Symmetry Effects in Aromatic Substitution

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Two main processes are involved in aromatic substitution reactions, the first being addition, say, of an electrophile, leading to the formation of a σ-complex; and the second, loss of a proton.

The first step usually controls the rate of the reaction but the second has to compete with a possible further attack, this time by a nucleophile, leading to overall addition. Now we would expect that the greater the positive charge on the aliphatic proton, H_a, [see Figure, (a)] the more acidic it would be, *i.e.*, the more easily could it leave the σ-complex as a proton. We can estimate the charge density on H_a quite easily using simple molecular orbital, theory, and from there we can try to predict whether substitution will compete favourably with addition.

For example, let us compare a typical $4n$ system, cyclobutadiene, with a typical $4n + 2$ system, benzene, in relation to their expected behaviour after electrophilic attack.

For simplicity, take orbital 1 to be the appropriate antisymmetric combination of two hydrogen atomic orbitals, as in hyperconjugation theory;[1] let all resonance integrals be unity except $\beta_{12} = \gamma$, equate all coulomb integrals, and finally, neglect non-nearest-neighbour interactions.

The charge distributions in these species are both given by the coefficients of the non-bonding orbitals[2,3] and are shown in the Figure.

One important feature immediately emerges; in the $4n$ system the non-bonding orbital is antisymmetric with respect to reflection through the plane of symmetry and has a node through the aliphatic carbon and its substituents. On the other hand, in the benzyl-like adduct, the non-bonding orbital is symmetrical about the plane of symmetry and in this case appreciable positive charge can accumulate on the aliphatic proton.

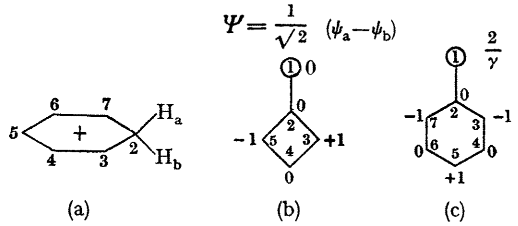

FIGURE. *Adducts of* H^+ *with* C_4H_4, C_6H_6, *and the un-normalised coefficients of the non-bonding orbitals.*

This gives us yet another contrast between the properties of rings containing $4n$ and $4n + 2$ carbon atoms, and the result is quite general within the framework of simple MO theory and does not depend on our particular simplifications.

It is interesting to note that a measure of the tendency towards substitution (and perhaps of aromatic character) is given by the methylene proton coupling constants in the e.s.r. spectra of the radical adducts (*e.g.* in cyclohexadienyl they are 47·72 G[4]). In adducts of $4n$ atom rings such coupling constants (and ease of substitution compared with addition) are expected to be low.

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