

Gillespie–Nyholm Aspects of Force Fields. I. Points-on-a-Sphere and Extended Hückel Molecular Orbital Analyses of Trigonal Bipyramids^{1,2}

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Abstract: Gillespie–Nyholm theory is applied systematically for the first time to a study of molecular vibrations. An analysis of bending force constants and barriers to Berry pseudorotation in trigonal bipyramids is carried out using a points-on-a-sphere (POS) variant of the theory. Parallel EHMO calculations for PF₅ and hypothetical XH₅ molecules are also performed for comparison purposes. Analytical POS expressions for symmetry force constants, F_{ij} , for bending are derived. The relative POS and EHMO force constants obtained are pleasingly in accord with each other and with *one and only one* of the several choices of force fields for PF₅ compatible with molecular vibrations (ν 's and ζ 's). A reassuring feature of both simple models is that the results obtained are insensitive to the force law assumed (POS case) or parameterization (EHMO case). Parallels between the hardness of the force law and d orbital involvement are drawn. Evidence is presented that the valence shell electron pair repulsion force law simulated by the POS interactions is substantially harder than coulombic (r^{-1}), the law frequently attributed to Gillespie–Nyholm theory. Barriers to Berry pseudorotation turn out to be much smaller than barriers calculated solely from the quadratic force constants, and they depend strongly upon the off-diagonal force constant F_{67} , a constant neglected in prior studies. The above results lead us to suggest that the simple POS scheme has the following virtues: (1) it provides a rough physical criterion for selecting the proper solution from among several alternative force field solutions derived from vibrational spectra; (2) it offers a plausible method for relating pseudorotational barriers to force constants, a heretofore elusive undertaking; and (3) it affords provocative evidence, in view of the striking parallel between point-repulsion calculations, MO calculations, and experiment, that the mutual avoidance (Pauli avoidance) of occupied, localized molecular orbitals is, as originally proposed by Gillespie and Nyholm, the proper basis for the valence shell electron pair repulsion theory.

Gillespie–Nyholm theory^{3–6} has been so successful in accounting for qualitative aspects of molecular structure that it was decided to apply it systematically, for the first time, to molecular force fields as well. An analysis of bending force constants of trigonal bipyramids therefore was initiated, using a POS (points-on-a-sphere) variant of the theory in which pairwise interaction energies between points-on-a-sphere are taken to simulate valence-shell-electron-pair repulsions. The most symmetrical trigonal bipyramids, the XY₅ systems with D_{3h} symmetry, furnish a particularly favorable case because, despite their simplicity, they possess a fairly rich array of (five) independent bending force constants. They are also of interest to chemists because they serve as model systems for understanding polytopal rearrangements of more complex phosphoranes,⁷ reaction pathways in hydrolyses of phosphate esters,⁸ the nature of the binding in hypervalent compounds,⁹ and other topical problems.

Several recent molecular orbital studies have ap-

peared^{10–13} which review the theories of binding in pentavalent phosphorus compounds and provide helpful analyses of their properties. A variety of physical methods including nmr,¹⁴ vibrational spectroscopy,^{14–19} and gas-phase electron diffraction^{6,14,20,21} have also been brought to bear on the structures, stereochemistries, and force fields of trigonal bipyramids but have fallen short of an unequivocal resolution of the problem as will be discussed below.

In phosphorus pentafluoride itself, the nmr spectrum shows that all fluorines are equivalent down to the lowest temperatures studied.¹⁴ This fact was interpreted by Berry²² as signifying a rapid intramolecular exchange of axial and equatorial fluorines by a mechanism now known as “Berry pseudorotation” proceeding

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(2) Presented in part at the Fourth Austin Symposium on Gas Phase Molecular Structure, Austin, Tex., Feb 28, 1972, Abstract M16.

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via $D_{3h} \rightarrow C_{4v} \rightarrow D_{3h}$ pathways. This mechanism (or a permutationally equivalent, but physically slightly different mechanism)⁷ is widely accepted, and chemists have addressed themselves to a study of the energy required to surmount the barrier between equivalent D_{3h} equilibrium structures. The most common way to gain information about molecular deformations is by studying their vibrational spectra, and Lord¹⁵ and Holmes,^{14,16} in particular, have discussed the relationship between vibrational studies and the pseudorotational problem.

Unfortunately, it turns out that there are two serious obstacles impeding the inference of barriers to pseudorotation from vibrational data. First, even in the simplest case, PF_5 , there is no unique solution relating frequencies and Coriolis coupling constants to quadratic force constants. Several alternative combinations fit the spectroscopic data perfectly, prompting Wilt, *et al.*, to state¹⁸ “. . . usually one is able to select on ‘physical grounds’ one of the solutions as ‘preferred’ . . . [but for PF_5] we believe it is impossible to choose realistically between solutions B and C.” Secondly, even if the quadratic force field were known exactly, the effect of anharmonicity would cause the true barrier to be markedly different from the barrier calculated from the quadratic force field alone. The reason for interest in applying a semiquantitative variant of the Gillespie-Nyholm theory to the problem is that there are indications that it cannot only provide a physical basis for selecting the correct force field from the existing mathematical alternatives¹⁸ but that it may also be able to give a useful characterization of the anharmonic corrections needed to estimate the barrier. Whether right or wrong, the model affords an extraordinarily simple way of looking at the electronic interactions underlying the force field and any success that it attains should lead to immediate physical insight.

