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Commentationes

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S.C.F. M.O. Study of Hafner's Hydrocarbons

By

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SCF MO calculations have been made for Hafner's hydrocarbons using neglect of differential overlap after the manner of Pople and Pariser and Parr. $\pi \rightarrow \pi^*$ transitions have been calculated by a limited configuration interaction method. The results show that agreement between predicted spectra and observed spectra is quite good for the heptalene derivative and reasonably good for the pentalene derivative. It is suggested that both molecules are aromatic in contradiction to predictions by Craig's rule.

SCF MO-Rechnungen mit zero differential overlap nach der Methode von Pople, Pariser und Parr wurden für Hafner's Kohlenwasserstoff angestellt. Mittels begrenzter Konfigurationswechselwirkung wurden die $\pi \rightarrow \pi^*$-Übergänge berechnet, wobei die Ergebnisse im Fall des Heptalen-Derivates verhältnismäßig gut, in dem des Pentalen-Derivates jedoch nur ungefähr mit dem Experiment übereinstimmen. Darüber hinaus sprechen die Resultate im Gegensatz zur Craig'schen Regel dafür, daß beide Moleküle aromatischen Charakter haben.

Nous avons effectué des calculs SCF MO pour les hydrocarbures de Hafner, en négligeant le recouvrement différentiel d'après Pople et Pariser et Parr. Quelques transitions $\pi \rightarrow \pi^*$ ont été calculées par interaction de configurations limitée. L'accord avec l'expérience est assez bon pour le dérivé de l'heptalène, et raisonable pour le dérivé du pentalène. Les deux molécules semblent être aromatiques, contrairement à la règle de Craig.

Introduction

In the present paper, we report results of Pople-SCF calculation [*6*] of two rather interesting molecules (I) and (II) (Fig. I) called Hafner's hydrocarbons which satisfy the criterion suggested to be characteristic of pseudoaromatic molecules [*3*] *i.e.* these molecules should have a non-totally symmetrical π electron ground state wavefunction. Ali and Coulson [*1*] studied these molecules by the valence bond method using only three Kekulé structures and by simple Hückel M.O. method and found that, according to the results of very limited valence bond calculation, (I) should be classed as normal aromatic while (II) could be pseudoaromatic. The simple Hückel M.O. method leads to totally symmetric ground state wavefunctions for (I) and (II) as they contain even number of π electrons and there is no orbital degeneracy. Further, it was found that by including overlap in simple Hückel M.O. method, electronic spectra of (I) could be fairly well understood on the basis of parameters derived from the spectra of azulene while the predicted spectra of (II) was quite different from the observed spectra.

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Since it is difficult to see whether the divergence between predicted and observed spectra for (II) is due to application of a relatively crude theory or a genuine peculiarity of the ground state wavefunction of (II), it would be of interest to study these molecules by the SCF method where electron interaction is incorporated explicitly in the calculation. Further, both molecules have C_{2v} point group symmetry and electronic states have A_1 or B_2 symmetry*.

Within the framework of Hückel MO theory, it is not easy to visualise how a B_2 ground state could arise. However, if we allow configuration interaction between the B_2 states and between the A_1 states built out of single electron excitations from bonding SCF MO's to virtuall SCF MO's, it could possibly happen that a B_2 wavefunction has lower energy than the lowest A_1 wavefunction. Hence the results of SCF MO calculation with configuration interaction would be illuminating for the above reasons.

Methods of Calculation

The matrix elements of the Hartree-Fock operator F in the basis of orthogonalised $2p_z$ atomic orbitals are given by [6]

$$F_{ii} = \omega_i + \tfrac{1}{2} P_{ii} \gamma_{ii} - \tfrac{1}{2} \gamma_0^{(C)} + \sum_{j \neq i} (P_{jj} - Z_j) \gamma_{ij}$$

and

$$F_{ij} = \beta_{ij} - \tfrac{1}{2} P_{ij} \gamma_{ij}$$

where $\omega_i - \sum_{j \neq i} Z_j \gamma_{ij}$ and β_{ij} are the elements of the bare framework Hamiltonian H_{core} and γ_{ij} are the two electron repulsion integrals.

$$\gamma_{ij} = [ii \mid jj] = \iint \varphi_i^* (1) \; \varphi_j^* (2) \frac{1}{r_{12}} \varphi_i (1) \, \varphi_j (2) \, dv_1 \, dv_2 .$$

