Correspondence

The Structures of PF_5, CH_3PF_4, and $(CH_3)_2PF_3$

Sir:

The structures of PF_5, CH_3PF_4, and $(CH_3)_2PF_3$ have recently been accurately determined by Bartell and Hansen[1] by the electron diffraction technique. They discuss their results in terms of a theory first proposed by Havinga and Wiebenga[2] to describe interhalogen compounds and extended by Rundle[3] to cover other molecules, but they mention that their results can also be explained by the electron-pair repulsion theory.[4] In this note we show that this latter theory, in fact, gives a better explanation of all the structural features of these molecules than does Rundle's theory. The molecular parameters for these three molecules are shown in Figure 1. The important features that have to be explained are the following: (1) The molecules are trigonal bipyramids, or distorted trigonal bipyramids. (2) Methyl groups occupy equatorial positions. (3) Axial bonds are longer than the corresponding equatorial bonds. (4) All the bond lengths increase, and the ratio of the length of the axial bonds to the length of the equatorial bonds r_{ax}/r_{eq} increases as the number of a CH_3 substituents increases. (5) Methyl substitution causes the P–F bonds to be bent away from the CH_3 groups.

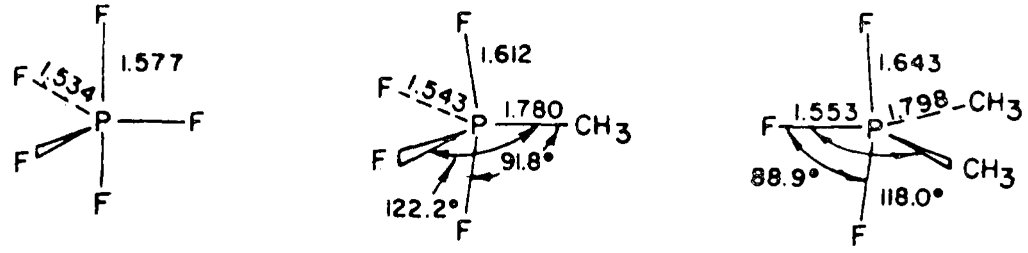

Figure 1.

Rundle[3] assumes that only p orbitals are involved in the bonding and that the axial bonds are three-center four-electron bonds with a bond order of approximately $^1/_2$. The remaining four bonding electrons bind the three equatorial ligands and so the bond orders are $^2/_3$. Thus, the axial bonds are expected to be more polar and longer than the equatorial bonds, and the least electronegative ligands would be expected to go to the equatorial sites. Thus (2) and (3) are explained. Point (1) is not satisfactorily explained, as there is no obvious reason why the molecule should adopt a trigonal-bipyramid shape and indeed the three p orbitals would seem to lead more naturally to the square-pyramid shape. Bartell and Hansen[1] attempt to explain (4) by assuming that the 3s orbital is also involved in bonding. If it contributes equally to all five bonds, then the equatorial bonds have an order of $^2/_3 + {}^1/_5$, while the axial bonds have an order of $^1/_2 + {}^1/_5$. If, on substituting fluorine by methyl, the latter by virtue of its smaller electronegativity forms a bond with considerable s character, the remaining bonds would, in the extreme case, have bond orders of $n_{eq} = 1$ and $n_{ax} = {}^1/_2$. Although this explains the increase in the ratio of axial to equatorial bond lengths, it would seem to imply that the equatorial bonds should decrease in length as n_{eq} increases from $^{13}/_{15}$ to 1, whereas they are, in fact, observed to increase in length. Point (5) cannot be explained at all, without invoking additional steric effects, and, in any case, the structures of the closely related ClF_3 and SF_4 molecules cannot be explained on this basis.

The electron-pair repulsion theory assumes that the interactions between the electron pairs in the valency shell of the central atom determine its stereochemistry.[4] Electron pairs bonding electronegative ligands are smaller and take up less space on the surface of the central atom than electron pairs binding less electronegative ligands.[4] It has been shown that the most probable arrangement of five equivalent electron pairs is the trigonal bipyramid.[5,6] Thus, any molecule in which there are five single bonds to equivalent ligands is expected to be a trigonal bipyramid. The axial electron pairs in this arrangement are not equivalent to the equatorial pairs, and, in particular, since the former have three nearest neighbors at 90°, while the latter have only two such neighboring pairs, equilibrium can only be attained if the axial pairs are at a greater distance from the nucleus than the equatorial pairs. Thus, in all such trigonal-bipyramid molecules the axial bonds are longer than the equatorial bonds.[6,7] Moreover, the smallest electron pairs, which have the smallest interactions with other electron pairs, tend to go into the axial positions, and the larger electron pairs occupy the equatorial positions where there is more room for them. Thus, the most electronegative ligands, which have the

---

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

(2) E. E. Havinga and E. H. Wiebenga, *Rec. Trav. Chim.*, **78**, 724 (1959).

(3) R. E. Rundle, *Acta Cryst.*, **14**, 585 (1961); *Record Chem. Progr.*, **23**, 195 (1962); *J. Am. Chem. Soc.*, **85**, 112 (1963).

(4) 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**, 4671 (1963).

(5) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960).

(6) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

(7) R. J. Gillespie, *Can. J. Chem.*, **39**, 318 (1961).

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).

(9) On leave from McMaster University, Hamilton, Ont., Canada.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MANCHESTER
MANCHESTER, ENGLAND
R. J. GILLESPIE[9]

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.

---

(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).