Previous applications of the points-on-a-sphere model have been successful in accounting for structures in a variety of molecular systems. Gillespie, using the most primitive criterion possible, that of maximizing the least distance between any two points on a sphere, was able to rationalize structures of XY_n molecules,^{3,4} Claxton and Benson²³ and, later, Thompson, *et al.*,^{24,25} and Jacob, *et al.*,²⁶ using a simple analytical law to express POS repulsions, were able to make some useful structural correlations in the case of seven coordination. Ligand repulsive energies for eight monodentate ligands were examined by a POS approach by Hoard and others.²⁷ The POS model has also been applied quite successfully by Blight and Kepert²⁸ to predict structures of complexes with bidentate ligands. For the above reasons it seems justified to pursue the model further,

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even though it appears almost offensively oversimplified at first glance.

Procedure

Practical Considerations. A rigorous theoretical treatment of the full, anharmonic force field and barrier to pseudorotation in XY_5 molecules seems to be feasible today, at most, for the hypothetical molecule PH_5 . In several studies of PH_5 , calculations of the barrier^{11,12} and of a few of the 13 possible quadratic force constants¹² have already been performed to near Hartree-Fock accuracy with fair geometry optimization. Analogous treatments of PF_5 and more complex systems would be enormously expensive and of only qualitative accuracy, making it worthwhile to consider the simpler model discussed in the introduction, the POS (points-on-a-sphere) model, and, for sake of comparison, the very different EHMO model.²⁹ These simpler models are not believed to be capable of treating bond stretches in any but the most qualitative manner; there is evidence, however, that they provide useful gauges of the energetics of bond bending.²³⁻³⁰ Therefore, the present study will be limited to pure bending deformations. All bonds in the EHMO calculations will be taken to be identical in length, despite experimental evidence that axial bonds are somewhat longer than equatorial bonds, to sidestep the problem of stretching displacements in the $D_{3h} \rightarrow C_{4v}$ deformations. Similarly, the POS model, in its restriction of repelling points to a spherical surface, suggests equal bond lengths. Since the difference between axial and equatorial bond lengths is only about 3% in PF_5 ,²⁰ such simplifications will presumably not greatly distort the results.

Points-on-a-Sphere Force Constants for XY_5 . Valence shell electron pair repulsions are represented in the present variant of the POS model by pairwise additive potential energy terms of the form r_{kl}^{-n} , where r_{kl} is the distance between points k and l which are constrained to move on the surface of a sphere. As will be discussed subsequently, the principal bond-bond repulsion is not expected to be coulombic and, hence, the exponent n is a free parameter unlikely to be close to unity. The force field of the molecule for bending displacements can be identified with the POS potential energy for the system of five points, if it is assumed that

$$V_T = K \sum_{k < l} r_{kl}^{-n} \quad (1)$$

the XY bond lines radiate from the center of the sphere through the points on a sphere. The model implication that bonds are not bent is not meant to be taken very literally and the success or failure of the model should not be interpreted too hastily in terms of the old problem of bond bending. Bending force constants F_{ij} can be determined by identifying the molecular potential energy of deformation, through quadratic terms in the symmetry coordinates S_i , or

$$(V_T - V_T^0) = (1/2) \sum_i \sum_j F_{ij} S_i S_j \quad (2)$$

with the POS potential energy in eq 1, for small displacements from D_{3h} symmetry. The symmetry co-

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ordinates adopted were

$$(A_2'') \quad S_4 = 6^{-1/2}(\Delta\beta_{15} - \Delta\beta_{16} + \Delta\beta_{25} - \Delta\beta_{26} + \Delta\beta_{35} - \Delta\beta_{36}) \quad (3)$$

$$(E') \quad S_{6a} = 6^{-1/2}(2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{13}) \quad (4)$$

$$(E') \quad S_{7a} = 12^{-1/2}(2\Delta\beta_{15} - \Delta\beta_{25} - \Delta\beta_{35} + 2\Delta\beta_{16} - \Delta\beta_{26} - \Delta\beta_{36}) \quad (5)$$

$$(E'') \quad S_{8a} = 12^{-1/2}(2\Delta\beta_{15} - \Delta\beta_{25} - \Delta\beta_{35} - 2\Delta\beta_{16} + \Delta\beta_{26} + \Delta\beta_{36}) \quad (6)$$

following the conventions of Hoskins and Lord¹⁵ illustrated in Figure 1, where $\Delta\alpha$ and $\Delta\beta$ represent equatorial-equatorial and axial-equatorial angles, respectively.

It was possible to derive analytical expressions for the F_{ij} by deforming the molecule along the symmetry coordinate S_i and S_j , by expressing the resultant quantities r_{kl}^{-n} as functions of the various angular displacements $\Delta\alpha$ and $\Delta\beta$, and by relating the $\Delta\alpha$ and $\Delta\beta$ values to S_i and S_j . This was accomplished by calculating the r_{kl}^2 from the Cartesian coordinates of points k and l via the three-dimensional Pythagorean theorem and then employing the binomial expansion to obtain r_{kl}^{-n} through quadratic terms in the displacements. The difference between V_T and V_T° , the reference D_{3h} energy, is a function only of the constant K , the sphere radius R , the exponent n , and the symmetry coordinates. The force constants thus obtained are given, in units of $(2K/R^n)$, by the expressions

$$F_{44} = \left[3^{-n/2} \left(\frac{n}{4} \right) + 2^{-n/2} \left(\frac{n^2}{8} + \frac{n}{4} \right) \right] \quad (7)$$

$$F_{66} = \left[3^{-n/2} \left(\frac{n^2}{24} + \frac{n}{6} \right) \right] \quad (8)$$

$$F_{67} = - \left[2^{-n/2} \left(\frac{n}{\sqrt{24}} \right) \right] \quad (9)$$

$$F_{77} = \left[2^{-n/2} \left(\frac{n^2}{8} + \frac{n}{4} \right) + 2^{-n} \left(\frac{n}{6} \right) \right] \quad (10)$$

$$F_{88} = \left[2^{-n/2} \left(\frac{n^2}{8} + \frac{n}{4} \right) \right] \quad (11)$$

Formulas for the doubly degenerate representations were checked by solving with the S_{ib} (not listed above) as well as the S_{ia} coordinates.

