models”. Nevertheless, one idea that we do believe is extremely relevant was published in 1994 by Vogt, Fitch, and Cockcroft.⁶ In their report they concluded that at very low temperature, 1.5 K, the lowest energy configuration of a hepta-coordinated compound, ReF_7 , is “a distorted pentagonal bipyramid”.

Our premise is that a **MUCH** simpler basis exists—using ONLY solid geometry and Coulomb’s law: “Like charges repel each other”.

In the study of the geometry of three-dimensional objects,⁷ one finds that there exist exactly five regular convex

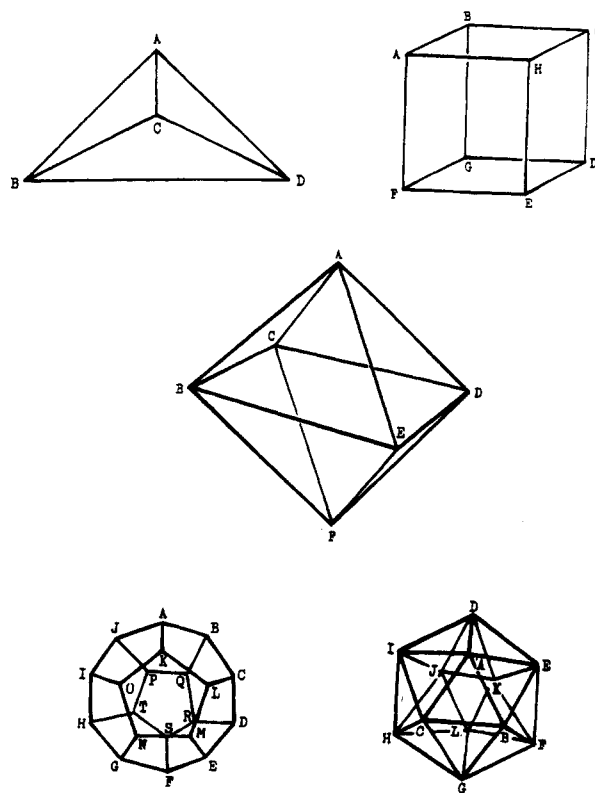


Figure 1. The five regular convex polyhedra.

polyhedra (Figure 1). This has important implications in chemistry in that if a central atom is covalently attached to n identical ligands AND, if, in addition, there are no free electrons—which, in most instances, for purposes of bonding, seem to act like phantom ligands, then these ligands will try to find positions as far away from each other as possible. In other words, simply what is referred to, in elementary chemistry textbooks, as Valence Shell Electron Pair Repulsion.

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2. REVIEW OF THE GEOMETRICAL BASIS FOR VSEPR

Consider the scenario that we have a central atom with n fluorine atoms as ligands. Because fluorine is the most electronegative atom, each fluorine atom will try to repel all of the remaining fluorine atoms—with the concomitant geometry of the molecule being that all of the angles in each of the planes formed by two fluorines and the central atom will be equal. This translates into the following:

(a) In forming beryllium (di)fluoride, BeF_2 , the two electrons in its outer shell of beryllium will assume a linear orientation; i.e., there exists a 180° angle between Be and the two bonded F atoms.

(b) Boron, which has three electrons in its outer shell, forms boron (tri)fluoride—a coplanar molecule having 120° angles with boron at the vertex and any two fluorine atoms on the angle sides.

(c) Carbon, which has four electrons in its outer shell, forms carbon (tetra)fluoride—a three dimensional molecule with the relevant model having the carbon atom at the center of a tetrahedron and the four fluorine atoms at the vertices; i.e., the central angle is approximately $109^\circ 28'$. (Precisely, the value of this "tetrahedral angle" is $\cos^{-1} -1/3$.) Notice that such a geometry minimizes the interaction between every set of two F atoms.

This description does not continue as we progress across row no. 2 of the Periodic Table, because the nucleus of the atom is not large enough to be able to accommodate such an increasing number of ligands; instead electrons will form pairs that act like strongly-negative phantom ligands. For example, nitrogen, with five electrons in its outer shell, will form three covalent bonds and have an unshared pair of electrons left over. This strong electronegativity center causes the neutral nitrogen atom to form only three covalent bonds—which are distorted out of the plane by repulsion from this electron pair. Such a molecule is, therefore, represented as a trigonal pyramid. Furthermore, nitrogen also, by giving up one of its electrons and forming, especially with hydrogen, the ammonium ion, can have four covalent bonds. Note that by so forming the ammonium ion, the simple (static and stable) geometric picture of ligands directed toward the vertices of a regular polyhedron (the tetrahedron) is achieved.

