# Bipyramidal Heptacovalent Bond Orbitals

George H. Duffey

## TABLE II.

| Anions | Graphical (Li-Na-K) | Pascal | Xanion Graphical (Mg-Zn-Cd) | Graphical (Ca-Sr-Ba) |
|---|---|---|---|---|
| Formate | 20.50 | 16.90 | 20.00 | 15.00 |
| Acetate | 34.00 | 28.76 | 29.50 | 25.00 |
| Propionate | 44.00 | 40.62 | 39.75 | 44.00 |
| Butyrate | 55.50 | 52.48 | 52.50 | 52.50 |
| Palmitate | 189.0 | 194.8 | 185.0 | 187.5 |
| Stearate | 206.0 | 218.5 | 209.0 | 212.0 |
| Oleate | 197.0 | 207.9 | — | — |
| Oxalate | 34.40 | 27.94 | 38.00 | 34.00 |
| Malonate | 45.50 | 39.80 | 52.00 | 53.00 |
| Succinate | 58.80 | 51.66 | 60.00 | 36.00 |
| Tartrate | 68.00 | 60.88 | 60.00 | 68.00 |
| Citrate | 79.50 | 79.17 | — | — |
| Benzoate | 72.50 | 67.72 | 70.00 | 68.50 |
| Salicylate | 81.00 | 73.93 | 75.50 | 74.50 |
| Cinnamate | 89.00 | 80.03 | — | — |
| Hippurate | 98.50 | 92.35 | — | — |

## TABLE III.

| Series | $\chi Li^+$ $\chi A$ | $\chi B$ | $\chi Na^+$ $\chi A$ | $\chi B$ | $\chi K^+$ $\chi A$ | $\chi B$ |
|---|---|---|---|---|---|---|
| Formate | 1.10 | 1.0 | 3.97 | 5.00 | 10.62 | 9.00 |
| Acetate | 1.18 | 1.14 | 5.19 | 5.70 | 10.55 | 10.26 |
| Propionate | 1.87 | 1.26 | 4.90 | 6.30 | 13.23 | 11.34 |
| Butyrate | 1.65 | 1.54 | 6.10 | 7.70 | 14.54 | 13.86 |
| Palmitate | 2.40 | 1.74 | 7.40 | 8.70 | 16.90 | 16.66 |
| Oleate | 2.40 | 2.24 | 13.10 | 11.20 | 18.20 | 20.16 |
| Stearate | 3.10 | 3.06 | 17.10 | 15.30 | 26.30 | 27.54 |
| Benzoate | 1.36 | 1.06 | 5.07 | 5.30 | 10.12 | 9.54 |
| Salicylate | 1.49 | 1.24 | 4.74 | 6.20 | 12.65 | 11.16 |
| Cinnamate | 2.39 | 2.14 | 9.65 | 10.70 | 21.70 | 19.26 |
| Hippurate | 2.74 | 2.54 | 13.30 | 12.70 | 21.00 | 22.86 |
| Oxalate | 1.81 | 1.70 | 8.40 | 8.50 | 15.62 | 15.30 |
| Malonate | 1.84 | 1.60 | 8.15 | 8.00 | 13.75 | 14.40 |
| Succinate | 1.70 | 1.75 | 9.01 | 8.75 | 15.40 | 15.75 |
| Tartrate | 2.29 | 2.10 | 11.99 | 10.50 | 17.26 | 18.90 |
| Citrate | 2.12 | 1.96 | 10.40 | 9.80 | 17.05 | 17.64 |

### Ikenmeyer's Relation

Ikenmeyer's relation[3] has been examined in the case of alkali salts of organic acids and the graphs obtained are shown in Fig. 2. These curves show none of the linearity which is obtained by the authors' method of plotting. There is, however, a general similarity between the curves for each element of a group in the periodic table.

[3] K. Ikenmeyer, Ann. d. Physik 1, 169 (1929).

### SUMMARY

The linear relation between $\chi_m$ and the number of electrons in the cations established in Part I of this paper was observed to hold good for the alkali salts containing a common organic anion. From this relation, values have been calculated for the susceptibilities of the cations and anions in these salts.