Extended Hückel MO Force Constants for PF_5 . Since the EHMO method is based on a simulated Hamiltonian,²⁹ it is not obvious what parameterization will yield the optimum force constants. The crucial point of the present paper, however, is not the absolute values of individual force constants but, rather, the distribution of force constants among the various symmetry coordinates. Previous studies have shown that chemically interesting trends are often insensitive to the exact EHMO parameterization even if absolute values of calculated observables are very sensitive.^{13, 29, 31} Therefore, two quite different sets of parameters were investigated. Set I parameters, listed in Table I, employed H_{ii} values for s and p orbitals based on the

(31) L. S. Bartell, L. S. Su, and Hsiukang Yow, *Inorg. Chem.*, **9**, 1903 (1970).

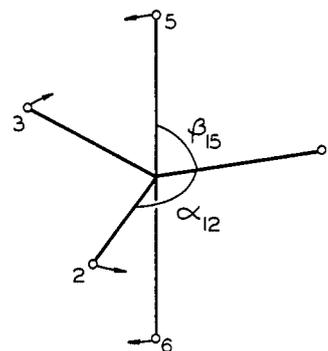


Figure 1. Numbering scheme for internal coordinates of the XY_5 molecule. Arrows indicate equatorial (S_{6a}) and axial (S_{7a}) displacements of E' symmetry with positive amplitude according to eq 4 and 5 carrying the molecule from a reference D_{3h} structure toward C_{4v} .

Table I. Orbital Parameters for Set I Calculations

Orbital	Exponent	$-H_{ii}$, eV
F_{3s}	1.968	29.68
F_{3p}	1.716	19.98
F_{3d}	1.10	7.00
F_{2s}	2.538	36.36
F_{2p}	2.468	15.64

VOIP of Basch, Viste, and Gray³² shifted by the charge parameter q to yield a moderately small charge on the phosphorus for a D_{3h} structure. Bond lengths were taken to be 1.551 Å, the mean length reported for PF_5 .²⁰ Set I used s and p orbital exponents, from Clementi and Raimondi,³³ shifted slightly, following Slater's rules, to account roughly for the atomic charges, and phosphorus 3d parameters were taken from Bartell, Su, and Yow.³¹ Set II parameters were those of Hoffmann, Howell, and Muetterties.¹⁰ They gave a superior ν_4 bending constant (case excluding 3d) but fairly large charges. It was observed that the total molecular energy for parameter set I decreased monotonically as the PF distance increased to 2.75 Å. For set II a minimum was observed at about 2.4 Å whether d orbitals were included or excluded. Although there is little physical significance to the minimum energy in EHMO calculations,³⁰ in prior work it has been observed that deformation energies may be better behaved in the vicinity of structures with minimum EHMO energy.³⁴ Therefore, for set II, a compromise PF internuclear distance of 2.0 Å, longer than the experimental value and somewhat shorter than $r_{\min}(\text{EHMO})$, was adopted.

Force constants were calculated as sketched in the previous section except that numerical EHMO energies at finite deformations were computed instead of analytical energies at infinitesimal deformations. The EHMO results, unlike POS, suffered both from round-off errors at small (1°) deformations and from anharmonicity at larger (6°) deformations. Conventional spectroscopic force fields are subject to the latter problem, also, of course. Molecular orbital calcula-

(32) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).

(33) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(34) L. Lohr, private communication.

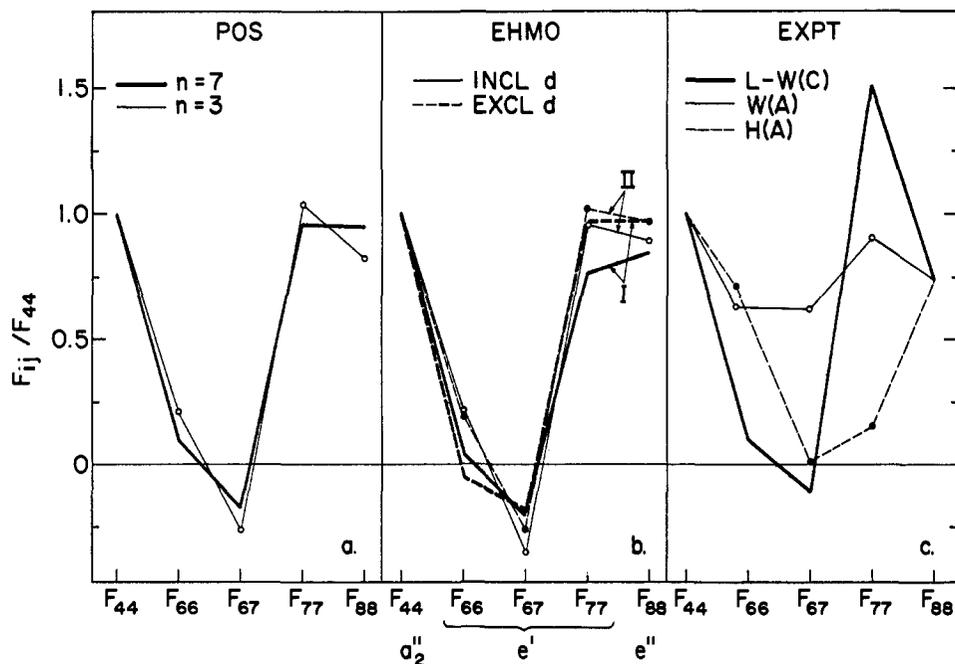


Figure 2. Bending force constant profile for PF_5 . (a) Points-on-a-sphere results for two values of repulsion hardness parameter n . (b) Extended Hückel results for set I (heavy lines) and set II (light lines) parameters. (c) Alternative experimental results including Levin-Wilt (C) field,¹⁸ Wilt (A) field,¹⁸ Holmes (A) field.¹⁸ The Holmes (B) field is similar to Levin-Wilt (C)

tions were performed both including and excluding d orbitals.

