THE ROLE OF SIGMA ELECTRONS IN AROMATIC SUBSTITUTION

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The recent development of generalised Huckel theories, e.g. that of Hoffmann (1), and their application to the changes which take place during molecular interactions, e.g. by Fukui et al. (2), promises to increase our understanding of many chemical reactions. Unfortunately, the results obtained from computors for specific problems take time to be digested and the important factors determining the course of a reaction are still liable to remain obscure. For this reason a rather simplified approach has been developed in which direct computation of energies is avoided and in which we only have to estimate the coefficients of a single non-bonding orbital (3). In this letter we hope to demonstrate the part which sigma electrons play in electrophilic substitution reactions of aromatic molecules.

In our model we imagine that an electrophile Y^+, with only one empty molecular/atomic orbital available for bonding, approaches the carbon atom C1 of an aromatic ring, from a direction approximately at right-angles to the molecular plane. In this case we can assume that the direct interaction involves only the $2p_\pi$ and 2s orbitals of C1. For simplicity we take the same value for all coulomb integrals of the orbitals involved in which case the charge distribution is given by a non-bonding orbital, mainly localised on Y, as long as the separation is large enough. We are, of course, considering the first part of the reaction. Both π- and σ- type atomic orbitals appear in the non-bonding orbital and their coefficients can be calculated easily, and more or less separately, because the diagonal terms of the secular equations are approximately zero.

We define the problem in terms of the usual carbon sp^2 and $2p_\pi$ atomic orbitals and one atomic orbital for the attacking agent and each substituent (see diagram).
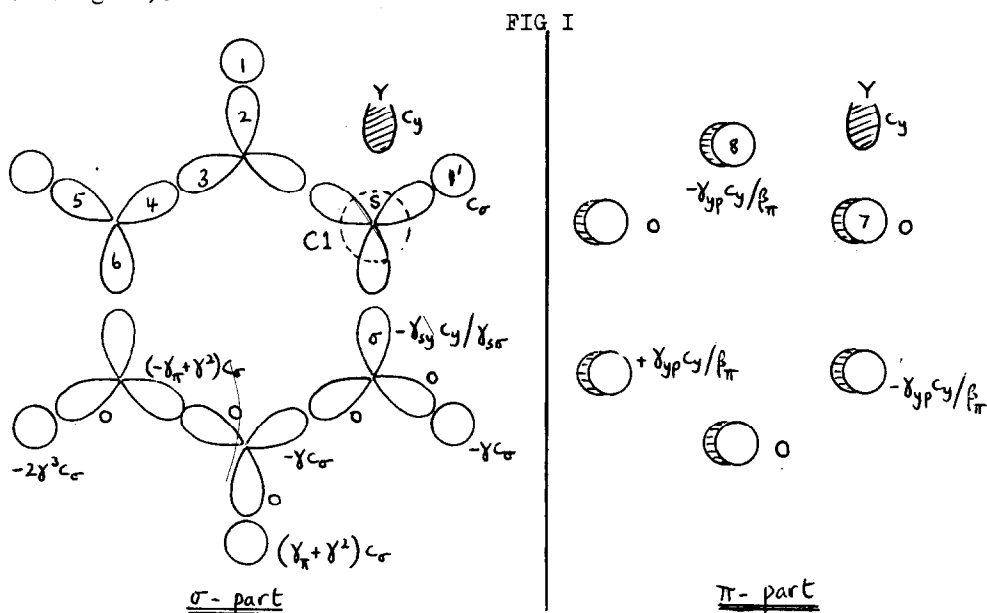
FIG I

FIG I : Diagram of the atomic orbitals involved in the non-bonding orbital with approximate expressions for their coefficients.

The non-zero resonance integrals which, from results of nuclear spin-spin coupling constant calculations (4), should be sufficient for determining the coefficients of these orbitals, are of the following types:- $\beta_{12} = \beta_{34} = 1$; $\beta_{23} = \gamma$; $\beta_{15} = -\beta_{26} \approx \frac{1}{2}$ $\beta_{78} = \gamma_\pi$; $\beta_{7\pi} = \beta_\pi$; $\beta_{97} = \gamma_{9p}$; $\beta_{95} = \gamma_9$ approximate expressions for the coefficients are shown in FIG I.

Looking at the π- part first, if there is a halogen atom attached to the carbon atoms ortho or para with respect to Cl, then the positive charge transmitted to these positions (as shown) will tend to counterbalance the negative charge there arising from the partial sharing of the lone pair(s) of the halogen. We would expect this to lower the energy compared with the situation in benzene itself, or when the attack is meta with respect to the substituent. As with more 'static' (5) theories of these reactions we therefore expect preferential attack on the ortho and para positions.

Now the charge distribution is given by the squared coefficients of atomic orbitals in the lowest unoccupied orbital of the system of two reactants. It is interesting to note that in the carbon $2p_\pi$ orbitals, the relative distriution ortho: meta: para remains approximately constant as Y^+ approaches, right up until the σ-complex intermediate has been formed.

However, we have to consider also the drift of positive charge into the sigma skeleton of the original molecule, more particularly on to the substituents. Confining ourselves only to the sigma part, if any substituents are more electronegative than hydrogen, then their   atomic orbitals will accomodate this positive charge less easily than a hydrogen 1s orbital, and the situation will be less favourable than that in benzene. Presumably the greater the tendency is for concentrating (partial) positive charge in a more electronegative orbital, the higher will be the energy, and therefore we expect the attack to be most favoured when the least positive charge is transmitted on to these electronegative substituents. From calculations of coupling constants in magnetic resonance spectra (4) the following orders of magnitude are found for the parameters γ_π and γ :

$$\gamma_\pi \approx 1/4 > \gamma$$

From the coefficients given in the diagram we therefore obtain the following order for the charges in the σ atomic orbitals :

$$c_1^2 \gg c_{meta}^2 > c_{ortho}^2 > c_{para}^2$$

We expect then, that the most favourable position for electrophilic attack will be para to a strongly electronegative substituent.

Now we must reintroduce the π-type atomic orbitals for the non-bonding orbital is a linear combination :

$$\Psi_{NBO} = \sum c_i \Psi_{\sigma i} + \sum c_r \Psi_{\pi r} + c_y \Psi_y$$

Where $\Psi_{\sigma i}$, $\Psi_{\pi i}$ are the ith σ-type, π-type atomic orbitals, respectively, of the original aromatic molecule. These are effectively linked by the electrophile Y^+.

Combining the activating influence in the π-system with the

deactivating effect in the σ-electron system we arrive at the following order of expected reactivity in electrophilic substitution (or addition) reactions :

zeroth (Cl) $<$ meta $\ll$ ortho $<$ para

This is the order which is generally observed (6) in 'activated' benzene derivatives and does not appear to have been explained very well before.

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