smallest bonding electron pairs, always go into the axial positions and the less electronegative ligands occupy the equatorial positions. The substitution of a fluorine by a methyl group decreases the effective electronegativity of the phosphorus and allows all the bonding pairs to move away from the phosphorus slightly, thus increasing all the bond lengths. In addition, however, the axial fluorine bonds are closer to the large methyl group bond than the equatorial fluorine bonds, hence they suffer a greater repulsion and increase more in length than the equatorial bonds. They are also pushed away from the methyl group so that the axial FPF bond angle becomes less than 180° in just the same way as the large lone pairs cause the same angle in the SF_4 and ClF_3 molecules to be less than 180°.[7,8]

Thus, the electron-pair repulsion theory accounts for all the observed structural features of these molecules without having to make any arbitrary assumptions concerning the types of atomic orbitals that take part in the bonding. The electron-pair theory merely assumes that each bond is due to an electron pair and that these electron pairs occupy orbitals, *i.e.*, have charge clouds, whose size is determined simply by the electronegativity of the atom, or group, which they are bonding to the central atom. The stereochemistry is determined by the arrangement of these electron pairs that minimizes their interactions taking into account, where necessary, their different sizes.

(8) R. J. Gillespie, *J. Chem. Phys.*, **37**, 2498 (1962).

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RECEIVED MARCH 28, 1966

Gillespie's Model, Molecular Orbitals, and Molecular Structure

Sir:

It is true that Gillespie's valence shell electron pair repulsion model[1] predicts the qualitative structural characteristics of PF_5, CH_3PF_4, $(CH_3)_2PF_3$, and the related molecules SF_4 and ClF_3, among others. It does this unambiguously and with fidelity. In our paper on fluorophosphorane structures[2] we placed, perhaps, insufficient emphasis on this fact and highlighted, instead, the alternative molecular orbital (MO) approach of Rundle.[3,4] There is no question that Gillespie's model, with a minimum of empirical ground rules, has somehow managed to capture the essence of a surprising amount of stereochemistry. Gillespie's rules are not always followed,[5] but the success of his model should stimulate us to search for the meaning behind his generalizations.

While the author agrees in large measure with Gillespie's statements in the preceding note[6] about the virtues of his own model, he holds very different views on the implications of a simple MO approach. The present disagreement boils down to what it is legitimate to attribute to the Rundle MO model. Gillespie's main arguments against Rundle's model are not, in fact, arguments against a bonafide MO model at all. None of the bond order parameters discussed by Hansen and this author[2] and reasonably criticized by Gillespie[5] was derived from MO theory. They were simplified valence bond, or theory of resonance, values introduced for purely illustrative purposes and interpreted by conventional valence bond arguments.[7] In brief discussions Rundle himself was content to apply such a patchwork scheme, but in approaching new problems he had considerably more faith in molecular orbital theory. Just how far Rundle actually proceeded in the cases at hand will never be known. Nevertheless, we have recently applied the simple Hückel MO model he taught us to a variety of "Gillespie-type" systems and have discovered patterns of significance in stereochemistry. Since these results are interesting in their own right and quite different from the results attributed by Gillespie to Rundle's model, it seems fitting to discuss them here.

For purposes of comparison with Gillespie's model, we introduce the simplest possible Hückel MO model capable of being formulated with adjustable ligand electronegativity. Following the spirit of Gillespie's approach, we place all ligands on the surface of a sphere about the central atom and consider only σ orbitals in the valence shell. The secular equation $|h_{ij} - E_k\delta_{ij}| = 0$ uses h_{ii} elements of $\alpha + n\beta$, α, and $\alpha + \delta\beta$ for central atom s orbitals, central atom p orbitals, and ligand orbitals, respectively. For bonded interactions, the elements h_{ij} are taken as $\beta\xi_{ij}$. The function ξ_{ij} expresses the self-evident dependency of h_{ij} on the relative orbital orientations and is unity for central s orbital interactions. It varies from 0 to 1 for central p orbital interactions. It is, of course, the angular dependency in the roots E_k which stems from the ξ_{ij} that determines the preferred bond angles; bond distance shifts can be inferred from Coulson bond orders. We may, perhaps, expect n to be in the range 5–10 and the electronegativity parameter δ to be 0–3 in this Hückel model neglecting all nonbonded interactions. The choice of parameters cannot be properly discussed in this brief note but, fortunately, the main points are not strongly dependent on the choice. Note that in our model the molecular shape *does not depend at all* on the value of the resonance integral β or on the details of atomic orbitals.

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(1) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); *J. Am. Chem. Soc.*, **85**, 467 (1963).

(2) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1775 (1965).

(3) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

(4) R. E. Rundle, *Acta Cryst.*, **14**, 585 (1961); *Record Chem. Progr.*, **23**, 195 (1962); *Surv. Progr. Chem.*, **1**, 81 (1963).

