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On Certain Charge Distribution Anomalies in Conjugated Heteroatomic Molecules

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It is shown by examination of the diagonal elements of the Hartree-Fock matrix in the Pople-Pariser-Parr π electron method that there exists a simple justification of the auxiliary electronegativity parameters sometimes used in Hückel approximation calculations.

Die Untersuchung der Diagonalelemente der HF-Matrix der PPP-Methode liefert eine Rechtfertigung für die Anwendung des „induktiven" Heteroatomparameters in der Hückel-Methode für den Fall, daß das Heteroatom 2π-Elektronen beisteuert.

L'examen des éléments diagonaux de la matrice de Hartree-Fock dans la méthode Pople-Pariser-Parr montre qu'il existe une justification simple des paramètres d'électronégativité auxiliaries utilisés parfois dans la méthode de Hückel.

Introduction

Let us consider two types of simple conjugated molecules; each molecule containing one atom other than carbon. Type I (of which pyridine, acrolein and formaldehyde are examples) has N atoms and N π electrons comprising the conjugated system. Type II (of which furan, pyrrole and thiophene are examples) has N atoms and $N+1$ π electrons comprising the conjugated system. If, in carrying out simple Hückel calculations, one chooses the coulombic parameters in the following way:

$$\alpha_r = \alpha_0 + h_r \beta_0$$

$$h_r \begin{cases} \neq 0 \text{ for the heteroatom} \\ = 0 \text{ otherwise} \end{cases}$$

then one finds that the calculated charge distributions in type I molecules appear to be reasonable on the basis of simple chemical intuition whereas those of type II appear unreasonable on a like basis. As specific examples we consider pyridine and furan. In the majority of calculations reported on the former molecule the coulombic parameters have been chosen such that $h_N > 0$ (e.g., 0.2 to 0.5) [2]. This invariably leads to the qualitative results

$$q_1 > q_2 < q_3$$

(q_i is the π electron charge density on the i^{th} atom, where the heteroatom (nitrogen in this case) is numbered 1 and the other atoms are numbered consecutively therefrom). Since it is known experimentally that pyridine tends to substitute predominantly in the 3-position (3- and 3,5-substitution products), this charge distribution appears reasonable. In the case of furan one usually sets $h_O > 0$ (e.g., 0.2 to 1.0) [2, 8]. This invariably leads to the qualitative result

$$q_1 > q_2 < q_3$$

which, however, is in apparent disagreement with the experimental observation that furan has an unusually pronounced tendency to substitute in the 2-position only.

To reconcile charge distributions and chemical intuition (assuming one can trust either!) one has at least two choices, viz., 1) to postulate a mechanism for substitution on furan which involves the initial formation of a 3-product (kinetic control) followed by a relatively rapid rearrangement to a thermodynamically more stable 2-product, or 2) to suggest some alternative choice of electronegativity parameters. As shown by BROWN and COLLER [1], a simple solution of the second type is to introduce an *auxiliary* electronegativity parameter for the atoms which are nearest neighbors to the heteroatom, viz., in the case of furan

$$\alpha_2 = \alpha_5 = \alpha_0 + h_2\beta_0 \qquad 0 < h_2 < h_1$$

where the heteroatom is numbered 1. Physically, such a formulation implies an inductive effect due to the oxygen atom — an inductive effect which is transmitted to nearest neighbors. As shown by explicit calculations by BROWN and COLLER, use of $h_1 = 1.0$ and $h_2 = h_5 = 0.25$ leads to $q_2 > q_3$.

The charge distribution behavior discussed above has its theoretical foundations in the *alternating polarity effect* — an effect first discussed in terms of the Hückel method by COULSON and LONGUET-HIGGINS [3]. This effect, although normally restricted to alternant hydrocarbons, nevertheless has an analogue in non-alternants. For example, furan consists of an odd-membered ring so that an alternating polarity such as found in pyridine (even-membered ring) is not possible. Nevertheless, the polarities of the atoms in furan tend to alternate *insofar as possible* as one goes in either direction from the heteroatom. It is easy to see that the effect of the auxiliary electronegativity parameter is to change this pattern by shifting the center of alternation.

Surprisingly enough, the above anomalies (if this they be) are not encountered in the Pople-Pariser-Parr SCF generalization of the Hückel approximation. Calculations by MCWEENY and PEACOCK [5] on pyridine and by ORLOFF and FITTS [6] on furan lead to $q_2 < q_3$ for the former and to $q_2 > q_3$ for the latter — apparently in complete agreement with chemical intuition. Furthermore, ORLOFF and FITTS have noted that the SCF treatment of furan somehow includes what is effectively an auxiliary electronegativity parameter analogous to that of the Hückel method. It is the purpose of the present paper to show 1) why the auxiliary electronegativity parameter is implicit in the SCF formulation, and 2) under what conditions such a parameter ought to be used in the Hückel approximation.

