Molecular Orbitals for the Protonated Sandwich Compounds

C. J. BALLHAUSEN and J. P. DAHL

Universitetets fysisk-kemiske Institut, Copenhagen, Denmark

A set of orbitals for a "twisted" sandwich compound is proposed. These new orbitals explain the behaviour of sandwich compounds when protonated.

The recent discovery [1] of the existence of protonated "sandwich" compounds [2] has motivated the modified molecular orbitals given below. Whereas in ferrocene for instance the two rings in $Fe(C_5H_5)_2$ are found to be parallel, we propose here that in $Fe(C_5H_5)_2H^+$ the two rings are not parallel any more (Fig. 1). The two rings are twisted in such a way that the radius vectors from the metal atom to the center of the rings make an angle, ω.

a) *The Cp rings.* When the rings are placed as in Fig. 1 we treat the bonds to the two rings as being independent of each other. With $\varphi_r^{(S)}$ being the r'th $2p_z$-orbital on ring S (S = A or B) we write as usual [3] the orbitals on the rings as follows, neglecting overlap:

$$CpS(a_2) = \sqrt{\tfrac{1}{5}}\,(\varphi_1^S + \varphi_2^S + \varphi_3^S + \varphi_4^S + \varphi_5^S)$$

$$CpS(e_1') = \sqrt{\tfrac{2}{5}}\,(\varphi_1^S + \cos\frac{2\pi}{5}\,(\varphi_2^S + \varphi_5^S) + \cos\frac{4\pi}{5}\,(\varphi_3^S + \varphi_4^S))$$
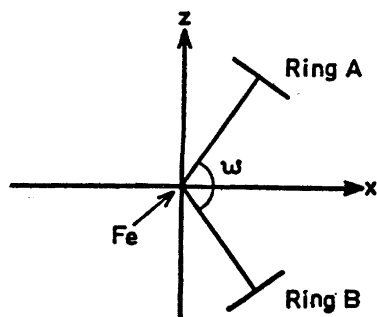

Fig. 1. Molecular structure of a twisted sandwich. The rings are drawn perpendicular to the xz plane, the radius vectors in the xz plane.

$$CpS(e_1'') = \sqrt{\tfrac{2}{5}} \ (\sin \frac{2\pi}{5} \ (\varphi_2^S - \varphi_5^S) + \sin \frac{4\pi}{5} \ (\varphi_3^S - \varphi_4^S))$$

$$CpS(e_2') = \sqrt{\tfrac{2}{5}}(\varphi_1^S + \cos \frac{4\pi}{5} \ (\varphi_2^S + \varphi_5^S) + \cos \frac{2\pi}{5} \ (\varphi_3^S + \ _4^S))$$

$$CpS(e_2'') = \sqrt{\tfrac{2}{5}}(\sin \frac{4\pi}{5} \ (\varphi_2^S - \varphi_5^S) - \sin \frac{2\pi}{5} \ (\varphi_3^S - \varphi_4^S))$$

The energies are found [3] to be:

$$CpS(a_2) = a + 2\beta$$

$$CpS(e_1) = a + 2\beta \ \cos \frac{2\pi}{5}$$

$$CpS(e_2) = a - 2\beta \ \cos \frac{\pi}{5}$$

With β negative the order is $E(a_2) < E(e_1) < E(e_2)$. As the e_2 orbital is anti-bonding we shall not use it in the bonding scheme.

b) The metal atom. The following valence orbitals will be used for the metal atom; all $3d$ orbitals, all $4p$ and the $4s$ orbitals. Utilizing these nine orbitals we now construct hybrid orbitals guided by the following principles:

We want to construct 3 hybrids $\psi_A(a_2)$, $\psi_A(e_1')$ and $\psi_A(e_1'')$ of which $\psi_A(a_2)$ only overlaps with $CpA(a_2)$. This can be done in a unique way. Then we construct a hybrid $\psi_A(e_1')$ which is orthogonal upon $\psi_A(a_2)$, and which only overlaps with $CpA(e_1')$ and in the same way $\psi_A(e_1'')$ is made up, only having overlap with $CpA(e_1'')$. Then we construct the corresponding three orthogonal hybrids $\psi_B(a_2)$, $\psi_B(e_1')$ and $\psi_B(e_1'')$, only overlapping with $CpB(a_2)$, $CpB(e_1')$ and $CpB(e_1'')$, respectively.

We now demand that the two sets of hybrids should be orthogonal upon each other, and transform into each other by reflection in the xy-plane. A necessary condition for this to take place turns out to be that the angel ω should lie between 135° and 180°.

Finally we construct three new hybrids, which are orthogonal upon each other and upon the six ring-hybrids. Of these ψ_O is cylindrical around the x-axis, and ψ_y and ψ_{-y} go into each other by reflection in the xz plane.

For ω equal to 135° these three non-bonding hybrids look as follows, calling

$$\text{tg} \frac{\pi}{8} = a$$

$$\psi_O = a \ \psi(4s) - \sqrt{1 - a^2} \ \psi \ (4p_x)$$

$$\psi_y = \frac{1}{\sqrt{2}} \ a \ \psi \ (4p_y) - \frac{1}{\sqrt{2}}\sqrt{1-a^2} \ \psi \ (3d_{xy}) - \sqrt{\tfrac{1}{8}} \ \psi \ (3d_{z^2}) - \sqrt{\tfrac{3}{8}} \ \psi(3d_{x^2-y^2})$$

$$\psi_{-y} = -\frac{1}{\sqrt{2}} \ a \ \psi \ (4p_y) + \frac{1}{\sqrt{2}}\sqrt{1-a^2} \ \psi \ (3d_{xy}) - \sqrt{\tfrac{1}{8}} \ \psi \ (3d_{z^2}) - \sqrt{\tfrac{3}{8}} \ \psi \ (3d_{x^2-y^2})$$

