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APPLICATION OF REFINED MO METHOD TO HAFNER'S HYDROCARBONS

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Abstract—Calculations have been made for Hafner's hydrocarbons using a refined form of the Hückel MO method in which dependence of 'Coulomb' integral on charge density and 'resonance' integral on bondlength via bond order have been allowed for in a selfconsistent manner. Bondlengths, $\pi \rightarrow \pi^*$ spectra, stability and reactivity of the molecules as given by the refined MO method have been compared with the simple Hückel MO method results.

INTRODUCTION

RECENTLY, Ali and Coulson[1] have studied theoretically the Hafner's hydrocarbons (I and II) using the simple Hückel molecular orbital method and correlated the reactivity of the molecules with π-charges and bond orders. The π-bond orders were also used to predict the bondlengths. However, it is known that the Hückel MO method in its simplest form is not genuinely selfconsistent for non-alternants in the sense that though the carbon atoms are assumed to have equal π-electron densities and therefore, equal "coulomb" integrals and the "resonance" integral for each bond is assigned a uniform value of β, the results show that the charges and bond orders are very far from being uniform throughout the molecule. Hence it is necessary to allow for the variation of the "coulomb" integral and "resonance" integral with bondlength in a somewhat self-consistent manner. Following the pioneer works,[2–5] Den Boer-Veenendaal and Den Boer[6] among others have studied the effect of allowing such variation in other chemically interesting molecules and shown that the results obtained had some interesting chemical content from the viewpoints of structure, reactivity and stability. Such a selfconsistent procedure would constitute a way of incorporating electron correlation within the framework of Hückel MO method. The functional dependence of "Coulomb" integral on charge densities and "resonance" integral on bondlength were taken to be the following:

$$\alpha^{(r)} = \alpha_0 + 1{\cdot}4\,[1 - q^{(r-1)}]\beta_0$$
$$\beta^{(r)} = \beta_0 \exp\,[-2{\cdot}683(0{\cdot}12 - 0{\cdot}18p^{(r-1)})]$$

where $q^{(r-1)}$ and $p^{(r-1)}$ are electron densities on an atom and bond order of a bond in the $(r - 1)$th stage of iteration, α_0 and β_0 being the "coulomb" integral for benzene carbon atom and "resonance" integral for benzene carbon-carbon distance of 1·40 Å.

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[1] M. A. Ali and C. A. Coulson, *Mol. Phys.* **4**, 65 (1961).
[2] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949).
[3] A. Streitweiser, *Molecular Orbital Theory for Organic Chemists* p. 115. J. Wiley, New York (1961).
[4] D. A. Hutchinson, *Acta Cryst.* **15**, 949 (1962).
[5] M. A. Ali and C. A. Coulson, *Tetrahedron* **10**, 41 (1960).
[6] P. C. Den-Boer-Veenendaal and D. H. W. den-Boer, *Mol. Phys.* **4**, 33 (1961).

The above relations have been used previously by Hutchinson[4] and Poole.[7] So one proceeds iteratively from the simple Hückel result q_p and p_{rs} to construct a new Hückel matrix whose solutions are used in the next step to construct a newer Hückel matrix. This iterative process for α and β selfconsistency is said to be complete if α and β obtained are selfconsistent to desired accuracy. A programme for this type of selfconsistent procedure has been developed by Poole on the Oxford University "Mercury" Computer. The present calculations were done using the above programme and the accuracy is upto five figures. In diagram II, the charge densities and bond orders for I and II obtained by the present selfconsistent calculation and Hückel calculation are compared; the righthand side numbers in each figure give charge densities and the left-hand side numbers give bond orders.

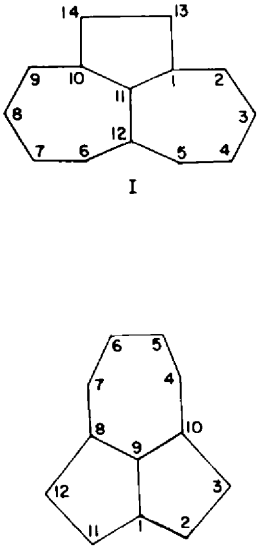

Diagram I

DISCUSSION

(a) The molecular diagram shows that the introduction of α and β selfconsistency tends to even out the charge densities at different centres and bond orders are changed appreciably from the simple Hückel MO values. It is of interest to note that the order of variation of charge densities of high value is still preserved.

(b) In the case of II, the HMO bondorder of bonds 12–11 and 2–3 is 0·745 while the SCF value is 0·7868. So there should be a tendency for the double bonds to get fixed in these positions. Hence one of the five membered rings would tend to act as a reactive olefinic bridge joining 1 and 8 positions in azulene. In the case of I, the HMO bond orders of the bond 13–14 is 0·683 while the SCF value is 0·6539. This shows that the five membered ring participates in conjugation more fully in I than in II.

