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Bipyramidal Pentacovalent Bond Orbitals

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The Pauling-Slater theory of directed valence is applied to the trigonal bipyramid structure. Covalent molecules of the type AB_5 are considered. It is assumed that the bonding orbitals are of composition $sp^{1+2n}d^{3-2n}$, and the bond strengths are determined as a function of n .

ELECTRON diffraction measurements have indicated that some molecules have the configuration of a trigonal bipyramid. Among these are PF_5 , PF_3Cl_2 , PCl_5 , $Fe(CO)_5$, and $MoCl_5$. It is of interest to apply the method of directed valence bonds as developed by Pauling^{1,2} and Slater³ to this structure.

Consider spd hybrid orbitals for bonds directed from a central atom to the corners of a regular trigonal bipyramid. Assume that the two axial bonds are equivalent and that the three other bonds are equivalent to each other but not, in general, to the axial bonds. Also assume that the configuration is $sp^{1+2n}d^{3-2n}$ where $0 \leq n \leq 1$. When it is introduced, this assumption limits the discussion to a set of orbitals having the symmetry⁴ D_{3h} . Differences in the radial parts of the wave functions will be neglected and the angular parts hybridized to give the desired structure.

The angular parts of the s , p , and d wave functions, normalized to 4π , are given by the equations

$$s=1, \quad (1)$$

$$p_x = \sqrt{3} \sin\vartheta \cos\varphi, \quad (2)$$

$$p_y = \sqrt{3} \sin\vartheta \sin\varphi, \quad (3)$$

$$p_z = \sqrt{3} \cos\vartheta, \quad (4)$$

$$d_z = [(5)^{1/2}/2](3 \cos^2\vartheta - 1), \quad (5)$$

$$d_{xy} = [(15)^{1/2}/2] \sin^2\vartheta \cos 2\varphi, \quad (6)$$

$$d_{x+y} = [(15)^{1/2}/2] \sin^2\vartheta \sin 2\varphi, \quad (7)$$

$$d_{x+z} = (15)^{1/2} \sin\vartheta \cos\vartheta \cos\varphi, \quad (8)$$

and

$$d_{y+z} = (15)^{1/2} \sin\vartheta \cos\vartheta \sin\varphi, \quad (9)$$

where ϑ and φ are the angles used in polar coordinates. The axis of the bipyramid will be chosen as the z axis.

Three equivalent bonds lying in the xy plane and separated by angles of 120° may be represented by the functions⁴

$$\psi_1 = [(1/\sqrt{3}) \sin\alpha]s + [(\sqrt{2}/\sqrt{3}) \cos\beta]p_x - [(1/\sqrt{3}) \cos\alpha]d_z + [(\sqrt{2}/\sqrt{3}) \sin\beta]d_{xy}, \quad (10)$$

$$\psi_2 = [(1/\sqrt{3}) \sin\alpha]s - \{[1/(6)^{1/2}] \cos\beta\}p_x + [(1/\sqrt{2}) \cos\beta]p_y - [(1/\sqrt{3}) \cos\alpha]d_z - \{[1/(6)^{1/2}] \sin\beta\}d_{xy} - [(1/\sqrt{2}) \sin\beta]d_{x+y}, \quad (11)$$

$$\psi_3 = [(1/\sqrt{3}) \sin\alpha]s - \{[1/(6)^{1/2}] \cos\beta\}p_x - [(1/\sqrt{2}) \cos\beta]p_y - [(1/\sqrt{3}) \cos\alpha]d_z - \{[1/(6)^{1/2}] \sin\beta\}d_{xy} + [(1/\sqrt{2}) \sin\beta]d_{x+y}. \quad (12)$$

If it is assumed that the maxima of the p and d functions for the axial bonds lie on the z axis, the axial bonds may be represented by the

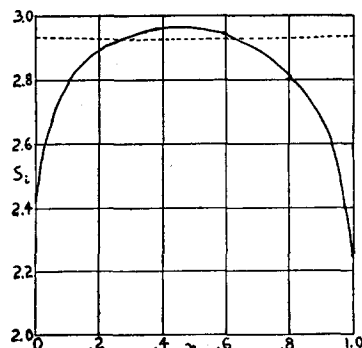


FIG. 1. Trigonal bipyramidal orbitals. The solid line represents S_e , the strength of an equatorial bond. The dotted line represents S_a , the strength of an axial bond. Each of these is plotted against n where the arrangement is $sp^{1+2n}d^{3-2n}$.

¹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).

² L. Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931).

³ J. C. Slater, *Phys. Rev.* **37**, 481 (1931).

⁴ See G. Kimball, *J. Chem. Phys.* **8**, 188 (1940).