We chose $\omega_i^{(C)} + \frac{1}{2} \gamma_0^{(C)}$ as zero of energy and the unit of energy as $\beta = -4.79$ ev, $\omega_i^{(C)}$ and $\gamma_0^{(C)}$ being the electronegativity parameter for carbon-atom in benzene and one centre two electron repulsion integral for carbon-atom in benzene respectively. Following McWeeny and Peacock [4], β_{ij} was assigned the value. -2.395 ev for i, j neighbour atoms and zero otherwise. Two centre two electron integrals were calculted using the prescription suggested by Pariser and Parr [5]. One centre two electron integral was given the value as used by McWeeny and Peacock [4]. All other two electron integrals were set equal to zero. The Hückel P matrix was used as the starting point in the well-known iterative process.

Molecular Geometry Assumed in the Calculation

The structure of these molecules has not yet been determined. For the purpose of the present calculation we have assumed that the molecules are planar with equal bondlengths of 1.39 Å. Since the molecules contain seven membered ring and five membered ring, the polygonal angles cannot be equal. In Fig. 1 we show the interbond angles assumed for both molecules. With the distances calculated

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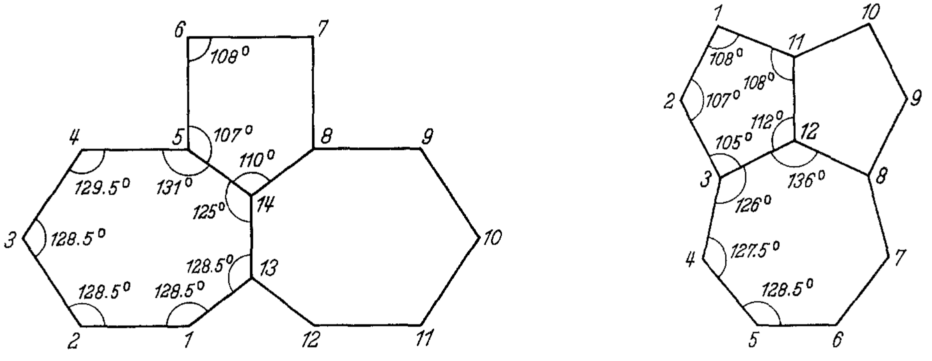
* σ_v plane is the plane perpendicular to the molecular plane and passing through twofold symmetry axis of the molecule while σ_v' is the plane of the molecule. Orbitals are of symmetry a_2 or b_1. Notation is the same as in Quantum Chemistry by H. Eyring, J. Walter and G. E. Kimball, John Wiley and Sons Inc. New York, 1944, page 384.

from the postulated geometry, all necessary two electron repulsion integrals between two different atomic centres can be computed by the method of PARISER and PARR [5].



Molecule I

Molecule II

Fig. 1

Results

The group theoretical symmetry designation and energies of SCF MO's in units of $\beta = -4.79$ ev along with McWEENY-PEACOCK notation for the three highest filled and the three lowest unfilled SCF MO's are given in Tab. 1. The relevant elements of SCF charge density and bond order matrix and Hückel charge density and bond order matrix are given in Tab. 2. A glance at the results shows that some inversion of order of sequence of charge densities on atoms takes place on inclusion of self-consistency procedure, as compared with Hückel MO results.

Table 1. *SCF MO energies*[a]

Molecule (I)			Molecule (II)		
Energy	Symmetry	McWeeny-Peacock Notation	Energy	Symmetry	McWeeny-Peacock Notation
2.061	b_1		2.043	b_1	
1.724	a_2		1.694	b_1	
1.670	b_1		1.614	a_2	
1.424	b_1		1.077	b_1	*C*
1.268	a_2	*C*	1.019	a_2	*B*
0.942	b_1	*B*	0.796	b_1	*A*
0.648	a_2	*A*	− 0.688	a_2	*A'*
− 0.721	b_1	*A'*	− 0.835	b_1	*B'*
− 0.947	b_1	*B'*	− 1.397	a_2	*C'*
− 0.964	a_2	*C'*	− 1.717	a_2	
− 1.512	a_2		− 1.845	b_1	
− 1.742	b_1		− 1.943	b_1	
− 1.831	a_2				
− 1.934	b_1				

[a] in units $\beta = -4.79$ e.v. Zero of energy is $\omega i_i^{\prime(c)} + \frac{1}{2}\gamma_0^{\prime(c)}$; MO's with positive energies in units of β are bonding and with negative energies are antibonding.