Pseudorotational Energies. The energetics of the Berry pseudorotational mechanism²² for interchanging axial and equatorial ligands *via* e' deformations was studied at several levels of approximation. First, the lowest energy C_{4v} structure along the Berry path ($D_{3h} \rightarrow C_{4v} \rightarrow D_{3h}$) was found by direct solution of the problem. To the extent that the POS and EHMO models represent the anharmonic force fields, E_B incorporates the full influence of anharmonicity on the pseudorotational barrier. Several quadratic approximations ΔE_B^{qa} were then investigated to find how serious the anharmonic corrections are likely to be.

In the case of the POS model, calculations could be performed exactly. If a C_{4v} structure is imposed on MX_5 , the potential energy derived from eq 1 is, in units of $(2K/R^n)$

$$V_T(C_{4v}) = [2(2 \sin \theta/2)^{-n} + (2 \cdot 2^{n/2} + 1)(2 \sin \theta)^{-n}] \quad (12)$$

where θ is the angle between the apical and basal bonds. Solving for the minimum energy of eq 12 with respect to variations in θ leads to θ_m characterizing the geometry of the minimum energy C_{4v} structure and to ΔE_B for the POS model. The structure and barrier, of course, depend upon n .

Corresponding values were found for the EHMO model by obtaining the energy at 5° increments and passing a parabola through the lowest three points to locate θ_m and ΔE_B .

Quadratic approximations were based on the e' quadratic force field

$$V_a = (1/2)(F_{66}S_{6a}^2 + F_{77}S_{7a}^2 + 2F_{67}S_{6a}S_{7a}) \quad (13)$$

If C_{4v} symmetry is imposed on the various $\Delta\alpha$'s and $\Delta\beta$'s of eq 3-6, the θ dependence of S_{6a} and S_{7a} can be

written as

$$S_{6a} = 6^{1/2} \left(\frac{2\pi}{3} - \theta \right) \quad (14)$$

and

$$S_{7a} = 2 \cdot 3^{-1/2} \left[\left(\theta - \frac{\pi}{2} \right) + \arcsin(\cos^2 \theta) \right] \quad (15)$$

These expressions inserted into eq 13 form the basis of the quadratic approximation for the minimum energy C_{4v} structure.

Results

Force Constants. Results for force constants, expressed in terms of the ratios F_{ij}/F_{44} , are shown in Figure 2. Ratios rather than absolute values were chosen for representation because, as discussed in the foregoing, the POS model yields only relative values and the absolute values yielded by the EHMO model are not expected to have any quantitative merit. Nevertheless, the force constants derived from EHMO set I, while low, were for the most part within a factor of 2 of the experimental constants. Set II was run at $r_{\text{PF}} = 2.0 \text{ \AA}$, a value much longer than the 1.551 \AA observed mean bond length, and it gave constants about fourfold smaller than those of set I. Lest it be feared that the constants in set II fell to such a small value that they were dictated mainly by surviving $F \cdots F$ nonbonded interactions known to be incorporated in EHMO calculations,³⁵ it may be noted that the F_{ij} fell by a factor of roughly $(r_{\text{FF}})^{-5}$. The EHMO nonbonded interactions for $\text{Ne} \cdots \text{Ne}$ and $\text{F} \cdots \text{F}$, on the other hand, fall more rapidly than this [roughly as $e^{-2.37/a_0}$ or r^{-10} at $r_{\text{FF}} \approx 2.2 \text{ \AA}$].^{36,37}

(35) R. S. Mulliken, *Rec. Chem. Progr.*, **13**, 67 (1952); *J. Amer. Chem. Soc.*, **72**, 4493 (1950); **77**, 877 (1955).

(36) L. S. Bartell, presented at the Colloquium in Conformational Analyses in Organic Molecules, Polymers, and Crystals, CNRS, Paris, France, June 1970.

(37) T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963).

Table II. Structure and Activation Energy^a of C_{4v} Pseudorotation Intermediate According to the Points-on-a-Sphere Model

Hardness, <i>n</i>	Exact		<i>F</i> ₆₇ ^b	Quadratic approximation		
	θ_m	ΔE_B		θ_m^{qa}	ΔE_B^{qa}	$\Delta E_B^{qa}/\Delta E_B$
2	103.6°	1.556	Exact	104.0°	5.17	3.32
			Zero	102.8°	14.79	9.50
4	102.4°	1.826	Exact	102.2°	6.34	3.47
			Zero	100.4°	15.24	8.35
7	100.8°	0.990	Exact	99.7°	3.84	3.88
			Zero	97.2°	8.40	8.48
10	99.5°	0.317	Exact	97.6°	1.50	4.73
			Zero	94.7°	3.30	10.43

^a Energy in units of (10⁻²K/R²). ^b Taken as its exact POS value or zero, retaining the exact values of *F*₆₆ and *F*₇₇.

Pseudorotation Barriers. Table II lists the barrier to Berry pseudorotation and θ_m for the lowest energy C_{4v} structure as calculated by the POS model as a function of *n*. Three levels of approximation are represented. First, ΔE_B , the exact barrier, is given with its corresponding θ_m . Then values based on the quadratic force field alone (eq 13), including and excluding the force constant *F*₆₇, are shown. The latter calculations illustrate the effect of neglecting anharmonicity and of neglecting the off-diagonal force constant, approximations that have been used in some published work. To parallel calculations based on experiment (where, of course, θ_m is not known exactly), the quadratic approximation calculations made use of θ_m values computed from the quadratic force field itself rather than the true, anharmonic θ_m values.