Similarly, oxygen, with six electrons in its outer shell forms two covalent bonds and two phantom centers of electronegativity. Oxygen, like nitrogen, is too small for its six outer shell electrons to accommodate six ligands and thus forms two covalent bonds and has two sets of paired electrons, which, acting as phantom ligands, forces the two ligands to be noncolinear. Furthermore, because there are only three points to consider (the oxygen atom and its two ligands), these three points uniquely determine a plane; i.e., there is no question of co- vs noncoplanarity.

Continuing to the last noninert element in row 2, fluorine, there is only one bond, and thus the geometry need not be considered.

With elements in Row no. 3, on the other hand, the central atom is larger, and there is sufficient room for more "geometrically interesting" structures. This, however, is mitigated by the fact that as we go down the columns of the periodic table, the prevalence of ionic, in contradistinction to covalent, compounds, especially on the left side of the

periodic table, obviates the need for discussing any "linear" AB_2 "molecules" in column 2 besides beryllium, etc.

Rather than following systematically across row 3, let us now consider the geometry of sulfur—which has six electrons in its outer shell. Unlike oxygen, sulfur is large enough to react with fluorine to form the simple compound SF_6 —whose geometry is such that the six fluorine atoms can be directed toward the vertices of an octahedron (or alternately toward the center point of the faces of a cube). In other words, because there exists a static, stable orientation of the ligands that fulfills the ideals of VSEPR, this is a chemically desirable orientation. Such a geometry is called "octahedral".

3. MOLECULAR "STRATEGIES" WHEN THERE DOES NOT EXIST A STATIC, STABLE GEOMETRY

Now let us focus on compounds having phosphorus as the central atom. We note, for example, that phosphorus forms two familiar compounds with fluorine: PF_3 and PF_5 . The first of these, like its analog with nitrogen, presents no geometric problems; HOWEVER, the pentafluoride is a different matter. The reason why this compound is different from all others we have discussed so far is that there does NOT exist a regular three-dimensional figure that has five equiposition points; i.e., no regular polyhedron with five vertices (to which the five ligands may be oriented) exists. Consequently, we canNOT produce equal angles and thus equal VSEPR. We should find a similar situation for compounds of the form AB_7 as well as for compounds of the form AB_9 and larger (with the exception of AB_{12} or AB_{20})—if they existed. Problems of this type are solved in nature by several different strategies, depending on the state of the molecule and the size of both the central atom and the ligands.

(1) Ionization: Consider two PF_5 groupings of atoms. If one of these F atoms were transferred from being attached to one of the P atoms to being attached to the other, the group giving up the F atom would lack the electronegativity of that particular F atom as well as the electrons which that fluorine atom provided; consequently, it could be represented as the PF_4^+ ion. Similarly, the phosphorus centered group gaining the extra fluorine atom and its electrons would be negatively charged; i.e., PF_6^- . Notice that the geometry requirements are now fulfilled since the PF_4^+ ion would have the fluorine atoms tetrahedrally-oriented, while the PF_6^- ion would have the fluorine atoms directed toward the vertices of an octahedron. Since the tetrahedron and the octahedron are two of the five regular polyhedra that exist in three-dimensional space, these two figures have the fluorine atoms set at a static, stable equilibrium position. In other words, such a strategy fulfills the idea of VSEPR.

An analogous situation exists for a fluorine compound having as the central atom an element in column 7. Here, again, there is not a regular three-dimensional geometrical figure with seven vertices; consequently, a static, stable, electrically neutral atom with the formula AF_7 is not possible; but AF_6^+ and AF_8^- ions are viable, PROVIDED the central atom (A) is large enough to accommodate eight fluorine ligands. This is exactly the situation that would be encountered if IF_7 were to ionized; i.e., the iodine atom is sufficiently large for such a geometry. Also, we find that only BrF_5 is attainable since five fluorine ligands (actually six, since the presence of exactly five equal ligands is

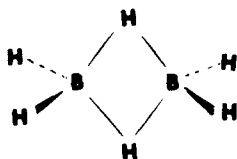


Figure 2. Diborane.