# Bipyramidal Heptacovalent Bond Orbitals

George H. Duffey
*Chemistry Department, South Dakota State College, Brookings, South Dakota*
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A set of seven orthogonal bond orbitals of symmetry $D_{5h}$ is considered. The orbitals are of type $sp^3d^3$. When the attached groups are all equivalent (such as in the bipyramidal $AB_7$ structure), the equatorial orbitals *and* the axial orbitals are strong. In general, the composition of an axial orbital differs considerably from the composition of an equatorial orbital. The discussion supports the view that $IF_7$ has a pentagonal bipyramidal structure.

SEVERAL arrangements of seven groups around a central atom are possible. Kimball[1] considered the $ZrF_7^{-3}$ and $TaF_7^{-2}$ structures. Recently, evidence[2] supporting a pentagonal bipyramidal structure for $IF_7$ has been presented.

In this paper the method of directed valence bonds[3] is used in discussing the pentagonal bipyramidal structure of symmetry $D_{5h}$. The fivefold axis is assumed to lie on the $Z$ axis. The $s$, $p$, and $d$ wave functions are

[1] G. Kimball, J. Chem. Phys. 8, 188 (1940).
[2] Lord, Lynch, Schumb, and Slowinski, J. Am. Chem. Soc. 72, 522 (1950).
[3] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

defined in the same way as in previous papers[4] by the author.

The five equivalent bonds lying in the $xy$ plane, separated by angles of $2\pi/5$, may be represented by the functions

$$\psi_1 = \{[1/(5)^{\frac{1}{2}}]\sin\alpha\}s + [\sqrt{2}/(5)^{\frac{1}{2}}]p_x - \{[1/(5)^{\frac{1}{2}}]\cos\alpha\}d_z + [\sqrt{2}/(5)^{\frac{1}{2}}]d_{xy}, \quad (1)$$

$$\psi_2 = \{[1/(5)^{\frac{1}{2}}]\sin\alpha\}s + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 72°\}p_x + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 72°\}p_y - \{[1/(5)^{\frac{1}{2}}]\cos\alpha\}d_z + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 144°\}d_{xy} + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 144°\}d_{x+y}, \quad (2)$$

[4] See G. H. Duffey, J. Chem. Phys. 17, 196 (1949).

TABLE I. Results of calculations on pentagonal bipyramidal orbitals.

| Function maximized | Amount[a] of $s$ in an equatorial orbital | $S_1$, Strength of an equatorial orbital | Amount[a] of $s$ in an axial orbital | $S_6$, Strength of an axial orbital |
|---|---|---|---|---|
| $5S_1+2S_6$ | 0.1311 | 2.976 | 0.1723 | 2.920 |
| $S_1$ | 0.0889 | 2.991 | 0.2778 | 2.806 |
| $S_6$ | 0.1667 | 2.933 | 0.0833 | 2.957 |

[a] Note that the $p$ content of any equatorial orbital is $\frac{3}{5}$; the $p$ content of any axial orbital is $\frac{1}{2}$.

$$\psi_3 = \{[1/(5)^{\frac{1}{2}}]\sin\alpha\}s + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 144°\}p_x$$
$$+ \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 144°\}p_y - \{[1/(5)^{\frac{1}{2}}]\cos\alpha\}d_z$$
$$+ \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 72°\}d_{xy} - \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 72°\}d_{x+y}, \quad (3)$$

$$\psi_4 = \{[1/(5)^{\frac{1}{2}}]\sin\alpha\}s + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 144°\}p_x$$
$$- \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 144°\}p_y - \{[1/(5)^{\frac{1}{2}}]\cos\alpha\}d_z$$
$$+ \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 72°\}d_{xy} + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 72°\}d_{x+y}, \quad (4)$$

$$\psi_5 = \{[1/(5)^{\frac{1}{2}}]\sin\alpha\}s + \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 72°\}p_x$$
$$- \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 72°\}p_y - \{[1/(5)^{\frac{1}{2}}]\cos\alpha\}d_z$$
$$+ \{[\sqrt{2}/(5)^{\frac{1}{2}}]\cos 144°\}d_{xy}$$
$$- \{[\sqrt{2}/(5)^{\frac{1}{2}}]\sin 144°\}d_{x+y}. \quad (5)$$

In testing these functions for orthogonality and in determining their composition, use the relation

$$\cos 144° + \cos 72° = -\tfrac{1}{2}. \quad (6)$$

This relation can be proved with the help of well-known trigonometric identities.