Table 2. *Elements of SCF and HMO charge density and Bond order matrix P*

Molecule (I)			Molecule (II)		
	SCF	HMO		SCF	HMO
P_{11}	1.094	1.048	P_{11}	0.896	0.960
P_{22}	0.888	0.899	P_{22}	1.150	1.148
P_{33}	1.094	1.049	P_{33}	0.898	0.940
P_{44}	0.860	0.882	P_{44}	0.942	0.886
P_{55}	1.102	1.091	P_{55}	0.966	0.907
P_{66}	1.064	1.122	$P_{11,11}$	1.146	1.161
$P_{13,13}$	0.862	0.884	$P_{12,12}$	1.146	1.156
$P_{14,14}$	0.938	0.934	P_{12}	0.756	0.746
P_{12}	0.744	0.722	P_{23}	0.504	0.512
P_{23}	0.548	0.568	P_{34}	0.592	0.599
P_{34}	0.740	0.719	P_{45}	0.684	0.656
P_{45}	0.502	0.524	P_{56}	0.622	0.637
P_{56}	0.600	0.581	$P_{3,12}$	0.440	0.467
P_{67}	0.694	0.683	$P_{11,12}$	0.606	0.582
$P_{1,13}$	0.480	0.517	$P_{1,11}$	0.490	0.503
$P_{13,14}$	0.584	0.555			
$P_{5,41}$	0.462	0.477			

Calculation of π Electronic Spectra

In calculating energies and wavefunctions of excited states, transitions between six molecular orbitals were considered, the three highest occupied and the three lowest empty orbitals being used. All nine single excited configurations involving the promotion of a single electron were considered. The method employed is similar to that first formulated by Pople for alternant hydrocarbons and extended to heteromolecules by McWeeny and Peacock [*4*].

Let (A), (B), and (AB) denote in order the columns of atomic orbital coefficients representing molecular orbitals A, B and the column whose ith element is the product of the ith elements of (A) and (B). The energies (relative to that of the ground state function) of singlet and triplet configurations in which one electron has been excited from an orbital I into an orbital K can be written in the approximation of neglecting differential overlap as

$$\begin{aligned} {}^{1,3}E_{I\to k} &= (I \to K \mid H \mid I \to K) \\ &= \varepsilon_k - \varepsilon_I - [(II)^\dagger \gamma(KK) - (IK)^\dagger \gamma\,(IK)] \pm (IK)^\dagger \gamma\,(IK) \end{aligned}$$

where ε_K, ε_I are the orbital energies and γ is the matrix of two elect ronrepulsion integrals γ_{ij} between atomic orbitals i and j.

The off-diagonal elements of the configuration interaction matrix are given by

$${}^{1,3}(I \to K \mid H \mid J \to L) = -\,[(IJ)^\dagger \gamma\,(KL) - (LJ)^\dagger \gamma\,(KI)] \pm (LJ)^\dagger \gamma\,(KI).$$

The energies and wavefunctions of the first five singlets are shown in Tab. 3 where $\Phi\,(C \to A')$ etc. stands for the singlet configurational wavefunction in which one electron has been promoted from bonding MO C to antibonding MO A'. The calculated singlet – singlet spectra is compared with the observed spectra in Tab. 4. The observed f values were estimated from the absorption curves in

Table 3. *Energy, symmetry and wavefunction of first five single excited wavefunctions*