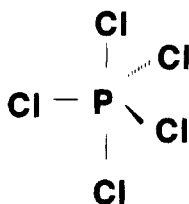


Figure 3. Phosphorus pentachloride as a trigonal bipyramid.

untenable) are within the size constraints that the bromine atom can hold in place; however, BrF_7 would be too crowded and thus bromine cannot combine with the seven (actually eight) fluorine atoms it would need to in order to form the hepta-fluoride.

(2) A second way found in nature to accommodate like ligands that are not one of the five "permitted" numbers (those that correspond to the number of vertices of a regular polyhedron in three dimensional space) is to polymerize; usually as dimers. Consider, for example, that instead of the ligands around a boron atom being fluorine atoms—with their high electronegativity, now, the like ligands are hydrogen atoms. We note that the molecule BH_3 does not exist as a single group; instead two such groups aggregate forming the molecule diborane (B_2H_6) (Figure 2)—a molecule having two constitutionally different hydrogen atoms as well as having two drastically different types of bonding between a boron atom and neighboring hydrogen atoms. Instead of investigating the physics behind these differences, we shall focus only on the fact that such a strategy allows for a viable geometry when we recognize that there are four hydrogen atoms about each boron. In other words, by the "strategy" of forming three-center two-atom bonds, it is possible to orient these centers of electropositivity as far apart as possible from each other and still have them oriented toward the vertices of one of the five regular polyhedra (the tetrahedron). A similar situation exists for aluminum chloride—which forms the dimer Al_2Cl_6 .

(3) A third method in which the requirements of angle equality **COULD** be obtained is through a process that is really the precursor of both fluxion and pseudorotation and is the focal point of this report; namely, we first consider that, **WHEN** a static stable equilibrium does not exist, **THEN** the ligands are in a state of constant rapid motion, bending and twisting relative to the central atom. **HOWEVER**, the integration over time of each of the possible orientations averages out to a common value; even though at an any instant these angles are, in fact, not equal. In order to better appreciate this picture, let us begin with the traditional view of PCl_5 being represented as a trigonal bipyramid (Figure 3). In such a model, the angles (having the P atom as the vertex) between two of the "equatorial" Cl atoms is 120° , while the angle between an axial and an equatorial atom is only 90° . This model seemed to be corroborated in 1940 by Rouault⁸ by measurements that showed that the axial bonds were, in fact, longer than the equatorial bonds. Further study by Van der Voorn and Drago⁹ of $\text{PCl}_{5-n}\text{F}_n$ with n

ranging from 0 to 5 confirmed this longer axial vs equatorial bonding, with the more stable isomers being those with the more electronegative substituents being axial. They⁹ also included a detailed evaluation of the interpretations (especially in term of s vs p vs d orbitals) supplied at the time by some of the more prominent chemists working on this problem at that time (Muetterties,¹⁰ Gillespie,¹¹ Cotton,¹² etc.).

At this point, however, it is important to note that one logical conclusion of the trigonal bipyramidal model of PCl_5 is that we should be able to radioactively tag a single Cl atom and then isolate two isomers—one with this "different" ligand being axial and the other equatorial. We *should*; however, Shriver, Atkins, and Langford¹³ correctly noted that "one problem with the experimental determination of the shape of a molecule is that different techniques sometimes lead to apparently conflicting conclusions". For example, NMR spectra correspond to a much long time duration than, say, IR or Raman spectra. Consequently, what may appear as a single form in NMR may be isolatable with the faster techniques. In other words, expectations about molecular shape often carry implications about both the time scale and the temperature at which such a molecule is being isolated. For example, as early as 1970, Jacob and Bartell,¹⁴ upon recording the electron diffraction in the gas phase of rhenium heptafluoride, noted a "puckering of the ring of the five fluorines" with up to 9° out of the plane displacement and a "movement of each axial fluorine from the reference axis of about 8° ".

Additionally, just last year, as was mentioned earlier,⁶ with a low enough temperature, Vogt et al. were able to achieve the isolation of a particular conformer. Their description of ReF_7 as "a distorted" (in contradistinction to a geometrically ideal) pentagonal bipyramid has fundamentally important geometrical implications that should not, as has been the past experience, be passed off lightly. Meanwhile, let us re-examine, from the geometric bias that we started with, the underlying philosophy of fluxions.