All of the nine possible hybrids are very strongly space directed. The ring hybrids are directed straight against the rings. ψ_O is directed towards the

negative end of the x-axis, while ψ_y and ψ_{-y} are directed, respectively, in between the positive and negative ends of the y-axis and the negative end of the x-axis (Fig. 2).

c. *Molecular orbitals*. Using the orbitals of the (Cp) rings given in a) and the metal hybrids given in b) we construct the six bonding molecular orbitals:

$$\Phi_S(a_2) = \cos\varphi\ \psi_S(a_2) + \sin\varphi\ CpS(a_2)$$
$$\Phi_S(e_1') = \cos\chi\ \psi_S(e_1') + \sin\chi\ CpS(e_1') \qquad (S = A,B)$$
$$\Phi_S(e_1'') = \cos\xi\ \psi_S(e_1'') + \sin\xi\ CpS(e_1'')$$

Of course we get six antibonding molecular orbitals as well, but their energy must be so high that we need not consider them.

These six bonding molecular orbitals contain twelve electrons. This electronic structure is common for all sandwich compounds and we will look apart from them in what follows [4]. We remark in passing that the total overlap of these twelve bonding electrons with the rings is nearly equal both in the "straight" and "twisted" form of the sandwiches. We get for instance for $\omega = 150°$, $S_{twisted}=1.87$ and for $\omega = 180°$, $S_{straight} = 2.00$. This indicates that the bonding of the rings to the metal-atom is not very dependent upon whether the molecule is "straight" or "twisted".

The remaining electrons in the sandwich compound are treated as "chemically active" electrons [4], and furthermore the hybrids ψ_0, ψ_y and ψ_{-y} are supposed to have a lower energy than the non-bonding ring orbitals $CpS(e_2')$ and $CpS(e_2'')$.

The number of electrons in surplus of the twelve used already are

3 in $(C_2H_5)_2$ Ta
4 in $(C_2H_5)_2$ W
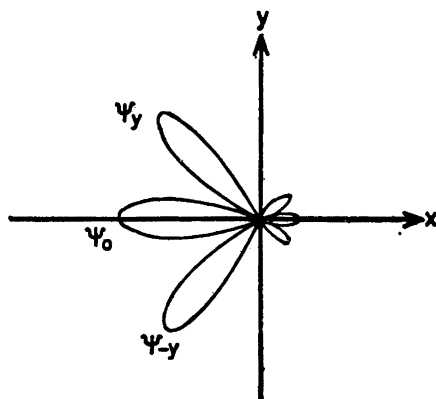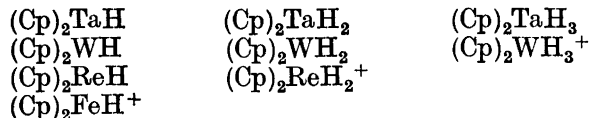5 in $(C_2H_5)_2$ Re
6 in $(C_2H_5)_2$ Fe

Fig. 2. Hybrid orbitals not used for ring bonding in a "twisted" sandwich molecule.
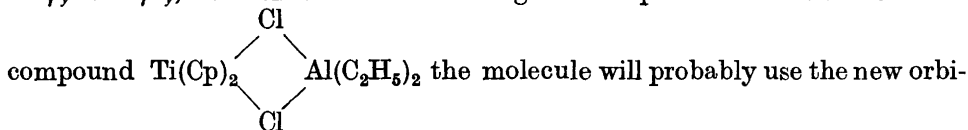
These electrons are then placed in the ψ_0, ψ_y and ψ_{-y} orbitals. These hybrids can now be used for further bonding purposes, *e.g.* ferrocene can take one proton up, presumably in ψ_0.

If we suppose that the maximum number of protons and hydrogens which can be bonded is determined by the condition that we can only have one positive charge on the hydrides we should be able to make the following compounds, of which the majority have already been prepared [1]:

$(Cp)_2TaH$ $(Cp)_2TaH_2$ $(Cp)_2TaH_3$
$(Cp)_2WH$ $(Cp)_2WH_2$ $(Cp)_2WH_3{}^+$
$(Cp)_2ReH$ $(Cp)_2ReH_2{}^+$
$(Cp)_2FeH^+$

Notice that in $(Cp)_2TaH_3$ and $(Cp)_2WH_3{}^+$ one of the hydrogen atoms is bonded differently from the other two. The latter two on the other hand are bonded equivalently. This again is confirmed by experiments [1]. It is furthermore remarkable that in order to obtain these results no f-orbitals need to be used.

Some suggestions. We suggest that the two Cl^-'s in $(Cp)_2TiCl_2$ are bonded to ψ_y and ψ_{-y}, and hence that the two rings are not planar. Furthermore in the

compound $\text{Ti(Cp)}_2 \diagdown\!\!\!\!\diagup\begin{smallmatrix}Cl\\\\Cl\end{smallmatrix}\diagup\!\!\!\!\diagdown \text{Al(C}_2\text{H}_5)_2$ the molecule will probably use the new orbi-

tals ψ_y and ψ_{-y} for the chlorine bonds since it is known that the rings are not planar [5].

REFERENCES

1. Wilkinson, G. *Private Communication.*
2. Wilkinson, G. and Cotton, F. A. *Progr. Inorg. Chem.* Vol. 1 Interscience, New York 1959
3. Moffitt, W. *J. Am. Chem. Soc.* **76** (1954) 3386.
4. Dahl, J. P. and Ballhausen, C. J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **33** (1961) No. 5.
5. Natta, G., Corradini, P. and Bassi, I. W. *J. Am. Chem. Soc.* **80** (1958) 755.