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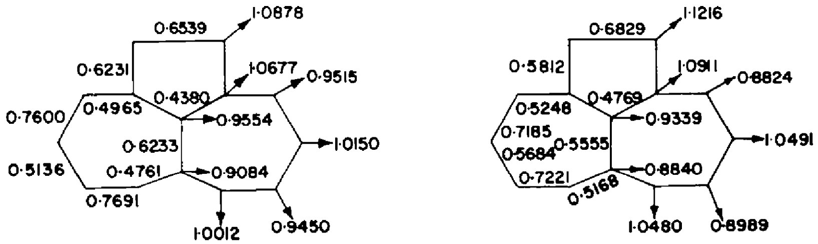
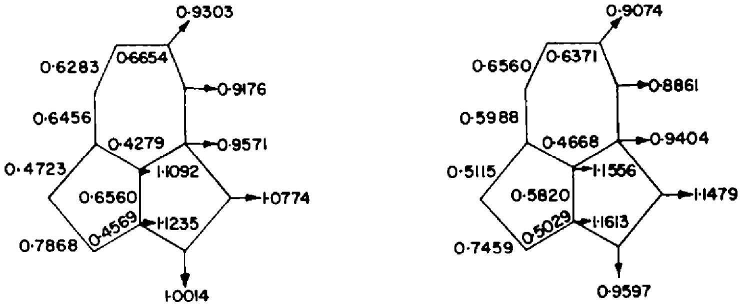
[7] M. D. Poole (unpublished), *Progress Report* p. 34. Wave Mechanics Group, Mathematical Institute, University of Oxford (1962–1963).

(c) The SCF bond orders of bonds 11–12 in I and 1–9 in II are—0·6233 and 0·6560 respectively as compared to HMO values 0·5555 and 0·5820. This shows that the central links in heptalene and pentalene framework in these molecules have intermediate character between single and double bonds as contrasted with the exclusive single bond character in the Kekule structures for these molecules.

(d) The SCF results show that in I, the charge densities q on positions 13, 3, and 5 are respectively in the order q_{13} (1·0878) > q_3 (1·0150) > q_5 (1·0012). So the greatest electrophilic activity will be displayed by atom 13 in agreement with simple HMO result and experiment. As has been pointed out by Ali and Coulson,[1] the electrophilic localization energy is lowest on position 5. So the disagreement between localization method and charge density method results for position 5 still remains. This disagreement could perhaps be resolved if calculation of localization energy is also made in a self-consistent manner. The greatest nucleophilic activity should be exhibited by position 2 again in agreement with HMO and localization energy results. The freevalence at position 2 is still highest and position 2 would display highest free radical reactivity.





SCF HMO

Diagram II: Charges and bond orders

(e) In I the SCF bond orders of bonds 8–9 and 7–6 are 0·7600 and 0·7691 respectively while in II the SCF bond orders of bonds 7–6 and 5–4 is 0·6283. Hence one would expect that I should display dienophile activity between position 9 and 6 while there should be little dienophile activity of II between positions 7 and 4 in agreement with experiment and para-localization energy calculated by Ali and Coulson.

(f) The bondlengths calculated from the selfconsistent bond orders are given in Table 1. The relation used is the following:

$$l = (1{\cdot}52 - 0{\cdot}18p)\ \text{Å}$$

We also give Hückel results for comparison. Experimental determination of bondlengths would be of considerable interest in this connection.

TABLE 1. BOND LENGTHS IN Å UNITS

Bond	SCF result	HMO result
Molecule: Penteno-heptalene		
13—14	1·402	1·397
13—1	1·408	1·415
1—2	1·431	1·426
2—3	1·383	1·391
3—4	1·428	1·418
4—5	1·382	1·390
11—12	1·408	1·420
1—11	1·441	1·434
5—12	1·434	1·427
Molecule: Pentenoazulene		
6—5	1·400	1·405
6—7	1·407	1·402
7—8	1·404	1·412
8—12	1·435	1·428
12—11	1·378	1·386
1—9	1·402	1·415
8—9	1·443	1·436
11—1	1·438	1·429

Orbital energies and spectra

In the simple Hückel scheme, the $\pi \rightarrow \pi^*$ transitions are assigned to one electron jumps from top occupied orbitals to lowest vacant orbitals. In Table 2 we compare the energies for all the bonding and the two lowest antibonding molecular orbitals for I and II for the SCF case and Hückel case. The results show that energies of molecular orbitals in the SCF case are somewhat different from that in the simple Hückel case. This results in bathochromic and hypsochromic shifts of $\pi \rightarrow \pi^*$ spectra as compared to that predicted by Hückel theory. The topmost occupied orbital is designated as A and the next occupied orbital as B. The lowest unoccupied orbital is designated as A' and the next unoccupied orbital B'. In the Table 3 we compare the $\pi \rightarrow \pi^*$ transition energies for electron jumps between A, B and A', B' orbitals for both molecules on the basis of SCF and Hückel results.