Energy (in cm^{-1})	λ in Å	Symmetry	Wavefunction
Molecule I			
12614	7927	B_2	$-0.044\,\Phi(C\rightarrow A') - 0.074\,\Phi(C\rightarrow B') - 0.026\,\Phi(B\rightarrow C') - 0.989\,\Phi(A\rightarrow A') - 0.116\,\Phi(A\rightarrow B')$
24947	4008	A_1	$0.039\,\Phi(C\rightarrow C') + 0.698\,\Phi(B\rightarrow A') - 0.188\,\Phi(B\rightarrow B') + 0.671\,\Phi(A\rightarrow C')$
27965	3576	B_2	$0.318\,\Phi(C\rightarrow A') + 0.018\,\Phi(C\rightarrow B') - 0.321\,\Phi(B\rightarrow C') - 0.100\,\Phi(A\rightarrow A') - 0.856\,\Phi(A\rightarrow B')$
32761	3052	A_1	$0.083\,\Phi(C\rightarrow C') - 0.664\,\Phi(B\rightarrow A') - 0.517\,\Phi(B\rightarrow B') + 0.501\,\Phi(A\rightarrow C')$
39866	2508	B_2	$0.637\,\Phi(C\rightarrow A') - 0.041\,\Phi(C\rightarrow B') + 0.749\,\Phi(B\rightarrow C') - 0.036\,\Phi(A\rightarrow A') - 0.062\,\Phi(A\rightarrow B')$
Molecule II			
13289	7525	B_2	$0.105\,\Phi(C\rightarrow A') - 0.017\,\Phi(C\rightarrow C') - 0.001\,\Phi(B\rightarrow B') + 0.990\,\Phi(A\rightarrow A') + 0.095\,\Phi(A\rightarrow C')$
24351	4106	A_1	$-0.145\,\Phi(C\rightarrow B') - 0.491\,\Phi(B\rightarrow A') - 0.011\,\Phi(B\rightarrow C') + 0.859\,\Phi(A\rightarrow B')$
30159	3315	B_2	$0.815\,\Phi(C\rightarrow A') + 0.028\,\Phi(C\rightarrow C') - 0.552\,\Phi(B\rightarrow B') - 0.100\,\Phi(A\rightarrow A') + 0.141\,\Phi(A\rightarrow C')$
31088	3216	A_1	$-0.638\,\Phi(C\rightarrow B') - 0.614\,\Phi(B\rightarrow A') + 0.081\,\Phi(B\rightarrow C') - 0.458\,\Phi(A\rightarrow B')$
42208	2369	B_2	$0.482\,\Phi(C\rightarrow A') + 0.077\,\Phi(C\rightarrow C') + 0.810\,\Phi(B\rightarrow B') - 0.079\,\Phi(A\rightarrow A') + 0.317\,\Phi(A\rightarrow C')$

reference (8) by using the formula

$$f = 2.2 \times 10^{-9} \Delta \nu \varepsilon_{max}$$

where $\Delta\nu$ is the bandwidth at half-maximum extinction and was assigned the uniform value of 3000 cm^{-1}.

Table 4. *Comparison of observed and calculated π electronic spectra*

Observed maximum in cm^{-1}	log (ε)	f_{obs}	Calculated maximum in cm^{-1}	f_{calc}
		Molecule I		
9320	1.672	≈ 0.0003	12614 (B_2)	≈ 0.01
9737	1.653			
11148	2.064			
12610	2.108	≈ 0.0008		
22075	4.10	≈ 0.066	24947 (A_1)	≈ 0.038
23753	4.00			
25445	4.09	≈ 0.066	27965 (B_2)	≈ 0.16
25840	4.15			
26954	4.17	≈ 0.066	32761 (A_1)	≈ 0.087
32051	2.81	≈ 0.0066	39866 (B_2)	≈ 0
33445	2.30			
		Molecule II		
21008	2.94	≈ 0.0062	13289 (B_2)	≈ 0
26110	3.33			
26667	3.11	≈ 0.014	24351 (A_1)	≈ 0
27397	3.21			
30211	3,80	≈ 0.041	30159 (B_2)	≈ 0.036
31250	3.82	≈ 0.041	31088 (A_1)	≈ 0.094
38023	4.65	≈ 0.297	42208 (B_2)	≈ 0.778

Discussion

The above results show that the SCF MO calculation interprets the general electronic spectra of (I) rather accurately while that for (II) is less satisfactory. Also the limited configuration interaction calculation shows that in both molecules, A_1 state is always the lowest, no B_2 state having lower energy than the ground A_1 state. Hence it is interesting to note that the overall agreement for (I) is very good and for (II) reasonably good. This would reinforce the suggestion that (I) and (II) are probably genuinely aromatic. However, since in the original arguments of Craig [3], the distinction between normal aromatic and pseudoaromatics is more apparent within the framework of the valence bond method, a more extended valence bond calculation using the dependence of coulomb and exchange integral on bondlength as suggested by Coulson and Dixon [2] is under way and we hope to report these results in the near future. Further, since the SCF MO's obtained are optimised for the A_1 state, the configuration interaction matrix set up with this MO basis set may be unfavourable for the B_2 state, it would be interesting to calculate SCF MO's for the lowest B_2 state using a single configuration wave-function by the openshell method outlined by Roothan [7].

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