PENTAVALENT BONDS

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PCl_5, PF_5, and $Fe(CO)_5$ are examples of molecules which possess the trigonal bipyramidal structure (1). In a molecule possessing this structure three bonds are directed to the three corners of the common base of the two pyramids and two bonds are directed to the vertices of the two pyramids. The former bonds are referred to as equatorial bonds, the latter as axial bonds. Symmetry considerations lead one to expect that, in general, an axial bond would not be equivalent to an equatorial bond.

In a recent paper (2) the author developed the theory of the trigonal bipyramidal structure . One **s**, $1 + 2n$ **p**, and $3 - 2n$ **d** orbitals were used. The composition of an axial bond and the composition of an equatorial bond as functions of **n** can be calculated from the theory.

These calculations have been carried out and the data are presented in Tables I and II. It is evident that for all values of **n** an axial bond differs considerably in composition from an equatorial bond. The composition of an axial bond is approximately constant as **n** varies. An axial bond is about 0.16 **s**, 0.50 **p**, and 0.34 **d** in character. The composition of an equatorial bond varies with **n**. When **n** is 1.000 an equatorial bond is about 0.23 **s**, 0.67 **p**, and 0.10 **d** in character.

TABLE I

Composition of an Equatorial Bond Orbital

n[a]	Amount of **s**	Amount of **p**	Amount of **d**
1.0000	0.235	0.667	0.098
0.9000	0.230	0.600	0.170
0.8000	0.228	0.533	0.238
0.4444	0.227	0.296	0.477
0.2000	0.227	0.133	0.639
0.1000	0.228	0.067	0.705
0.0000	0.233	0.000	0.767

TABLE II

Composition of an Axial Bond Orbital

n[a]	Amount of s	Amount of p	Amount of d
1.0000	0.147	0.500	0.353
0.9000	0.155	0.500	0.345
0.8000	0.158	0.500	0.342
0.4444	0.160	0.500	0.340
0.2000	0.159	0.500	0.347
0.1000	0.157	0.500	0.343
0.0000	0.150	0.500	0.350

[a]The overall composition of the five orbitals is $s\ p^{1+2n}\ d^{3-2n}$.

BIBLIOGRAPHY

1. L. Pauling, **The Nature of the Chemical Bond** (Cornell University Press, Ithaca, 1940).
2. G. H. Duffey, J. Chem. Phys. **17,** 196 (1949).