(5) L. S. Bartell, R. M. Gavin, Jr., H. B. Thomson, and C. L. Chernick, *J. Chem. Phys.*, **43**, 2547 (1965).

(6) R. J. Gillespie, *Inorg. Chem.*, **5**, 1634 (1966).

(7) C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954); H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960).

We must not expect such a naïve model to yield reliable energies and equilibrium molecular shapes when far more complex treatments have failed. We simply ask whether such a model, which has no more assumptions in it than Gillespie's model,[8] can exhibit the same set of correlations as Gillespie's model—namely, to recognize structural symmetries when they should exist and, in molecules which are unsymmetrical by virtue of lone pairs or ligand electronegativity differences, to predict directions (*not* magnitudes) of deformation. In comparisons with a quasi-steric model, it is of especial interest to find what can be done with a model which utterly neglects nonbonded interactions.[9] The answers, insofar as they pertain to points raised by Gillespie,[5] are briefly outlined below. The excuse for studying such a simple model at all is that the success of Gillespie's model hints of an underlying simplicity in nature.

(I) Gillespie maintains with some justification that the Rundle picture takes into account only p orbitals. Actually, in cases like XeF_2 and XeF_4 (but not XeF_6!) the p-orbital treatment gives a reasonably good result and the net s orbital contribution to bonding is nil. In cases where Gillespie lone pairs are unsymmetrically distributed and behave as stereochemically active ligands, the MO model gives clear warnings that p orbitals are insufficient. For correct results in these molecules it is absolutely essential to feed the MO model just as many electrons as are utilized in the Gillespie model. This requires the inclusion of the s orbital on the central atom. This orbital is given a considerably lower energy than the p orbitals, and mixing is small but vital. Note that no preconception of hybridization or directed valence is necessary. The preferred molecular geometry falls right out of the solutions of the MO secular equations. Also, popular belief notwithstanding, Rundle did not totally disregard s-orbital involvement as a glance at his MO correlation diagram for XeF_4 will confirm.[3]

(II) Gillespie infers from the directional properties of p orbitals that a simple p-orbital MO treatment of PF_5 should lead naturally to a square pyramid. Actually, a Hückel treatment limited to p orbitals makes the trigonal bipyramid appreciably more stable than the square pyramid with phosphorus in the equatorial plane. This result is independent of the MO parameters chosen. If the square pyramid is allowed to deform by increasing the angles between the axial and equatorial bonds while preserving C_{4v} symmetry, a lower MO energy can be obtained. An energy minimum is achieved at a square-pyramidal configuration which virtually minimizes the mean-square deviations between square-pyramidal angles and the most closely corresponding trigonal-bipyramidal angles. The deformed square pyramid is very slightly lower in MO energy than the trigonal bipyramid, but this energy difference is reversed as soon as the phosphorus s orbital is introduced.

(III) Gillespie questioned the ability of a simple MO model to explain effects of lone pairs and ligand electronegativity on bond angles. In fact, the MO model handles these effects correctly in cases studied to date. For example, in ClF_3, provided the s orbital is included, the MO result yields a T-shaped molecule with FClF angles *smaller* than 90°. The FClF angle tends to decrease as ligand electronegativity is increased, exactly as required by Gillespie's theory. If the s orbital and its complement of electrons are left out of the treatment of ClF_3, the molecule fans out to a planar equilateral triangle.

(IV) Gillespie points out that his model handles in a straightforward manner the effect of increasing methyl substitution on the equatorial bond length in $(CH_3)_nPF_{5-n}$. The theory of resonance, on the other hand, deals with the effect clumsily and, at best, ambiguously. Hückel MO calculations based only on p orbitals give a PF(eq) bond order shift in the wrong direction. Inclusion of the phosphorus s orbital is able to rectify the bond order shift, however, illustrating once again the important role of the s orbital. The parameterization which makes the MO results most regularly follow the electron pair repulsion results in all structural implications has not yet been investigated in detail.

All in all, it is quite astonishing and enlightening to find that the simple Hückel model (which altogether *neglects* explicit electron repulsions) closely parallels the Gillespie model (which considers *only* electron repulsions.) This parallelism includes not only molecular geometries but also distributions of electron pairs. Localized MO's constructed from the delocalized MO's exhibit very Gillespie-like shifts in centers of gravity. Perhaps further exploration along this line will uncover the deeper significance of the valence shell electron pair repulsion model.

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RECEIVED MAY 19, 1966

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(8) In ref 1 are listed a number of rules calibrated against nature. In addition, the force law between electron pairs and the placement of the pairs are left sufficiently indefinite to avoid certain difficulties encountered in a purely steric theory.

(9) The neglect of nonbonded repulsions has a certain merit. Nonsteric aspects of directed valence can be diagnosed, and plausible repulsions can be grafted on later to keep XeF_6 or ClF_3, for example, from deforming too far. There is some evidence that popular extended Hückel treatments so overemphasize nonbonded repulsions that nonsteric forces may not be allowed to play their full role.