TABLE I. Results^a of calculations on trigonal bipyramidal orbitals of type $sp^{1+2n}d^{3-2n}$.

n	$\cos\beta$	$\cos\alpha$	S_1 , strength of equatorial bond	S_4 , strength of axial bond
1.0000	1.0000	0.5424	2.249	2.937
0.9000	0.9487	0.5574	2.681	2.932
0.8000	0.8944	0.5615	2.812	2.930
0.4444	0.6667	0.5659	2.963	2.928
0.2000	0.4472	0.5637	2.887	2.929
0.1000	0.3162	0.5607	2.787	2.930
0.0000	0.0000	0.5485	2.418	2.935

^a These bond strengths may be compared with the following reported by Pauling (see reference 1). The best bond orbital obtainable from $s-p-d$ hybridization has a strength of 3.000. The best two equivalent orbitals, oppositely directed, obtainable on $s-p-d$ hybridization have a strength of 2.96.

functions⁵

$$\psi_4 = [(1/\sqrt{2}) \cos\gamma]s + (1/\sqrt{2})p_z + [(\sin\gamma \cos\delta)/\sqrt{2}]d_z + [(\sin\gamma \sin\delta)/\sqrt{2}]d_{xy}, \quad (13)$$

$$\psi_5 = [(1/\sqrt{2}) \cos\gamma]s - (1/\sqrt{2})p_z + [(\sin\gamma \cos\delta)/\sqrt{2}]d_z + [(\sin\gamma \sin\delta)/\sqrt{2}]d_{xy}. \quad (14)$$

The parameters in Eqs. (10), (11), (12), (13), and (14) are subject to conditions imposed by the orthogonality of the axial bond functions to the other bond functions. Thus if $\sin\delta \neq 0$, $\sin\beta = 0$. Also $\sin\alpha \cos\gamma = \cos\alpha \sin\gamma \cos\delta$. The assumption that the configuration is $sp^{1+2n}d^{3-2n}$ gives the relation $\sin^2\alpha + \cos^2\gamma = 1$. This gives the relations

$$\alpha = \gamma, \quad (15)$$

$$\cos\delta = 1. \quad (16)$$

Four orbitals orthogonal to $\psi_1, \psi_2, \psi_3, \psi_4$, and ψ_5 with $\cos\delta = 1$ can be set up as follows:

$$\psi_6 = [(\sqrt{2}/\sqrt{3}) \sin\beta]p_x - [(\sqrt{2}/\sqrt{3}) \cos\beta]d_{xy} + (1/\sqrt{3})d_{x+z}, \quad (17)$$

⁵ See R. Hultgren, Phys. Rev. 40, 891 (1932).

$$\psi_7 = -\{[1/(6)^{1/2}] \sin\beta\}p_x + [(1/\sqrt{2}) \sin\beta]p_y + \{[1/(6)^{1/2}] \cos\beta\}d_{xy} + [(1/\sqrt{2}) \cos\beta]d_{x+y} + (1/\sqrt{3})d_{x+z}, \quad (18)$$

$$\psi_8 = -\{[1/(6)^{1/2}] \sin\beta\}p_x - [(1/\sqrt{2}) \sin\beta]p_y + \{[1/(6)^{1/2}] \cos\beta\}d_{xy} - [(1/\sqrt{2}) \cos\beta]d_{x+y} + (1/\sqrt{3})d_{x+z}, \quad (19)$$

$$\psi_9 = d_{y+z}. \quad (20)$$

The relation between n and β is

$$\cos^2\beta = n. \quad (21)$$

Consider molecules or ions of the type AB_5 and assume that the energy of the $A-B$ bond is proportional to the product of the squares of the strengths of the orbitals of the two atoms.⁶ The strength of an equatorial bond equals S_1 , the value of ψ_1 when $\vartheta = \pi/2$, $\varphi = 0$. The strength of an axial bond equals S_4 , the value of ψ_4 when $\vartheta = 0$. The covalent bond energy of the molecule is then proportional to $3S_1^2 + 2S_4^2$. The results of maximizing this function for various values of $\cos\beta$ are given in Table I and Fig. 1.

If n can change without changing the electronic energy of the central atom, n will equal 4/9 for the most stable structure and the strength of an axial bond will equal 2.928, the strength of an equatorial bond 2.963. In general, however, a change in n will change the electronic energy of the central atom. For example, in PCl_5 , n would presumably not differ much from 1. When n equals 1, the strength of an axial bond equals 2.937, and the strength of an equatorial bond equals 2.249.

⁶ See H. Kuhn, J. Chem. Phys. 16, 727 (1948). The results obtained are not very sensitive to the form of assumption made at this point. For instance, if we assumed that the energy of the $A-B$ bond is proportional to the product of the strengths of the orbitals of the two atoms, the calculated bond strengths would not differ by more than 0.5 percent from the values reported here.