If it is assumed that the maxima of the $p$ and $d$ functions for the axial bonds lie on the $Z$ axis[4] and that the orbitals are of symmetry $D_{5h}$, the axial bonds may be represented by the functions

$$\psi_6 = \{[1/\sqrt{2}]\cos\beta\}s + (1/\sqrt{2})p_z + \{[1/\sqrt{2}]\sin\beta\}d_z, \quad (7)$$

$$\psi_7 = \{[1/\sqrt{2}]\cos\beta\}s - (1/\sqrt{2})p_z + \{[1/\sqrt{2}]\sin\beta\}d_z. \quad (8)$$

Let

$$\beta = \alpha, \quad (9)$$

so that these seven functions form an orthogonal set. Their over-all composition is $sp^3d^3$.

Two functions orthogonal to $\psi_1\cdots\psi_7$ can be set up as follows:

$$\psi_8 = d_{x+z}, \quad (10)$$

$$\psi_9 = d_{y+z}. \quad (11)$$

Let the maximum value of $\psi_1$ be called $S_1$, and the maximum value of $\psi_6$, $S_6$. Consider molecules or ions

of type $AB_7$. Assume the energy of each $A$-$B$ bond is given by Eq. (13) in "Hexacovalent bond orbitals III."[5] In general, $W$ for an axial bond differs from $W$ for an equatorial bond. However, if the degree of ionic character of an axial bond and of an equatorial bond are assumed to be equal and constant, the sum of the $W$'s and, incidentally, the sum of the $R$'s over all bonds in $AB_7$ are not changed when $\alpha$ is changed. Then the value of $\alpha$ giving the largest sum of the bond energies is found by maximizing $5S_1 + 2S_6$. The results are given in the first row of Table I. Note that the composition of an axial bond orbital is near the composition of a cylindrical octahedral bond orbital.

When a molecule $AB_7$ assumes the pentagonal bipyramidal structure, one might expect considerable repulsion to exist between the five equatorial $B$'s. It is of interest to compare this structure with the dodeca-hedral structure[3,6] as assumed by $Mo(CN)_8^{-4}$. Since in the dodecahedral structure there are fourteen angles equal to about 73°40', one would expect that a radius ratio which was favorable to the formation of a dodeca-hedral structure would probably be favorable to the formation of the pentagonal bipyramidal structure.

In $Mo(CN)_8^{-4}$ the ratio of the covalent radius[3] of carbon to the covalent radius of molybdenum is 0.56. In $IF_7$ the ratio of the covalent radius of fluorine to the covalent radius of iodine is about 0.50, a more favorable value. The pentagonal bipyramidal structure for $IF_7$ uses one $5s$, three $5p$, and three $5d$ orbitals of the iodine atom, the orbitals most readily available for hybridization in heptacovalent iodine. From Table I the strength of an equatorial orbital is 2.976 and the strength of an axial orbital is 2.920. We tentatively conclude that the pentagonal bipyramidal structure is a reasonable structure for $IF_7$.

In each of the metal atoms of $ZrF_7^{-3}$, $CbF_7^{-2}$, and $TaF_7^{-2}$ there are no unshared electrons in the valence shells and the $p$ orbitals are more unstable than the $s$ or $d$ orbitals. Hence each tends to use a heptacovalent configuration approaching type $spd^5$ rather than $sp^3d^3$, the type which might yield the bipyramidal structure.

The other results recorded in Table I are of some interest. For instance, in a pentagonal plane molecule of type $AB_5$, $\psi_1\cdots\psi_5$ are used as the bond orbitals, and the best value of $\alpha$ is found by maximizing $S_1$ if the $s$ and $d$ orbitals are of equal stability.

[5] G. H. Duffey, J. Chem. Phys. 18, 510 (1950).
[6] J. L. Hoard and H. H. Nordsieck, J. Am. Chem. Soc. 61, 2853 (1939).