Beginning with a trigonal bipyramidal arrangement, an axial and an equatorial Cl atom are only 90° apart. Consequently, if these two atoms were at the same distance from the phosphorus, they would experience greater Coulomb repulsion than that which occurs between two equatorial chlorine atoms. This would result in a rearrangement so that the axial distance is increased. Now, however, in order for each of the Cl atoms to remain bonded to the central P atom, this results in a pushing together of two of the originally equatorial Cl atoms—a phenomenon described by Berry.^{3c} If this angle were to be pushed to 90° and **THEN STOPPED**, now one of the originally equatorial Cl atoms would become axial and the rearrangement would be completed, with the net result that there was a new set of axial vs equatorial Cl atoms. **HOWEVER**, this process cannot be stopped without a sudden drastic cooling of the environment and thus would continue indefinitely, i.e., formation of a state of dynamic equilibrium.

One further item of note is that we *seem* to have a nearly identical situation with IF_7 —the obvious difference being that the equatorial angle is now less than 90° , namely 72° (Figure 4). The consequence of this is that the initial driving force is the Coulomb repulsion between two equatorial F atoms, rather than between an equatorial and an axial F, and also that now the equatorial bonds are longer.

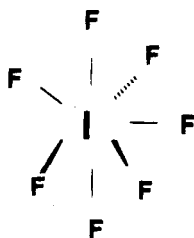


Figure 4. Iodine heptafluoride as a pentagonal bipyramid.

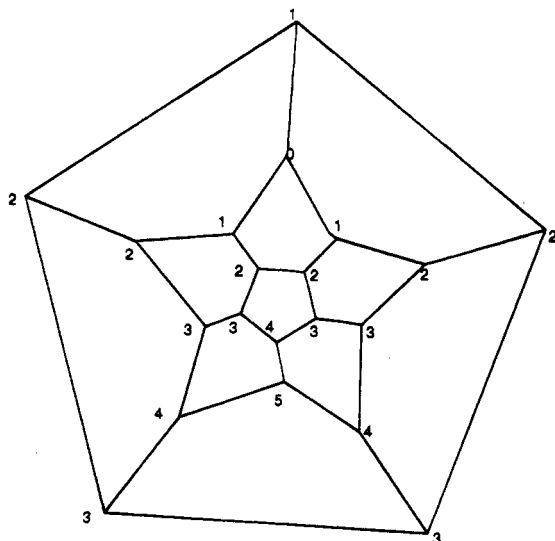


Figure 5. Minimum graph theoretical distance on a dodecahedron from a selected vertex.

4. AN IMPLICATION FROM GRAPH THEORY

There is, HOWEVER, one major difference in the graph theoretical description of a pentagonal bipyramid that mitigates against equating the pictures of trigonal vs pentagonal bipyramids. This is seen by examining the set of 20 vertices that exist on a regular dodecahedron. Before undertaking this examination, however, it should be noted that any bipyramid may be viewed as being derivated from an octahedron with two vertices held constant. We refer to these two selected vertices as being "axial", and relegate the remaining vertices to the "equatorial" plane. This is precisely the picture one gets from the traditional trigonal and pentagonal bipyramids; i.e., the equator has been respectively "expanded" or "shrunk" from the "square bipyramid" (octahedron). Instead of such a perspective, we note the existence of a semiregular pattern that can be imposed by derivating a set of vertices selected from the next higher regular polyhedron (the dodecahedron). This results in a set of seven vertices which may be designated as the desired equilibration points. Furthermore, we note that **when** this set has desirable properties of symmetry, it does not lend itself to the standard dichotomy into axial vs equatorial.

For simplicity, consider a Schlegel projection¹⁵ for the dodecahedron and randomly select one vertex (label it "0") as the starting point. Next, list the minimum graph theoretical distance to each of the other 19 vertices (Figure 5). This produces two sets (even and odd numbered vertices). In the even numbered vertex set, the only pairs of adjacent atoms are numbered "2". Select either one of each of these pairs plus all of the vertices numbered "0" and "4". This creates a set of seven vertices in which equilibration between the three sets of vertices numbered "2" could occur (Figure 6).

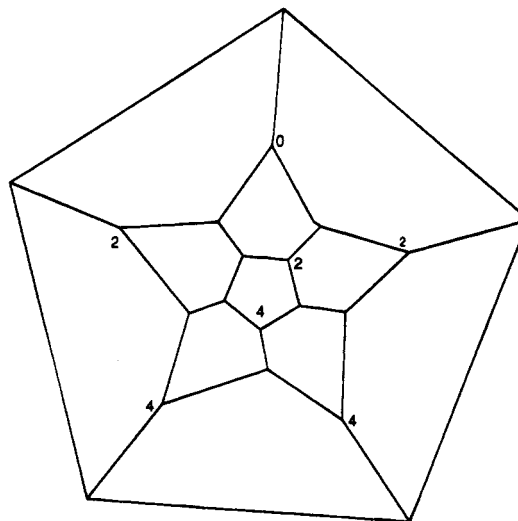


Figure 6. A set of seven symmetric libration points on a dodecahedron.