Corresponding barriers have not been tabulated for the molecular orbital calculations because the arbitrariness of the MO parameterization and certain numerical instabilities vitiate critical comparisons. Round-off errors of the order of 1 part per million in total EHMO energies coupled with anharmonicity made the smaller EHMO force constants subject to uncertainties of as much as 10 to 20%. Such uncertainties can render ΔE^{qa} uncertain in some cases by 100%. The POS model, being analytical, suffers from no such difficulty. Certain trends in the EHMO results could be observed. They are discussed in the next section.

Discussion

Force Constant Ratios. The most striking result is that the POS and EHMO models gave patterns of force constants very much alike over a large range of input parameters as can be seen in Figures 2a and 2b. This makes it easier to be optimistic about the physical significance of the results. All model calculations yielded a negative value for the interaction constant, *F*₆₇ (or positive value, if the equally valid convention of Holmes^{14,16} is used). The sign of the constant has a very decided Gillespie-Nyholm implication. It means that the symmetry coordinates *S*₆ and *S*₇ tend to have the same signs because, if they do, the potential energy is thereby reduced. More physically, it means that, as an equatorial bond angle opens up, a void is created in the coordination sphere into which the axial bonds tend to bend (or *vice versa*). These concerted e' motions start the molecule off along a Berry pseudorotational pathway. The larger the magnitude of this (negative) interaction constant, the smaller is the barrier to pseudorotation and, other constants being equal, the larger is θ_m for the C_{4v} structure.

Influence of d Orbitals. Several molecular orbital calculations exist which make it possible to study the effect of central atom d orbitals on the barrier to pseudorotation in MY₅ molecules.¹⁰⁻¹² In the case of PH₅, adding d orbitals to the basis set decreased the barrier somewhat both in the *ab initio* calculations of Allen, *et al.*,¹¹ and in the extended Hückel calculations of Hoffmann, *et al.*¹⁰ On the other hand, in EHMO calculations for PF₅, d orbitals increased the barrier in Hoffmann's calculations¹⁰ and in our set I but left it almost unchanged in set II. Whether any physically significant inferences can be drawn is discussed below. Hoffmann, *et al.*,¹⁰ attribute no particular meaning to the d orbitals except insofar as they stabilize both the *D*_{3h} and C_{4v} structures somewhat by dropping the energy of the nonbonding molecular orbital. We observed a consistent effect in our PF₅ calculations that may be worth recording. The d orbitals have scarcely any effect on the *changes* in energies of occupied molecular orbitals when the molecule is deformed a small distance along an e' equatorial bending coordinate, except in the case of the lowest e' (2p_F) pair of orbitals where the d orbitals increase the cost of the deformation. This particular pair of occupied orbitals is the pair which also seems to be most susceptible to a pseudo-Jahn-Teller destabilization^{5b,38,39} of *D*_{3h} symmetry in e' deformations and is the pair which led to the negative value of *F*₆₆ in set I calculations excluding d orbitals.⁴⁰ The d orbitals mitigate the pseudo-Jahn-Teller interaction by favoring p-d backbonding in the *D*_{3h} structure. An analogous effect is less important in the more primitive Gillespie-Nyholm case, PH₅, than in PF₅. Allen, *et al.*,¹¹ conclude for PH₅ that the d orbitals serve "only to overcome some inadequacies in the basis set and that no greater significance should be attached

(38) H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **235**, 537 (1956); V. Opik and M. H. L. Price, *ibid.*, **238**, 425 (1957); R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960).

(39) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

(40) The spontaneous equatorial e' deformation implied by the negative force constant *F*₆₆ in the set I calculations excluding d orbitals was analyzed by following the individual MO energies during an equatorial bend. The energy lowering has many contributing bits and pieces, the most important of which are second-order interactions^{5b,38,39} between a fairly low-lying occupied bonding e' MO (the one with large 2p σ coefficients) and the empty antibonding a₁'* and e'* MO's which strongly mix into the low-lying e' orbital during e' deformations. This mixing redistributes charge density favorably enough to make the deformation spontaneous. Note that the excitations are different from the ones proposed by Pearson³⁹ as the principal pseudo-Jahn-Teller culprit in PF₅. As noted in simple σ only Hückel calculations on MX₅ systems several years ago,^{5a} a C_{4v} structure with $\theta_m > 90^\circ$ is stabilized relative to *D*_{3h} if the central atom s orbital is sufficiently low lying (as it was in the present set I). If the central atom s orbital is raised (as it was in set II) the a₁'* MO is raised increasing the a₁'* - e' gap and reducing the pseudo-Jahn-Teller destabilization of *D*_{3h}.

to them." Nevertheless, d orbitals do introduce the possibility of electronic excitations with definite symmetry properties and, hence, may promote well-defined pseudo-Jahn-Teller softenings of deformations along certain symmetry coordinates. It is easy to envision XH_3 molecules in which the central atom d orbitals become more and more accessible for binding and in which they ultimately become dominant. During this transition toward increased d participation, the gap between the a_2'' (occupied) and e'' (empty) orbitals narrows rapidly (and the levels may even reverse). The associated interaction, as well as those noted in ref 40, is pseudo-Jahn-Teller active for e' deformations. It becomes strong when the gap narrows and ultimately leads to a spontaneous e' deformation. Therefore, it seems reasonable to conclude, for XH_3 at least, that increasing d orbital participation tends to lower the pseudorotational barrier.