It is seen from Table 3 that in molecule I all transitions except $A \rightarrow B'$ are shifted to longer wavelengths because of the selfconsistency procedure used while in molecule II $A \rightarrow A'$, and $A \rightarrow B'$ transitions are shifted to longer wavelengths while $B \rightarrow A'$ and $B \rightarrow B'$ transitions are shifted to shorter wavelengths. Further, on the average, the shifts in the transition energies in molecule II are much larger than in I. It may be pointed out in this connection that although the introduction of α and β selfconsistency in the Hückel procedure leads to more reliable results, the results do not allow semi-quantitative calculation of spectra. In view of this, we are at present engaged in carrying out a full SCF calculation including electron repulsion explicitly for these molecules, the results of which would be reported in the near future.

TABLE 2. COMPARISON OF SCF AND HÜCKEL ORBITAL ENERGIES IN UNITS OF β_0

SCF.		Symmetry	Hückel	
Molecule I				
2·3191		b_1	2·4476	
1·7601		a_2	1·7812	
1·7094		b_1	1·7709	
1·3359		b_1	1·3207	
1·1101		a_2	1·1361	
0·7039	(B)	b_1	0·7580	(B)
0·2371	(A)	a_2	0·2411	(A)
−0·2982	(A′)	b_1	−0·3292	(A′)
−0·7422	(B′)	a_2	−0·7092	(B′)
Molecule II				
2·3204		b_1	2·4804	
1·7215		b_1	1·7084	
1·6590		a_2	1·6825	
0·9050		b_1	1·0000	
0·8924	(B)	a_2	0·8308	(B)
0·4007	(A)	b_1	0·4805	(A)
- 0·2616	(A′)	a_2	−0·2846	(A′)
−0·5470	(B′)	b_1	−0·5940	(B′)

TABLE 3. $\pi \rightarrow \pi^*$ TRANSITION ENERGIES IN UNITS OF β_0

Transition	Transition energy (SCF)	Transition energy (Hückel)
Molecule I		
A → A′	0·5353	0·5703
A → B′	0·9793	0·9503
B → A′	1·0021	1·0872
B → B′	1·4461	1·4672
Molecule II		
A → A′	0·6623	0·7651
A → B′	0·9477	1·0745
B → A′	1·1540	1·1154
B → B′	1·4394	1·4274

Stability

The question remains whether the molecular ground state obtained by the SCF procedure is more or less stable than the ground state predicted by Hückel theory and the magnitude of stabilization energy. One cannot directly compare the total π-energies of the SCF case and the Hückel case because of σ-electrons and α and β variation. To do the calculation in a satisfactory and consistent manner, the simple

Hückel results is used to get α and β depending on Hückel charges and bond orders and the following relation, used in a different connection by den-Boer,[6] is utilized.

$$V_{\text{SCF}} - V_{\text{Hückel}} = -2aP' \sum_{i<j} [\beta_{ij}(\text{SCF}) - \beta_{ij}(\text{Hückel})] + \sum_{i} (q_i\alpha_i)_{\text{SCF}} - \sum_{i} (q_i\alpha_i)_{\text{Hückel}}$$

The results show that the $\alpha - \beta$ SCF procedure does confer extra stability to the ground state of these molecules by 0·1 β_0 (2·5 Kcal/mole) for molecule I and 0·11 β_0 (2·76 Kcal/mole) for molecule II. The values of a and p' are 0·37313 and $-$ 6·25 respectively. The stabilization energy between Hückel ground state and SCF ground state is small i.e. of the order of 2·5 Kcal/mole. Our previous work[5] in these lines has shown that even such small energy differences could play significant roles in questions of chemical structure and stability. It should be noted that we are comparing π-energies alone with some account of σ-π interaction while the σ-contribution to the energy of the molecule has been left out. In fact, one of the problems in this field is to explain the very shallow minimum of total π-energy. One would have expected deeper energy minimum on general intuitive grounds. However, it is necessary to show that the molecular ground state is stabilized by the Wheland SCF procedure. Otherwise, we could not put any reliance on the bondlengths predicted by this refined method. That the α and β SCF procedure would lead to lower energy compared to Hückel method can be understood by appeal to variational method since in the former procedure the equality of all "coulomb" and "resonance" integrals which is a constraint, has been relaxed and the wavefunction obtained is, therefore, better than the Hückel wavefunction in the variational sense.

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