Also, we can form a corresponding set using the odd numbered vertex set and equilibration between those vertices numbered "3". If we further have equilibration between these two sets, we have created a physical picture that will fulfill the intent of integrating over time to produce "equal angles".

Some interesting observations about this model (Figure 6) are as follows:

(1) If "0" is a member of this set then the diametrically opposed point "5" is NOT. In other words, using this symmetric model does not include the pentagonal bipyramid as a structure for AB_7 .

(2) Each of the selected seven vertices is exactly graph theoretical distance (GTD) = 2 or GTD = 4 from the other six members of this set. In other words, we note a symmetry which is aesthetically, if not actually chemically, very desirable.

(3) The remaining set of 13 other vertices can be nearly evenly partitioned into two sets based on GTD from the libration points. Six of these 13 vertices are adjacent to two libration points, and the remaining seven are adjacent to one and a GTD = 2 from a second of these libration points.

The above observations are equivalent to defining the intuitive concept of "almost regular" for a coordination that does not allow for orientation toward the vertices of a regular polyhedron. Naturally, an intuitive concept is not a substitute for the mathematical precision that we would like.

There does, however, exist another model of hepta-coordination shown in Figure 7, which, although not being symmetric, does include both vertices "0" and "5" in the set of equilibration vertices; i.e., this set of equilibration points does contain both of the axial atoms of the pentagonal bipyramid. Whether this set of equilibration points is actually preferable to the symmetric one—in that we still have all members of the equilibration set two units apart from one another while simultaneously having now a greater number of other vertices at a smaller GTD from the libration vertices: nine (designated as a) have GTD = 1,1; three (designated as b) have GTD = 1,2, but one (designated as c) is two units away from any of the selected libration points (GTD = 2,2)—has not yet been resolved to our satisfaction.

In an identical manner, we can find a pattern on this same dodecahedron in which five points are preferentially selected

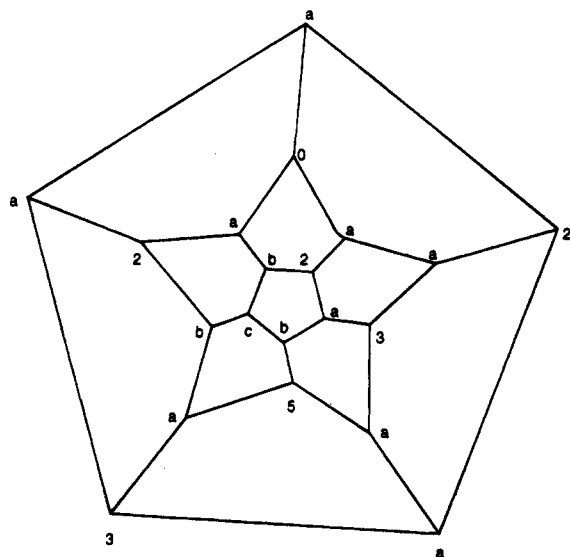


Figure 7. A set of seven unsymmetric libration points on a dodecahedron which contains a coaxial pair of vertices.

(Figure 8). Here, inasmuch as there does not exist a symmetric set of vertices all the same GTD from nearest neighbors, we chose as the pattern to select the vertices named "0" and "5" and two of the vertices marked "2". (Which two of the six potential vertices is limited only by the restriction that they not be adjacent.) There are now exactly two vertices named "3" that are equidistant from the selected "2"s and from "5". One of these is chosen as the fifth member of the desired set of libration points. By such a choice every one of the five points is either 2 (three of them) or 3 (two of them) GTD units away from two neighbors—which is the best optimization that we could find. One advantage of this model is that because we have picked both points "0" and "5" in the equilibration set, the idea of axial and equatorial is implied. The only difference from the traditional picture is that the equatorial atoms will equilibrate about the equatorial plane, rather than being static in it. Now in the case of low temperature or very short time integration, the trigonal bipyramid is the logical choice for the default structure—in marked distinction to the default structure for AB_7 .