Comparisons between POS and EHMO Models. In addition to the remarkable similarity between the POS and EHMO profiles of F_{ij} in Figure 2, there are other trends worth noting. Effects of varying n in the POS model mimic effects of varying d orbital participation in the EHMO model for MH_3 , and in a way that was tacitly recognized by Gillespie long ago.^{3,4} An intuitive grasp of the influence of n is simple. The higher the value of n , the "harder" are the POS repulsions, and $n = \infty$ represents a hard-sphere limit with no simple MO analog. For moderate n , interactions are small until the repelling points are close together. Thus, for a D_{3h} structure, the axial-equatorial repulsions (bonds at 90°) far outweigh the equatorial-equatorial repulsions (bonds at 120°) and axial bends are energetically more costly than equatorial in-plane bends (*i.e.*, $F_{77} > F_{66}$). If n is decreased more and more, the interactions get longer in range, axial and equatorial interactions become more nearly equivalent and softer, and the structure becomes more and more compliant. At $n = 0$ the repelling forces vanish and at negative n all bending deformations from D_{3h} are energetically favorable.

The above behavior for decreasing n roughly resembles that in a σ -bonded MH_3 associated with increasing d orbital participation. Stated another way, simple Gillespie-Nyholm aspects of structures and force fields deteriorate more and more as n decreases or as d orbital participation increases.⁴¹ Gillespie himself excluded complexes dominated by d orbital participation unless effects of d orbitals were taken into account by a ligand field model.⁴² We suggest that, rather than patching deficiencies of one simple model by introducing another of uncertain kinship, we can understand the breakdown of the POS model in a self-consistent Gillespie-Nyholm

(41) The fact that, in certain EHMO parameter ranges for PF_3 , a small d participation had an effect closely parallel to increasing n and improving instead of spoiling adherence to Gillespie-Nyholm theory, should not be allowed to detract from the main σ -bond arguments above. For one thing, the most conspicuous influence of d orbitals (set I) was observed with the poorest parameterization. Secondly, when π bonding is appreciable, new considerations are introduced. The VSEPR theory treats σ, π double bonds in the same way as single bonds except for the greater space requirement of the double bond in the coordination sphere (*cf.* $\text{F}_3\text{P}=\text{O}$ which, in EHMO calculations, does not require d orbitals to conform to VSEPR behavior). When ligands possess more than one valence electron, modest central atom d participation may induce π bonding and, hence, somewhat bulkier, less compliant bonds, as seen in set I, result for equatorial bonds. For axial bonds, however, the d- σ effect dominated even with set I parameters.

(42) R. J. Gillespie, *J. Chem. Soc.*, 4679 (1963).

framework. If we identify the repulsions in VSEPR theory with the mutual avoidances of localized molecular orbitals (bonds and lone pairs), we may expect sp^n hybrids to repel more or less in the fashion of points-on-a-sphere, for the principal lobes of sp^n hybrids radiate from the central atom in the direction of a well-defined point on the sphere around the atom. Pure p orbitals are imitated by points-on-a-sphere less well (and bonds modeled upon pure p bases lose their Gillespie-Nyholm aspects as discussed briefly in ref 5b) but, in practical cases, s orbitals are always available to participate with p orbitals in localized electron pairs. In contrast to sp^n hybrids, d orbitals radiate with no single dominant lobe, and the best avoidance of two d orbitals may correspond to bonds at 45 or 135° , neglecting ligand-ligand interactions. It may well turn out that the structures and energetics of systems of bonds involving d orbitals can be understood in terms of an orbital avoidance picture, but it is clear that the picture will not be the simple POS picture.

Discrimination between Alternative Experimental Force Fields. The fact that the POS and EHMO models for MX_3 yield profiles of force constants similar to each other and very similar to the F_{66}, F_{67}, F_{77} profile determined by Walker¹² in an *ab initio* study of PH_3 lends credence to the generality and physical plausibility of the approach. Encouraged by this success, we venture to judge alternative solutions of the spectroscopic problem plotted in Figure 2c. The outcome is obvious upon inspection. One and only one of the solutions, namely the Levin-Wilt (C) field,¹⁸ yields a profile resembling the POS and molecular orbital profiles. It has already been shown⁶ that electron diffraction data discriminate between the Holmes field A and Holmes field B¹⁶ in favor of field B [similar to Levin-Wilt (C)].¹⁸ Whether Wilt's field A¹⁸ and (nearly identical) field B can be similarly ruled out by diffraction data, confirming the present models, has not yet been tested. Neither is it established that the Levin-Wilt (C)¹⁶ field is optimized, for it is one of an infinity of similar solutions based on a plausible but arbitrary value of F_{57} . It is not inconceivable that the experimental profile will resemble the model profiles even more closely when element F_{57} (coupling a bend and a stretch) is finally established.^{42a}

Inference of VSEPR Force Law. The degree of hardness of valence shell electron pair repulsions summarized in the present POS variant has received some speculation in the literature. Bent has discussed directed valence in terms of the close packing of electron pairs, the various pairs being restricted to mutually impenetrable regions of various sizes.⁴³ Although the impenetrability suggests a hard force law, the regions are considered to be deformable. No clues are given for the treatment of force constants. Soft force laws are commonly invoked. Discussions in many papers regard valence shell electron pair repulsions as if they were strictly electrostatic with $n = 1$. Frequently this arises from a misconception of the VSEPR model of Gillespie and Nyholm and the failure to take into

(42a) NOTE ADDED IN PROOF. We have now carried out calculations of amplitudes of vibrations in PF_3 based on the Wilt field A. A comparison with electron diffraction amplitudes confirms the POS conclusion; Wilt fields A and B are ruled out.

