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HMO PERTURBATIONAL CONSIDERATIONS OF CORRELATIONS BETWEEN CHEMICAL SHIFTS AND SOME THEORETICAL INDICES OF REACTIVITY

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Recently, the correlations between chemical shifts in proton NMR spectra, t_r, and some theoretical indices of reactivity were obtained (1-4) for some conjugated hydrocarbons. In the case of benzenoid hydrocarbons this idea is of particular interest because of the Coulson-Rushbrooke theorem (5) which states that $q_r = 1$ for all r positions when calculations are made by use of HMO or SCF-PPP methods (6). Then the linear relation between t_r and q_r (7-9) is not fulfilled.

The aim of this paper is to substantiate the correlations between :

1) the chemical shifts t_r and free valence F_r, and

2) the chemical shifts t_r and the atom-atom self-polarizability $\pi_{r,r}$.

All the considerations are made in the simple HMO version of the perturbation theory.

Let us assume the magnetic field acting on a molecule as a perturbation; then the pi-electron energy of the molecule changes because of changes in the Coulomb integrals, $a_r \rightarrow a_r^o + da_r$, and the resonance integrals, $b_{rs} \rightarrow b_{rs}^o + db_{rs}$ (10,11). Thus in the HMO theory one can find the change in pi--electron due to this perturbation in the following form :

$$(\Delta E^{pi})_{tot} = \sum_r \Delta E_r^{pi} + \sum_{rs} \Delta E_{rs}^{pi} \qquad (1)$$

where the components ΔE_r^{pi} and ΔE_{rs}^{pi} arise from the perturbation of the two kinds of integrals. In the other hand the value $(\Delta E^{pi})_r$ can be defined as a sum of partial pi-electron energies being connected with local perturbations around the r-th atomic center bonded via bonds r-s with other atoms of a given molecule, e.g. :

$$(\Delta E^{pi})_r = \Delta E_r^{pi} + \sum_s \Delta E_{rs}^{pi} \qquad (2)$$

According to the general relationships of the perturbation theory within HMO method (12), one can write

$$(\Delta E^{pi})_r = q_r da_r + \frac{1}{2}\pi_{r,r}(da_r)^2 + \ldots + 2\sum_s p_{rs} db_{rs} + \sum_s \pi_{rs,rs}(db_{rs})^2 + \ldots \qquad (3)$$

Neglecting the second-order terms in (3) one obtains approximately :

$$(\Delta E^{pi})_r = q_r\, da_r + 2 \sum_s p_{rs}\, db_{rs} \qquad (4)$$

where the values da_r and db_{rs} can be regarded as structural characteristics of a suitable series of compounds. For instance the cyclic hydrocarbons could have the da_r and db_{rs} values approximately constant for angular and non-angular positions (for definition see (13)), respectively. Within a given class of the positions and compounds one can assume that $da_r = A$ and $db_{rs} = B$, where A and B are constants. Therefore eq.(4) might be rewritten as :

$$(\Delta E^{pi})_r = A\, q_r + B \sum_s p_{rs} \qquad (5)$$

Including the Coulson (14) definition of free valence $F_r = N_{max} - \sum_s p_{rs}$ one gets :

$$(\Delta E^{pi})_r = A\, q_r + B'\, F_r + C \qquad (6)$$

If the energy $(\Delta E^{pi})_r$ actually expresses the influence of external magnetic field H_o, then it should be proportional to the energy of the appropriate nuclear magnetic dipole, μ, e.g. $(\Delta E^{pi})_r \approx \mu\, H_r$, where H_r is the local magnetic field arising from pi electron ring current (see (15) Section six). As $H_r = -\sigma_r H_o$, where σ_r is the screening constant (15) and the chemical shift is defined as $t_r = \sigma_r - \sigma_{standard}$, one can also suppose a proportionality between the values $(\Delta E^{pi})_r$ and t_r. Using eq.(6) a general form of the empirical correlations between t_r and the reactivity indices q_r and F_r can be obtained :

$$t_r(\mathrm{ppm}) = a\, q_r + b\, F_r + c \qquad (7)$$

which has been found for nonalternant hydrocarbons and ions (2). For the benzenoid hydrocarbons $q_r = 1$ (5,6) and one gets

$$t_r(\mathrm{ppm}) = b\, F_r + c' \qquad (8)$$

which is in a good agreement with the correlation found (correlation coefficient $r = 0.970$) (1).

On the other hand, if the resonance terms in the perturbation expansion (3) are not taken into consideration, one gets the simple relation :

$$(\Delta E^{pi})_r = q_r\, da_r + \frac{1}{2} \pi_{r,r} (da_r)^2 \qquad (9)$$

provided the db_{rs} values are not significant or are assumed to vary linearly with the atomic terms.

Thus applying an assumption similar to that made in eq.(6), one can obtain the linear relation,

$$t_r(\mathrm{ppm}) = a''\, \pi_{r,r} + \mathrm{const.} \qquad (10)$$

which gives a good correlation coefficient, $r = 0.977$ (1).

The original methods for chemical-shift calculations based on HMO theory were proposed by Pople (10) and McWeeny (11). Our procedure could be considered as an extreme simplification of the McWeeny theory which leads to the following expression for the proton screening constant (15) :

$$\sigma_r = \sum_{r,s} p_{rs} f_1(s_{rs}, r_r, r_s) + \sum_{r,s} \sum_{t,u} b\, \pi_{rs,tu} f_2(s_{rs}, s_{tu}, r_r, r_s, r_t, r_u) \qquad (11)$$

where f_1 and f_2 are algebraic functions of area and distance parameters s_{rs}, s_{tu} and r_r, r_s, r_t, r_u, resp. Separating the first term in eq.(11) into the different terms for $r = s$ and $r \neq s$ one arrives at eq.(12) :

$$\sigma_r = q_r f_1' + \sum_{r \neq s} b\, p_{rs} f_1 \qquad (12)$$

which appears to be equivalent to eqs.(5) and (7) provided the functions f_1 and f_1' are approximately constant for a given kind of position and only the neighbouring s-terms are taken into consideration. Analogous assumptions taking the second term in eq.(11) into account give rise to relationships of the kind (10) or (9), respectively.

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