Further analysis of Figure 8 shows greater disparity in the distances of nonequilibration vertices from the selected set of equilibration vertices for AB_5 than existed for AB_7 coordination; namely, the set of equilibration points selected for Figure 8 has four of the 15 other vertices with GTD = 1,1 from two libration points (a), seven with GTD = 1,2 (b), and four with GTD = 2,2 (c). At present, we see no criterion for defining "better" (in terms of optimizing a relevant parameter) sets of the five equilibration points.

As an additional comment one notes that Balaban et al.¹⁶ illustrated the repositioning of B atoms in the pseudorotation of AB_5 compounds in graph form. Although, in retrospect, one would be correct in asserting that this produces a 20 vertex ("dodecahedral") graph, we know of no further analysis of the graph theoretical implications that was ever undertaken, until now.

5. SCHAFFLI ANGLES AND A SPECULATION ABOUT THE QUANTITATIVE NATURE OF PSEUDOROTATION

At this point it is interesting to notice that, by simple combinatorics, there are $C_2^7 = 21$ planar angles in AB_7 :

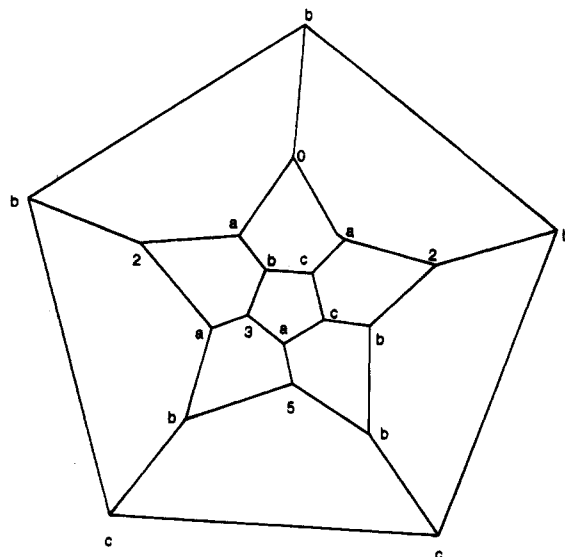


Figure 8. A set of five libration points on a dodecahedron.

Using the pentagonal bipyramid model, there are 16 simple planar angles (5 of these angles are 72° , 10 are 90° , and 1 is 180°) as well as five multiple angles, which due to their relationship to the Schaffli symbols for nomenclating polygrams,¹⁷ we have designated as "Schaffli angles". These five multiple angles are each 144° , but the effect of Coulomb attraction is mitigated by the fact that they are separated by an intervening ligand; consequently, in conformity with dividing the number of faces in a polygram by its "density",¹⁸ the measure of each such central angle is similarly divided by its density—in this case 2. In other words, in general each Schaffli angle contributes $1/d$ times its measure to the angle sum, and in this case $1/2 * 144^\circ = 72^\circ$. Ignoring, for the moment the interaction between the two axial B atoms (which are effectively blocked by the A atom), the average of these 20 angles is 81° . This means that there would be exactly a 9° out of the plane displacement as Jacob and Bartell had recorded.¹⁴ Furthermore, inclusion of the 21st angle between the axial B atoms yields an average angle of $85 \frac{5}{7}^\circ$ or a $4 \frac{2}{7}^\circ$ deviation from both the "north" and "south" polar points by the two B atoms that had been designated as "axial". In other words, the sum of these two angles between the "true polar" and the "designated axial" is $8 \frac{4}{7}^\circ$, which seems to further corroborate Jacob and Bartell's measurements.

6. CONCLUSION

A "not simple" dynamic model involving vibrations about equilibration points can be described to accommodate interpretation of coordinations unequal to orientation toward the vertices of a regular polyhedron; i.e., coordinations such as 5, 7, etc. Also, in a manner analogous to our earlier *strictly* geometric interpretation of Markovnikov vs anti-Markovnikov addition of HI to a double bond,¹⁹ we may consider that the "driving force" for pseudorotation is *strictly* geometric; i.e., there exists a much simpler interpretation of this observed chemical phenomenon than the one that is traditionally given in terms of orbital hybridization. Finally, there is a graph-theoretical difference in the fluxion model for hepta-coordination versus the one that is applicable for penta-coordination. This is expressed in the heuristic concept of "almost regular". Based upon such a heuristic, the

pseudorotational description for hepta-coordination gives a picture that is not best accommodated using a pentagonal bipyramidal model, as has been traditionally assumed; however, for penta-coordination the trigonal bipyramidal model still appears to be optimal.

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