(43) H. A. Bent, *Fortschr. Chem. Forsch.*, 14, 1 (1970); *J. Chem. Educ.*, 45, 768 (1968); 40, 446, 523 (1963).

account the close electrostatic balance (in nonpolar molecules) between repulsions (electron–electron and nuclear–nuclear) and attractions (electron–nuclear). This balance is one of the cornerstones of EHMO theory, and the fair qualitative success of EHMO theory lends some support to the dismissal of coulombic forces as the basis of VSEPR theory. On the other hand, because POS results do not depend heavily upon the value of n and because ligands in polar molecules may sometimes contribute a substantial coulomb force, coulomb-based models may enjoy substantial success in careful hands.^{44,45}

Thompson,⁴⁶ in drawing close parallels between Walsh diagrams and VSEPR theory *via* the bridge of easily visualized orbital localization schemes, has suggested the value of $n \approx 2$. His rationale is that electrons in localized orbitals may resemble particles in boxes with energy (kinetic energy) inversely proportional to the square of the box dimensions. As orbitals are forced together they are compressed along the line of approach. Thompson's kinetic energy argument, while very approximate, adds insights sometimes overlooked in valence theory.

Still other writers have discussed VSEPR repulsions as if they were atom–atom steric avoidances.⁴⁷ Although such interactions certainly exist, they are not considered by Gillespie^{3,4} and others^{5b} to be the principal ingredients in the force fields of molecules unless the central atom is small (first row) or the coordination number is high. Experimental^{37,48} and theoretical^{35,48} evidence favor a fairly hard ($n \approx 10$) interaction for atom–atom repulsions.

The only experimental value of n based on a VSEPR approach is a value of about 4 for IF_7 deduced from the amplitude of e_2'' and e_1' deformations observed in the gas-phase molecular structure.²⁵ In the case of XY_m compounds with $1 \leq m \leq 9$, only for $m = 7$ does the VSEPR–POS structure depend upon n . The interpretation of n for IF_7 , however, was somewhat clouded because the comparison of the experimental and POS calculated structures was based on a static POS geometry. The rather large puckering displacements of the equatorial fluorines in IF_7 are in part thermally induced and the latter component might distort the derived force law.

What, then, can be inferred about n from the present approach? Since one of the virtues is that results are fairly immune to deficiencies related to our ignorance of n , since the best function is probably not r^{-n} , anyway, and because the experiment itself leaves an appreciable uncertainty in force constants, we will have to be content with a rather rough and ready answer. The ratio of F_{66} to the larger force constants suggests a value of n in the vicinity of 7. A still larger value of n , perhaps as high as 12, would be required to reduce F_{67} to its

tentative experimental value while fitting F_{44} , F_{77} , and F_{88} in the mean. Similar inferences would be made from the *ab initio* force constants F_{66} , F_{77} , and F_{67} calculated for PH_5 from Walker.¹² The EHMO calculations are not in conflict with $n \approx 7$.

It is unknown to what extent the analysis for n is distorted by the POS assumption of equivalent bonds save for direction. Axial “three-center four-electron” bonds are conceived by some as being distinctly different in kind from the “normal” equatorial bonds in penta-valent compounds.⁹ Presumably this problem can be avoided in, say, analogous studies of MX_4 and MX_6 molecules for which all bonds in the equilibrium structure are equivalent. Unfortunately, in neither case is the force field as rich in bending constants as MX_5 , a fact which reduces checks of internal consistency. Our prejudice is that the value of n is probably smaller than 12 and possibly smaller than 7, but this prejudice cannot easily be defended on the basis of the present data. It is more constructive to consider it quite remarkable that such a severely oversimplified model as POS worked at all (and gave qualitatively acceptable results at even, say, $n = 3$) than it is to dwell upon finer distinctions. In PF_5 and PH_5 , however, it seems fair to conclude that the effective VSEPR law is significantly harder than coulomb.

Quadratic Approximation for Barrier. It is evidently so difficult to establish experimentally the true quadratic components of the molecular force field that we must be somewhat pessimistic about measuring the even less accessible cubic and higher order force constants well enough to calculate accurate barriers to pseudorotation. Therefore, it is helpful to have some plausible guide lines to gauge the effect of neglecting anharmonicity. Often, estimates of only the diagonal elements of the force constant matrix are available, so a practical test of the effect of neglecting off-diagonal elements is of some value. The success of the POS model in accounting for quadratic force constants is no guarantee that its higher-order constants are reasonable, but if the underlying basis is roughly correct, the ratio of higher order terms to quadratic terms must be dictated in large measure by geometry and considerations of continuity. For this reason, especially in view of the paucity of other information, it is reasonable to apply the POS model to the problem. The results tabulated in Table II are encouraging since, again, we find an insensitivity to the value of n adopted whether we look at results including or excluding the off-diagonal elements F_{67} . Neglect of anharmonicity makes the apparent pseudorotational barrier too high by perhaps fourfold, and neglect of F_{67} may augment the error by yet another factor of 2. Whether the POS model ratios of $\Delta E_B^{qa}/\Delta E_B$ are quantitatively accurate or not, they illustrate the difficulty in obtaining rigorously accurate barriers from vibrational spectra.

Inference of Barrier to Pseudorotation in PF_5 . Reaffirming the pitfalls of applying a speculative model to equivocal data, we hazard, nevertheless, an estimate to the Berry barrier in PF_5 . Adopting the force constants of the Wilt–Levin (C) field,¹⁸ of 0.26, 0.31, and 4.17 mdyn $\text{\AA}/\text{rad}^2$ for F_{66} , F_{67} , and F_{77} , respectively [which should be reevaluated using the newer frequencies of Miller, *et al.*¹⁹] we calculate $\theta_m = 97.0^\circ$ and $\Delta E_B^{qa} = 22.1$ kcal/mol. If we then apply the POS values for

(44) A. W. Searcy, *J. Chem. Phys.*, **28**, 1237 (1958); **31**, 1 (1959); A. E. Parsons and A. W. Searcy, **30**, 1635 (1959).

