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UNIFIED THEORY OF THE THERMODYNAMIC AND KINETIC CRITERIA OF AROMATIC CHARACTER IN THE [4n+2]ANNULENES

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Abstract: It is shown that there is a direct relationship between the resonance energies and the HOMO-LUMO energy gap in the [4n+2]annulenes - thereby demonstrating the connection between the thermodynamic and kinetic criteria of aromatic character.

It is generally assumed that there is a one-to-one correspondence between the thermodynamic and kinetic criteria of aromatic character (TCAC and KCAC, respectively).[1-3] That is, resonance energies (TCAC) are taken to provide a measure of chemical stability and reactivity (KCAC). Insofar as we are aware, this relationship has never been rigorously demonstrated, although the experimental evidence clearly supports a qualitative connection.[4-6] Recently, it has been shown that there is an analytic relationship between the resonance energies (TCAC) and ring currents (magnetic criterion of AC) of [4n+2]π - electron annulenes which leads naturally to a unified theory of aromatic character.[7] It therefore seemed of interest to try to extend this work and to seek a quantitative correlation between the thermodynamic and kinetic criteria of aromatic character. For the TCAC the REs will be employed while for the KCAC the energy gap (ΔE) between the highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO) will be utilized. It has been shown that ΔE does provide a measure of chemical stability and reactivity (stable compounds have large values of ΔE whereas reactive compounds have small values).[8] Other quantities[3,9] have also been correlated with ΔE.

The resonance energy (RE) of the [N = 4n+2]annulenes is given by[7]

$$RE = \frac{\pi^2 p_{rs}\beta}{3N} = \frac{2\pi^2\beta}{3N^2\sin(\pi/N)} \qquad (1)$$

where p_{rs} is the bond order, N is the number of atoms and β is the carbon-carbon resonance integral (negative). The HOMO-LUMO energy gap (ΔE) in the [N = 4n+2]annulenes is given by

$$\Delta E = -4\beta \sin (\pi/N) \tag{2}$$

Therefore by combination of eqs 1 and 2 we obtain

$$RE = - \frac{(\pi p_{rs})^2 \Delta E}{24} \tag{3a}$$

or

$$\Delta E = - \frac{24\ RE}{(\pi p_{rs})^2} \tag{3b}$$

Thus establishing a direct relationship between resonance energies and the HOMO-LUMO energy gap in the [4n+2]annulenes. At large ring size and in the absence of bond alternation eqs 3 may be simplified (even for benzene the error is less than 9%), to give

$$RE = - \Delta E/6 \tag{4a}$$

$$\Delta E = - 6\ RE \tag{4b}$$

The relationship between the reduced ring currents (RCs),[7] and the other quantities takes a particularly simple form

$$\frac{\pi^2 RC}{3S} = RE = - \frac{\Delta E}{6} \tag{5}$$

The above equations serve to unify the magnetic, thermodynamic, and kinetic criteria of aromatic character in the original subjects of the Huckel rule – the [4n+2]annulenes.

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