The Auxiliary Heteroatomic Parameter

The diagonal elements of the matrix representation of the π electron Hartree-Fock operator in an assumed orthogonalized orbitals basis is given by [9, 10]

$$F_{rr} = N_r\omega_r + R_{rr}\gamma_{rr} + \sum_{s \neq r} (2R_{ss} - N_s)\gamma_{rs} \, .$$

The various terms are identified as follows: N_r is the number of electrons *formally* donated to the conjugated system by atom r, ω_r is the valence state ionization potential of atom r, R_{rr} is a diagonal element of the first-order density matrix (represented in the same basis as the Hartree-Fock operator) and γ_{rs} is a two-electron, two-center coulombic repulsion integral. It should be noted that $q_r = 2R_{rr}$, i.e., the diagonal elements of the first-order density matrix (in this particular representation) are one-half the charge densities. In an earlier paper [4] we reported that SCF calculations on furan with the summation terms in F_{rr} omitted led to $q_2 < q_3$, i.e., to the same qualitative results as obtained by the Hückel method *sans* auxiliary electronegativity parameter. This fact provides the clue to the explanation of the apparent charge distribution anomalies.

When $r = 1$ (oxygen atom), the summation portion of F_{11} contains only terms such as $(2R_{ss} - 1)\gamma_{rs}$ (with $s \neq 1$) all of which are small since $2R_{ss}$ is not too far from unity for *all* carbon atoms. However, for the carbon atoms themselves (for which $r \neq 1$) there will be one term in F_{rr}, viz., $(2R_{11} - 2)\gamma_{r1}$ which will be negative since $2R_{11} < 2$ and which will be largest when r is a nearest neighbor of the oxygen atom (since γ_{r1} is largest when atoms r and 1 are closest). It is the term $(2R_{11} - 2)$ γ_{r1}, where r is a nearest neighbor to atom 1, which accounts for the so-called inductive effect. We therefore conclude that it is necessary and meaningful to employ auxiliary electronegativity parameters in carrying out simple Hückel calculations on type II molecules. In fact, it is just this conclusion which forms the justification of the ORLOFF and FITTS scheme for constructing Hückel matrices from SCF matrices of suitably chosen model molecules [7].

In the case of a type I molecule such as pyridine, the elements $(2R_{11} - 1)\gamma_{r1}$ are positive (since $2R_{11} > 1$) and thus serve to make atoms which are nearest neighbors to nitrogen less electronegative than nitrogen. In the Hückel method this would be represented by $h_2 < 0$. However, $2R_{11} - 1$ is not large enough in pyridine (as contrasted to $2R_{11} - 2$ in furan) to have a dominant effect. The primary difference between type I and type II molecules is, of course, that $N_1 = 1$ for the former and $N_1 = 2$ for the latter. The heteroatom in type I contributes the same number of π electrons to the system as does any other atom and thus, in spite of $h_1 > 0$, the increase of charge $(2R_{11} - 1)$ does not become unduly large. In type II the heteroatom contributes *twice* as many electrons to the system as does any other single atom; consequently the absolute value of the charge change $(2R_{11} - 2)$ is greater than the corresponding charge change $(2R_{11} - 1)$ in type I molecules. It is evident that the use of an auxiliary electronegativity parameter is the Hückel approximation's only way of taking into account the effect of the number of electrons formally donated by an atom to the conjugated system. The effect of this N_r term is to modify the alternating polarity trend. When $N_r = 1$ the usual alternating polarity trend leads to qualitatively correct results and no modification is needed. When $N_r = 2$ a modification is required to change the trend. Strictly speaking, the auxiliary electronegativity parameter should not be interpreted in terms of an inductive effect (at least not in the usual sense) but rather as an "electron overflow" effect — an effect resulting from the tendency of the electrons to become delocalized as much as possible. Otherwise one would be forced to say that atoms more electronegative than carbon have inductive effects of opposite signs in molecules of types I and II. From a more formal viewpoint, one can also attribute the need for an auxiliary electronegativy parameter on a given atom r to a perturbation of the local field by the nearest neighbor atoms — a perturbation whose magnitude depends largeley on N_s.

Incidentally, McWEENY and PEACOCK [5] were the first to show how one could use SCF calculations to obtain Hückel electronegativity parameters such that the two methods led to similar charge distributions. However, McWEENY and PEACOCK considered only the main electronegativity parameter in which case the summation portion of F_{rr} is of minor effect and may be neglected in either type I or type II molecules.

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