(45) Y. Takahata, G. W. Schnuelle, and R. G. Parr, *J. Amer. Chem. Soc.*, **93**, 784 (1971); G. W. Schnuelle and R. G. Parr, *ibid.*, in press.

(46) H. B. Thompson, *Inorg. Chem.*, **7**, 604 (1968); *J. Amer. Chem. Soc.*, **93**, 4609 (1971).

(47) One of the more successful of such treatments is that of R. F. Zahrobsky, *ibid.*, **93**, 3313 (1971).

(48) H. Margenau and N. R. Kestner, “Theory of Intermolecular Forces,” 2nd ed, Pergamon Press, Oxford, 1971; “Intermolecular Forces,” J. O. Hirschfelder, Ed., Interscience, New York, N. Y., 1967.

($\theta_m - \theta_m^{qa}$) and $\Delta E_m^{qa}/\Delta E_m$ corresponding to $n = 7$ [or 10] we estimate θ_m to be 98.1° (or 98.9°) and ΔE_B to be 5.7 kcal/mol (or 4.6 kcal/mol). These values compare with previous estimates by Holmes, *et al.*, (field B) of 91.4° and 15.3 kcal/mol in which a guess of the effect of anharmonicity was made, but in which F_{67} was neglected since it was not known at the time.¹⁵ A more recent value of 3.0 kcal/mol based on an observed bending anharmonicity in VF_5 scaled to PF_5 has also been estimated by Holmes.¹⁴ It will be interesting to investigate whether a transition metal complex conforms to the POS model as well as do compounds of nonmetals. In any event, we have more or less bracketed the barrier to pseudorotation in PF_5 and find a value low enough to permit facile intramolecular exchange but a value somewhat higher than given by the EHMO method.

Concluding Remarks

The POS variant of the valence shell electron pair repulsion model has shown sufficient promise in its application to force fields of XY_5 compounds that further studies are underway. Unanswered in the present investigation are its merits in treating simpler cases where *all* bonds are equivalent by symmetry (*cf.* SnCl_4 , TeF_6), decidedly more complex cases where auxiliary ideas are needed to interpret observations in a consistent way (*cf.* IF_7), and cases in which bonds are nonequivalent chemically as well as geometrically (*cf.* IOF_5). Preliminary results for the latter com-

pound⁴⁹ reveal that the POS and EHMO models are again strikingly parallel in their predictions of force fields and, moreover, are successful in accounting for radial forces governing the distribution of bond lengths as well as angular forces.

Applied to XY_5 molecules the POS scheme has the following salutary features. (1) It accounts in an elementary way for the symmetry and distribution of bond lengths^{3,4} and force constants. (2) It provides a rough physical criterion for selecting the proper solution from among several alternative force field solutions derived from vibrational spectra. (3) It offers a plausible method for relating pseudorotational barriers to force constants, a heretofore elusive undertaking. (4) It affords provocative evidence, in view of the harder than coulomb repulsions found and close correspondence between POS calculations, *ab initio* MO calculations, EHMO calculations devoid of coulomb interactions, and experiment, that the mutual avoidance (Pauli avoidance) of occupied, localized molecular orbitals is, as originally proposed by Gillespie and Nyholm, the proper basis for the valence shell electron pair repulsion theory.

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(49) L. S. Bartell, F. B. Clippard, and E. J. Jacob, *Acta Crystallogr.*, in press.

Reaction Pathways for the Photochemical Conversion of Ortho-Substituted Benzylideneanilines to Azoles

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Abstract: Benzylideneanilines substituted in the ortho position of the aniline ring by hydroxy, sulfhydryl, or amino groups are photochemically converted to the corresponding azoles. The possible reaction pathways depend on the substituent. Benzylidene-*o*-hydroxyaniline is stable at room temperature. Two photons are required to convert it first to the thermally unstable 2-phenylbenzoxazoline and then to 2-phenylbenzoxazole. Benzal-*o*-sulfhydrylaniline (Ib) is unstable at room temperature. It converts thermally to 2-phenylbenzothiazoline (IIb). Illumination of IIb yields 2-phenylbenzothiazole and Ib. Benzylidene-*o*-aminoaniline is stable at room temperature. Only one photon is required for the ring closure to 2-phenylbenzimidazole. The corresponding imidazoline could not be detected as an intermediate. It is either too short lived or nonexistent. All photo-reactions are accompanied by *trans* \rightarrow *cis* photoisomerizations of the Schiff bases.

Benzylideneanilines (I) substituted in the ortho position of the aniline ring by a hydroxy (Ia), mercapto (Ib), or an amino group (Ic) are photochemically converted to the respective heterocycles 2-phenylbenzoxazole (IIa), 2-phenylbenzothiazole (IIb), and 2-phenylbenzimidazole¹ (IIc). (The reason for including the azoline II in Scheme I will be explained below.)

The reaction takes place in degassed as well as in air-

saturated solutions. In the latter case the quantum yield is higher and stoichiometric amounts of H_2O_2 are found; without oxygen the formation of hydrogen has been observed by means of gas chromatography. The products were identified by comparison with authentic samples.

The reaction depends somewhat on the nature of the solvent. Ib and Ic yield in hexane as well as in ethanol the corresponding azoles, whereas Ia photohydrolyzes in ethanol into *o*-hydroxyaniline and benzaldehyde and

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